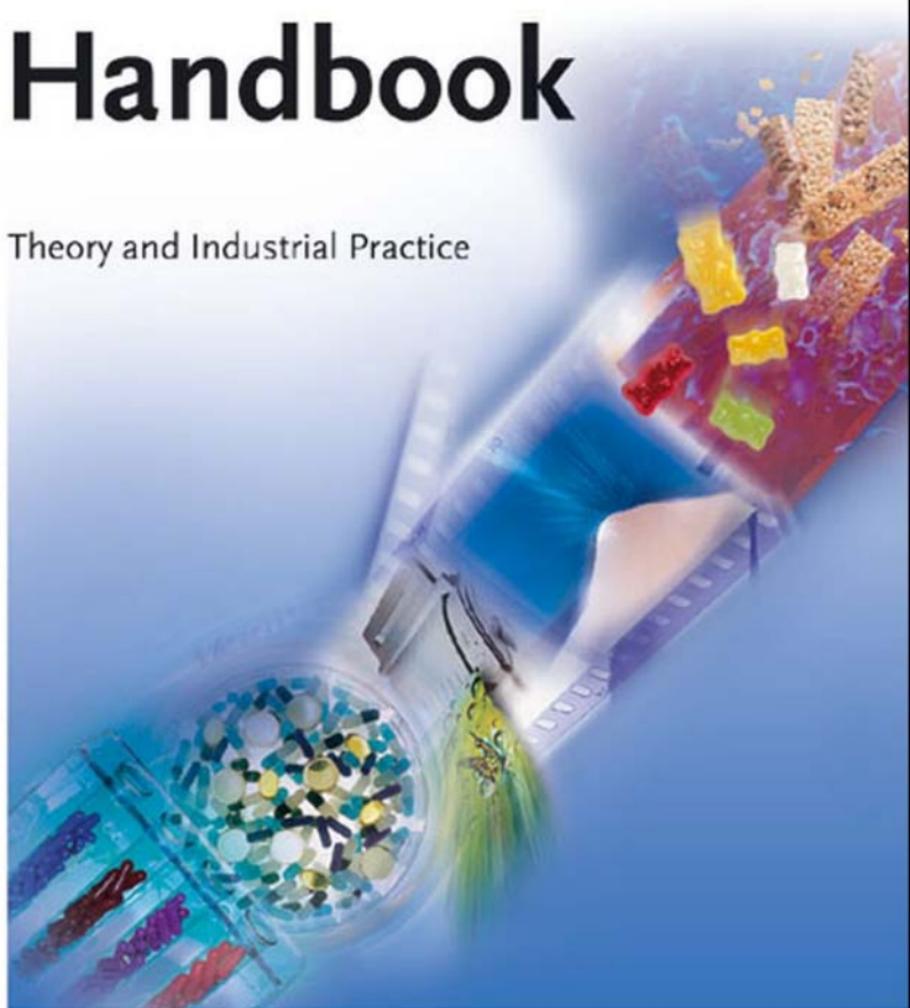


Reinhard Schrieber, Herbert Gareis

WILEY-VCH

Gelatine Handbook

Theory and Industrial Practice



Reinhard Schrieber and Herbert Gareis

Gelatine Handbook

Theory and Industrial Practice



WILEY-VCH Verlag GmbH & Co. KGaA

Reinhard Schrieber and
Herbert Gareis
Gelatine Handbook

1807–2007 Knowledge for Generations

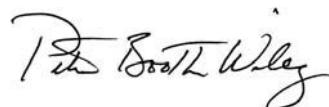
Each generation has its unique needs and aspirations. When Charles Wiley first opened his small printing shop in lower Manhattan in 1807, it was a generation of boundless potential searching for an identity. And we were there, helping to define a new American literary tradition. Over half a century later, in the midst of the Second Industrial Revolution, it was a generation focused on building the future. Once again, we were there, supplying the critical scientific, technical, and engineering knowledge that helped frame the world. Throughout the 20th Century, and into the new millennium, nations began to reach out beyond their own borders and a new international community was born. Wiley was there, expanding its operations around the world to enable a global exchange of ideas, opinions, and know-how.

For 200 years, Wiley has been an integral part of each generation's journey, enabling the flow of information and understanding necessary to meet their needs and fulfill their aspirations. Today, bold new technologies are changing the way we live and learn. Wiley will be there, providing you the must-have knowledge you need to imagine new worlds, new possibilities, and new opportunities.

Generations come and go, but you can always count on Wiley to provide you the knowledge you need, when and where you need it!



William J. Pesce
President and Chief Executive Officer



Peter Booth Wiley
Chairman of the Board

Reinhard Schrieber and Herbert Gareis

Gelatine Handbook

Theory and Industrial Practice



WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Reinhard Schrieber

Rudolf-Epp-Strasse 38
69412 Eberbach
Germany

Dr. Herbert Gareis

GELITA AG
Uferstrasse 7
69412 Eberbach
Germany

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <<http://dnb.d-nb.de>>.

© 2007 WILEY-VCH Verlag GmbH & Co.
KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Typesetting Asco Typesetters, Hong Kong
Printing betz-druck GmbH, Darmstadt
Binding Litges & Dopf GmbH, Heppenheim
Cover Design Grafik-Design Schulz,
Fußgönheim
Wiley Bicentennial Logo Richard J. Pacifico

ISBN 978-3-527-31548-2

Contents

Gelatine – An Element of Our Life XI

1	Introduction	1
1.1	Gelatine – Yesterday, Today, and Tomorrow	1
1.1.1	The Future of Gelatine Has Just Begun – Its Multi-faceted History Is Proof	1
1.1.2	It All Began with Glue	1
1.1.3	Pure Luxury for Kings and Aristocrats	3
1.1.4	During the Napoleonic Wars, Gelatine Was Systematically Researched as a Source of Protein	3
1.1.5	Suddenly, Medicines No Longer Had a Bitter Taste	4
1.1.6	Gelatine Helped to Popularize Photography	5
1.1.7	Magically Appearing Text	7
1.1.8	Gelatine Literally on Everyone's Lips	9
1.1.9	An Essential Element of Our Daily Lives	11
1.2	The Development of the Gelatine Industry	12
1.2.1	Period 1800–1865	12
1.2.2	Period 1866–1900	13
1.2.3	Period 1901–1914	15
1.2.4	Period 1915–1918	17
1.2.5	Period 1919–1939	17
1.2.6	Period 1940–1948	21
1.2.7	Period 1949–1972	22
1.2.8	Period 1973–1993	29
1.2.9	Period 1994–2005	36
	References	43
2	From Collagen to Gelatine	45
2.1	Basic Chemical/Physical Principles and Technological Properties	45
2.1.1	Basic Chemical/Physical Principles	45
2.1.1.1	Chemical Composition and Molecular Structure of Collagen	45
2.1.1.2	The Conditioning Process and its Effects on the Amino Acid Composition of Gelatine	47

2.1.1.3	The Conditioning Process and its Effect on the Molecular weight Distribution of Gelatine	48
2.1.2	Technologically Important Properties and Characteristics of Gelatine	51
2.1.2.1	Gel Formation, Viscosity, and Texture	52
2.1.2.2	Gel Strength/Bloom Value	53
2.1.2.3	The Kinetics of Gel Formation	54
2.1.2.4	The Rheology of a Gelatine Solution	55
2.1.2.5	From Gelatine/Water to Complex Systems	56
2.1.2.6	Surface Properties	59
2.1.2.7	Amphoteric Behavior/Isoelectric Point	61
2.1.2.8	Protective Colloid Function	62
2.1.2.9	Adhesion Properties	62
2.1.3	Basic Principles for Selecting a Suitable Type of Gelatine	63
2.1.4	Chemically Modified Gelatines	63
2.2	Manufacture of Gelatine: Theory and Practice	66
2.2.1	The Raw Material “Ossein”	66
2.2.1.1	Maceration	66
2.2.1.2	Pressure Hydrolysis	69
2.2.2	The Raw Material “Hide Split”	69
2.2.3	The Raw Material Pigskin	71
2.2.4	Conditioning	72
2.2.4.1	Alkaline Pretreatment “Conditioning” for Type B Gelatine	73
2.2.4.2	Acid Pretreatment for Type A Gelatine	74
2.2.5	Traditional Extraction (Batch Process)	75
2.2.6	Continuous Extraction	78
2.2.7	Production of Fish and Fowl Gelatine	79
2.2.8	Processing the Extracted Gelatine	82
2.2.8.1	Filtration and Clarification	82
2.2.8.2	Deionization	83
2.2.8.3	Concentration	85
2.2.8.4	Final Sterilization	86
2.2.8.5	Drying Process for Granulated Gelatine	86
2.2.8.6	Standardization and Packaging of Granulated Gelatine	88
2.2.9	Manufacture of Leaf Gelatine	89
2.2.10	Instant Gelatine	91
2.2.11	Gelatine Hydrolysate	93
2.2.12	Environmental Aspects of Gelatine Manufacture	96
2.3	Quality Control and Certified Product Safety	99
2.3.1	The Quality Assurance Process	99
2.3.1.1	Raw Materials	103
2.3.1.2	Production	103
2.3.2	Standard Quality Tests on the Final Product	104
2.3.2.1	Gel Strength (Bloom Value)	104
2.3.2.2	Viscosity	106

- 2.3.2.3 pH 106
- 2.3.2.4 Water Content 107
- 2.3.2.5 Color and Clarity 107
- 2.3.2.6 Sulfur Dioxide and Peroxides 108
- 2.3.2.7 Odor and Taste 108
- 2.3.2.8 Inorganic Components 108
- 2.3.2.9 Conductivity 109
- 2.3.3 Microbiological Tests 109
- 2.3.4 Special Chemical/Technological Tests 110
 - 2.3.4.1 Gelation Point, Melting Point, Gelation Time 110
 - 2.3.4.2 Rheology 111
 - 2.3.4.3 The Foam Test 112
 - 2.3.4.4 Isoelectric Point 113
 - 2.3.4.5 Molecular-Weight Distribution 113
 - 2.3.4.6 Nitrogen Determination using the Kjeldahl Method 114
 - 2.3.4.7 Determination of Gelatine Protein 115
 - 2.3.4.8 Hydroxyproline 115
- 2.3.5 Special Tests for Photographic Applications 115
 - 2.3.5.1 Characterization of Photographic Properties 115
 - 2.3.5.2 Hardening Behavior 116
- 2.3.5.3 Gold Number 117
 - References 117

3 Practical Aspects 119

- 3.1 Basic Processing 119
 - 3.1.1 The Functional Properties of Gelatine Compared with Other Hydrocolloids 119
 - 3.1.1.1 Agar-agar 123
 - 3.1.1.2 Carrageenans 124
 - 3.1.1.3 Alginates 125
 - 3.1.1.4 Pectin 126
 - 3.1.1.5 Locust Bean Gum 127
 - 3.1.1.6 Gum Arabic 128
 - 3.1.1.7 Modified Cellulose 129
 - 3.1.1.8 Starch and its Derivatives 131
 - 3.1.1.9 Xanthan Gum 133
 - 3.1.1.10 Gellan Gum 133
 - 3.1.1.11 Conclusion and Outlook 134
 - 3.1.2 Dissolution Kinetics and the Rheological Behavior of a Gelatine Solution are Central to Process Optimization 137
 - 3.1.2.1 Process Steps for Dissolution 138
 - 3.1.2.2 Factors Influencing Dissolution – Particle Size 138
 - 3.1.2.3 Factors Influencing Dissolution – the Matrix 139
 - 3.1.2.4 Traditional Two-step Processing versus the Modern Hot-Melt Process 140

3.1.2.5	The Viscous Behavior of a Gelatine Solution During Further Processing	142
3.1.2.6	Setting Temperature and Setting Time	143
3.1.2.7	Process Optimization in Practice	144
3.1.2.8	Special: Processing Leaf Gelatine	148
3.1.3	The Typical Properties of Instant Gelatine Must be Taken into Account when Processing	150
3.1.4	Gelatine Hydrolysate – a Non-gelling but Versatile Product	155
3.2	Gelatine Applications	163
3.2.1	Confectionery and Gelatine Desserts	163
3.2.1.1	Fruit Gummies	163
3.2.1.2	Mallows	172
3.2.1.3	Bar Products	179
3.2.1.4	Gelatine Desserts	182
3.2.1.5	Other Confectionery Applications	186
3.2.1.6	Interaction with Other Ingredients	187
3.2.2	Dairy Products and Pastries	191
3.2.2.1	Stirred and Thermally Treated Fermented Milk Products	191
3.2.2.2	Stabilization Against Syneresis	192
3.2.2.3	Fermented Milk Drinks	194
3.2.2.4	Ice Cream and Whipped Desserts	194
3.2.2.5	Stabilization of Cream	196
3.2.2.6	Sandwich Spreads and Cheeses	198
3.2.2.7	Powdered Dairy Products	200
3.2.2.8	Gelatine in Combination with other Hydrocolloids	201
3.2.3	Meat and Delicatessen Products	203
3.2.3.1	Aspic Products	204
3.2.3.2	Gelatine Glazing and Dipping Masses	212
3.2.3.3	Binding of Cooking Juice	212
3.2.3.4	Water Binding in Fresh Meat	213
3.2.3.5	Pickled Products	214
3.2.3.6	Reduction of Baking, Frying, and Grilling Losses	215
3.2.3.7	Mayonnaise and Salad Dressings	217
3.2.3.8	Other Aspects	218
3.2.4	Beverages	218
3.2.4.1	Selecting the Most Suitable Type of Fining Gelatine	220
3.2.4.2	Determining the Optimal Quantity of Gelatine	221
3.2.4.3	Combined Gelatine-Silicic Acid/Bentonite Fining	222
3.2.4.4	Procedure for Fining with Gelatine	222
3.2.4.5	Dosage of Gelatine	223
3.2.4.6	Factors that Influence Fining Efficiency	224
3.2.4.7	Hot Fining of Fruit Juices	225
3.2.4.8	Pre-fermentation Fining with Liquid Gelatine Hydrolysates	225
3.2.5	The Traditional and Modern Nutritional Science of Gelatine	226
3.2.5.1	Gelatine and Nutrition – a Historical Review	226

3.2.5.2	Protein Requirement and Biological Value	228
3.2.5.3	Nutritional and Physiological Importance of Gelatine	230
3.2.5.4	Gelatine for Modern, Health-promoting Foodstuffs (Low-fat, Low-carb, Low-calorie)	234
3.2.6	Pharmaceuticals and Medicine	239
3.2.6.1	Gelatine in the Pharmacopoeias	239
3.2.6.2	Gelatine Capsules	240
3.2.6.3	Plasmas Substitutes	253
3.2.6.4	Vitamin Coating	254
3.2.6.5	Other Gelatine Applications in Pharmaceutical Technology	255
3.2.6.6	Medical Applications	255
3.2.7	Photography and Ink-jet Printing	259
3.2.7.1	Characteristics of Photographic Gelatine	260
3.2.7.2	The Photographic Process	260
3.2.7.3	The Manufacture of Photographic Emulsions	263
3.2.7.4	Coating	266
3.2.7.5	Ink-jet Media	268
3.2.8	Cosmetics	272
3.2.8.1	Structure of the Skin	273
3.2.8.2	Aging of the Skin	274
3.2.8.3	Structure of the Hair	275
3.2.8.4	Collagen in Cosmetic Applications – Direct Effects	277
3.2.8.5	Indirect Effects in Skin and Hair Care	281
3.2.8.6	Protein Surfactants	282
3.2.9	Technical Applications	283
3.2.9.1	Microencapsulation Using Complex Coacervation	283
3.2.9.2	Microencapsulation by Spray Drying	287
3.2.9.3	Adhesives and Building Materials	287
3.2.9.4	Paper Processing	288
3.2.9.5	Analytics	289
3.2.9.6	Gelatine Films and Coatings	290
3.2.9.7	Detergents and Cleansing Agents	294
3.2.9.8	Electro-plating and Suspension Polymerization	295
3.2.9.9	Environmental Protection	295
	References	299
4	The Role of Collagen Hydrolysate in the Prophylaxis of Osteoarthritis and Osteoporosis	301
4.1	Osteoarthritis	301
4.1.1	Genesis and Conventional Therapy	302
4.1.2	Preventive Treatment with Collagen Hydrolysate	303
4.1.2.1	Mode of Action	303
4.1.2.2	Clinical Studies	304
4.2	Osteoporosis	306
4.3	Processing into Food Supplements	307

4.4	Future Prospects	308
	<i>References</i>	309
5	Future Prospects – Global Megatrends and Opportunities	311
5.1	Increasing Population with an Increasing Proportion of Elderly People	311
5.2	No one Type of Grain can Cover all Nutrient Requirements	313
5.3	Health is an Invaluable Asset	313
5.4	Low-calorie, Low-fat, and Low-carb	314
5.5	The Digital Revolution Continues	315
5.6	Environmentally Friendly Production Processing Is Gaining Ground	315
5.7	Our Oil Reserves Are Shrinking	316
5.8	Gelatine's Flexibility will also be in Demand Tomorrow	317
	<i>Reference</i>	320
6	Glossary	319
	Subject Index	331

Gelatine – An Element of Our Life

Today, we encounter gelatine in practically all areas of modern life. In spite of this, many experts, product developers and technologists often spontaneously associate gelatine with gummy bears and pharmaceutical capsules; they are still not fully aware that this natural product has numerous other application possibilities.

In the future, however, interest in gelatine will not just be restricted to classical applications; new uses in health care and in specialized technical areas will result in gelatine and gelatine hydrolysates, due to their unique properties, becoming a focal point of interest for a much wider public.

This “Handbook of Gelatine” is intended to provide an insight into all current and numerous potential applications of this extremely versatile protein. It is designed to provide comprehensive background knowledge of the manufacture and the technological and physiological properties of the “multi-talent” gelatine and is directed principally to students, experts and technologists in the fields of industry, science and healthcare. The various processing possibilities and applications in the areas of nutrition, medicine, pharmaceuticals and photography are comprehensively described. The book also gives an overview of the worldwide historical development of the entire industrial sector.

In order to make our “Handbook” suitable for as wide a readership as possible, we have deliberately refrained from giving complex theoretical explanations. Instead, we have provided a well-founded scientific basis of the substance gelatine. In doing so, we have focused entirely on the practical aspects of working with gelatine. A glossary of terms relevant to this specialist area is also provided to aid understanding. Furthermore, specific literature references are given in each chapter; these will provide further information for those interested.

We would like to express our thanks to all who have contributed towards making this book possible. In particular, we would like to thank the employees of the GELITA Group worldwide and many other international companies involved in the manufacture of gelatine. All have made an enormous contribution towards describing the different facets of the wonderful natural product gelatine and the development of the industry.

We wish our readers many and valuable new insights, suggestions and help regarding gelatine and trust we have managed to fill any gaps that may have existed concerning gelatine and its applications.

Eberbach, November 2006

Reinhard Schrieber

Dr. Herbert Gareis

1

Introduction

1.1

Gelatine – Yesterday, Today, and Tomorrow

1.1.1

The Future of Gelatine Has Just Begun – Its Multi-faceted History Is Proof

The foodstuff gelatine has had a long and successful history. In ancient times it was used as a “biological adhesive”, and in the course of time it progressed to industrial manufacture and diverse applications. Some 8000 years ago, cave dwellers in what is now the Middle East were able to produce glue from animal tissues. Some 3000 years later, the Ancient Egyptians were well aware of its functionality and used a type of wood glue produced from collagen as an adhesive to glue their items of furniture together. And, at the court of Henry VIII of England (1491–1547), pickled dishes with “glittering calves’-foot jelly” were on the menu at every banquet. It was in the Napoleonic era, however, that gelatine experienced its first real boom: it was used as a source of protein to feed the French when meat became scarce during the blockade of their ports by the British navy. And, of course, modern pharmaceuticals and photography would be unthinkable today without gelatine.

The use of gelatine for health purposes has been documented since as early as the Middle Ages. For example, Hildegard von Bingen, Benedictine Abbess and universal scholar, recommended in her “Physica” around 1150 that “frequent and adequate” portions of a broth made from calves’ feet was good for joint pain. Today, science has proven just how right she was.

1.1.2

It All Began with Glue

However, archeologists have established that certain forms of crude gelatine were used much earlier. Chemical and microbiological analyses carried out at the Weizmann Institute in Israel on samples taken from a cave near the Dead Sea clearly show that its inhabitants in the New Stone Age knew much about the adhesive strength of collagen glue and used it for numerous purposes. Discoveries



Fig. 1.1 Gelatine has had a long and successful history. The granulated types are today's most common grades for industrial use.

in both Deir el Bahari (in the funerary temple of Queen Hatshepsut) and in Thebes [1] (today's Luxor) also unambiguously prove that animal glue was used in Egypt at the time (see Fig. 1.2). This form of glue, so-called glutin glue, is still produced today from the collagen of animal hides. In addition, some pyramid texts indicate that the Egyptians also used bones in the preparation of various broths and soups [2].

Thus, the use of gelatine for the preparation of food during the first few centuries AD can be clearly established. During this period, the bone and hide of animals was boiled to obtain glue. However, a different kind of product was also obtained – a raw extract that, when cooled, solidified to produce what in fact was the “original form” of edible gelatine.



Fig. 1.2 The Ancient Egyptians used glutin glues for furniture production. This glue is still produced today from the collagen of animal hides and bones in some countries, including Egypt.

1.1.3

Pure Luxury for Kings and Aristocrats

For centuries, gelatine was a luxury item; it was used to prepare an extravagant jelly for dishes presented at court and in aristocratic villas. It was only in the late 17th century that scientists started propagating its nutritional and physiological qualities.

In 1682 the French mathematician Denis, Papin invented a pressure cooking pot [3] called a “digester” that made it possible to cook bones until soft. Papin recommended using the stock produced for preparing soups; he even suggested to King Charles II of England in 1681 that “the jelly produced from bone be used as a general foodstuff for the people.”

1.1.4

During the Napoleonic Wars, Gelatine Was Systematically Researched as a Source of Protein

Gelatine's popularity as a foodstuff came about during the Napoleonic Wars. The blockade of the French ports by the British navy during the wars meant a shortage of meat protein for the population. Politicians and scientists initiated a search for possible alternatives and in fact found one – gelatine. In 1803 and 1818, the administrator of the Military Hospital in Paris, Anton Alexis Cadet de Vaux, published reports on “gelatine produced from bones and on the resulting bouillon”. A commission headed by the chemist d'Arcel used these to compile methods for manufacturing gelatine. Gelatine as a source of protein for nutritional purposes was then systematically researched and its manufacture and application improved. The obvious consequence was the industrial production of gelatine.

The first company to manufacture gelatine on an industrial scale was Coignet & Cie., founded in 1818 in Lyons, France. The company improved production in two areas: it was the first company to use “hide split” (so-called “glue leather”) as a raw material (see Section 2.2.2), and it introduced a process for the industrial drying of thick gelatine leaves. This remained the method of choice until



Fig. 1.3 Manufacture of gelatine was extremely work-intensive until the middle of the 20th century. Here, packing of the dried gelatine sheets.

the middle of the 20th century. The first products to be sold under the label "powder gelatine" were no more than ground thick leaves or bars of gelatine.

1.1.5

Suddenly, Medicines No Longer Had a Bitter Taste

Almost at the same time, the first new applications for gelatine were developed. The first breakthrough came about in 1833 when French pharmacist Mothes was granted a patent for the manufacture of gelatine capsules (French Patent No. 9690). These “original capsules” were produced by immersing a small leather sack filled with mercury into a concentrated solution of gelatine. The chilled and dried gelatine film which looked like a capsule was then stripped from the leather bag. These capsules enabled drugs to be dosed more easily and, for the first time, to be better protected from the effects of heat, cold, and humidity. More importantly, however, the medicines they contained no longer tasted bitter.

Later, American companies became technology leaders in the manufacture of capsules. In 1897 [4], the company Eli Lilly, based in Indianapolis, IN USA, started filling powders and granulates into very thin, two-part hard gelatine capsules. By 1913, the company had also developed and globally introduced the first automatic method for the production of hard gelatine capsules. The process for the simultaneous production of “bodies” and “caps” was introduced in 1931 by Parke, Davis & Company in Detroit, MI USA.

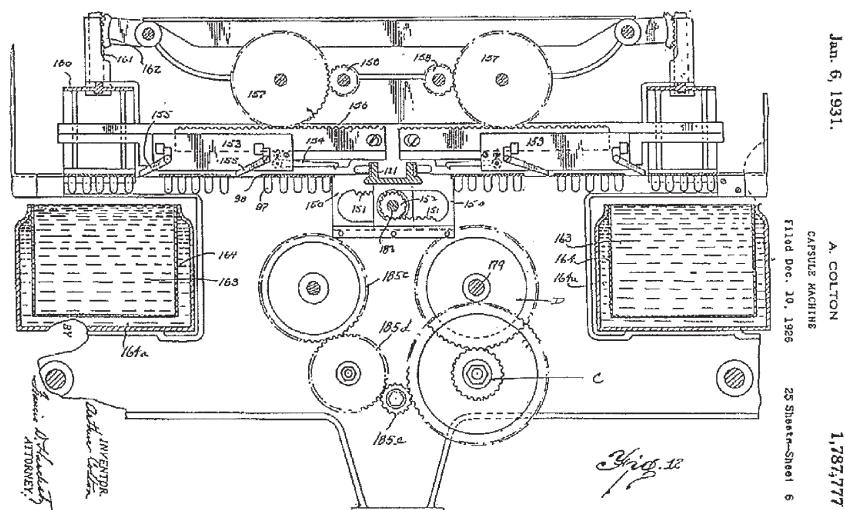


Fig. 1.4 Construction plan of a hard shell capsule machine from the patent application of Parke, Davis & Company, 1931.



Fig. 1.5 Two of the first soft shell capsule machines of Robert P. Scherer, who revolutionized the manufacture of soft gelatine capsules with his development.

Around 1930, a further pioneering invention revolutionized the manufacture of soft capsules: Robert P. Scherer invented a machine for the automatic and continuous manufacture and filling of soft gelatine capsules, a process that very soon spread throughout the world (see Fig. 1.5). Gelatine, however, was also used in other pharmaceutical applications: it was used, for example, for coating tablets and microcapsules, thus reliably protecting the active substances contained in them from the effects of light and atmospheric oxygen.

It is not only this effective barrier function that makes gelatine so valuable in pharmaceutical production; its high degree of compatibility and extremely low allergenicity make it an ideal component of drug systems. These particular properties have also been utilized in applications in medicine: since the 1940s, for example, gelatine sponges have become indispensable as hemostats against surgical bleeding (see Fig. 1.6). Interestingly, this has a connection with the early history of gelatine: during the 3rd century, the Chinese and Japanese used gelatine for this specific purpose [5]. A further example is in the area of emergency medicine, where gelatine-based substances are used as blood replacement agents or plasma expanders (see Fig. 1.7). These were intensively researched during the First World War [6] and successfully used on a large scale during the Second World War.

1.1.6

Gelatine Helped to Popularize Photography

The history of photography would also have been quite different without gelatine. The decisive breakthrough was made by Frenchman Louis Jacques Mandé Daguerre (1787–1851), who developed the “Daguerreotype” process of photographic printing. The process, however, was somewhat complex and difficult to handle. In addition, it was only possible to prepare unique original positives. These were expensive, and hence the hobby of photography was restricted to those who could afford it.



Fig. 1.6 Gelatine sponges are available in a variety of shapes to stanch surgical bleeding in different areas of the human and animal bodies.

Making photography uncomplicated, important for its widespread popularity, was made possible half a century later with the help of gelatine. From 1880 onwards, ready-to-use dry photographic plates coated with gelatine emulsion became available. With these, it was possible to produce negatives and therefore many positives. However, photography was only finally popularized by George Eastman who, in 1888, introduced his famous “Kodak Number 1” camera (see Fig. 1.8).

This made it possible for the amateur photographer to produce photos at reasonable cost as the easy-to-use camera worked with rolls of film instead of plates. An indispensable aspect of the exposure and development of the films was the coating of the photographic paper with high-quality gelatine. The gelatine used had to be chemically pure and particularly uniform in terms of its viscosity and texture. The companies involved in the photographic business, although many, like Kodak, had their own gelatine manufacturing plants, soon started to cooperate with specialists in photographic gelatine.

At the end of the 19th and beginning of the 20th centuries, such specialists were to be found particularly in Germany and France. The close cooperation that followed soon led to both industrial areas becoming closely knit, at least in part. In 1921, for example, George Eastman and Heinrich Stoess, after a long and successful transatlantic cooperation, founded together the first German-American joint venture after the First World War – the Odin Factory in Eberbach, Germany, the plant supplying Kodak with its photographic gelatine (see Fig. 1.9).

Also, Agfa AG, at the time one of the largest of Kodak's competitors in Europe, concluded a contract with DGF (Deutsche Gelatine Fabriken AG) in Göppingen



Fig. 1.7 Blood plasma substitutes based on gelatine are widely used for the temporary replacement of blood in the circulatory system after surgery or accidents.

and Schweinfurt in Germany whereby DGF AG agreed to supply all of Agfa's requirements for photographic gelatine. In 1964, in fact, Agfa AG itself started producing gelatine: it acquired completely the company Koepf & Söhne and from then until the year 2000 produced part of its total requirement of gelatine at its own plant in Heilbronn, Germany.

1.1.7

Magically Appearing Text

The contracts between Kodak and Stoess on the one hand and Agfa and DGF on the other were quite different in nature. However, they had one thing in common: as with all documents at the time, they were duplicated using carbon paper. This changed dramatically in the 1960s: Barrett Green and Lowell Schleicher of the company NCR invented the microcapsule for carbonless paper that was based on the reaction between gelatine and gum arabic (US Patent No. 72 800 457). This enabled special dyes to be embedded in microscopically small capsules that were

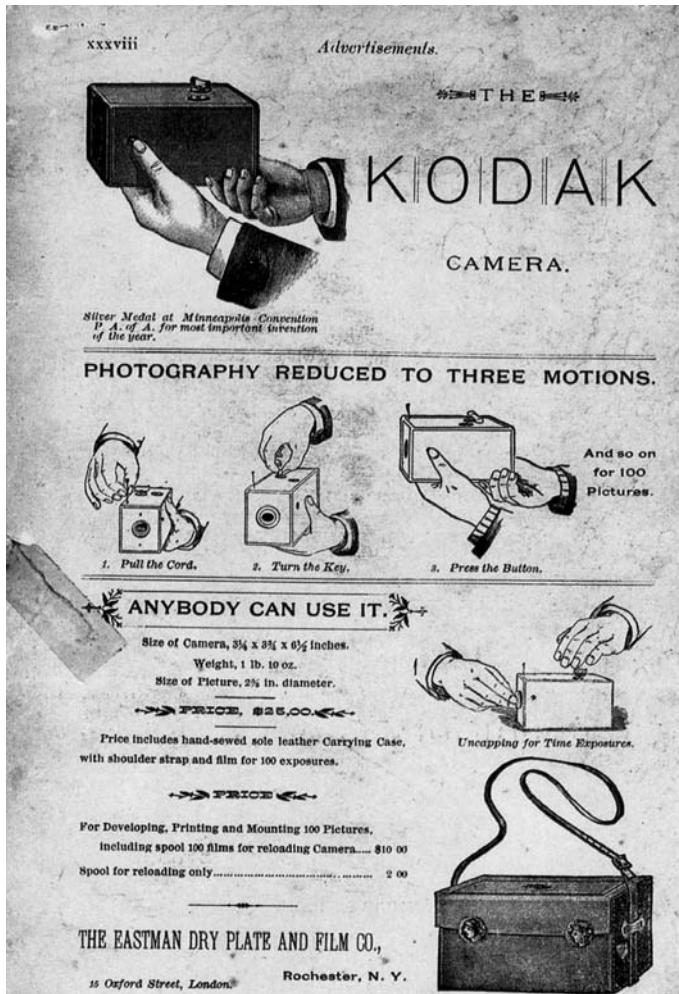


Fig. 1.8 Advertisement for the “Kodak Nr. 1” camera which worked with rolls of film instead of plates. This made it possible to produce photos in an easy way and at reasonable cost.

coated onto the reverse side of the paper to be written on (see Fig. 1.10). The pressure exerted by either the pen or the typewriter keys caused the capsules to rupture, hence releasing an initially colorless amount of ink. A special coating on the upper side of the copy then rendered the ink visible, and the text appeared as if by magic! This ended the period of black “carbon fingers” in many a typing pool.

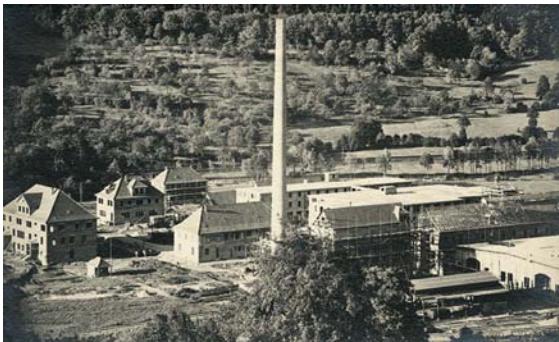


Fig. 1.9 In 1921, George Eastman and Heinrich Stoess established a joint venture – the Odin Factory in Germany. The plant supplied Kodak's factories world-wide with its photographic gelatine for close to 20 years.



Fig. 1.10 Carbonless paper forms are covered on the back with gelatine microcapsules filled with ink. The capsules collapse and release the incorporated dye as a result of the pressure of the pen when writing.

1.1.8

Gelatine Literally on Everyone's Lips

A further important step that made gelatine ubiquitous in its use was the introduction of household packs of granulated gelatine in the United States in 1890 through the efforts of Charles Knox (see Fig. 1.11) and in Germany, during the period of worldwide economic recession, through DGF AG. This single event made gelatine into a basic and very popular ingredient for numerous foodstuffs and brought about its use on a worldwide basis.

Another major move to make gelatine more widely known was made by Peter Cooper in the United States when, in 1845, he obtained the first patent for a gelatine dessert. In 1897, the product was improved by adding fruit flavors and was named JELL-O®. The first recipe book was published in 1904. Sales of JELL-O® are currently about 300 million boxes per year in the United States. A different way of offering gelatine desserts to the public was developed in Great Britain by



Fig. 1.11 Household packs of granulated gelatine were introduced in 1890 by C. Knox and soon became very popular in the United States.

the company Rowntree. Starting with a similar product to JELL-O® in 1923, they started marketing concentrated cubes called Jelly Tablets in 1932. These also contained different fruit flavors (see Fig. 1.12). Although the product was very successful in Great Britain, it never managed to be marketed on a broader scale abroad.

Ever since, not only the food industry but also gelatine manufacturers have been continuously developing new applications for gelatine. Further aspects of its multifunctional properties were discovered and made available via new products to consumers. Many of these products were literally on everyone's lips:



Fig. 1.12 Jelly Tablets are concentrated gelatine cubes containing sugar and different fruit flavors. After mixing with hot water and then chilling, the dessert is ready to eat.



Fig. 1.13 Today, gelatine is a very popular ingredient in numerous foodstuffs. Confectionery products are by far the largest application area for gelatine around the world.

marshmallows were introduced into the United States in the early 1900s and became extremely popular by the 1950s, in 1930 the now-famous gummy bears were introduced, and by the 1970s gelatine enabled fruit yogurts without the filmy layer of whey on the surface to be developed (Fig. 1.13).

At the end of the 1970s, hydrolyzed gelatine became one of the top topics on the talk shows on American TV. The result: the calorie-reducing “liquid protein” created a record-breaking demand. Gelatine was also significantly involved in the worldwide success of the low-fat margarines and sandwich spreads invented by Lage Sundstroem in Sweden that, by 1984, were being produced on an industrial scale (US Patent No. 4071634). Gelatine was the emulsifier and stabilizer used to ensure the consistency and spreadability demanded by consumers.

1.1.9

An Essential Element of Our Daily Lives

Today, gelatine is a modern product with a very wide range of uses. It is an essential element of our daily lives, even if this is not obvious at a first glance. Match heads contain gelatine and digital holiday snapshots can be printed on top-quality, gelatine-coated ink-jet photographic paper or, traditionally, on classical photographic paper in the photo laboratory. Gelatine has also been proven to be effective as a cleansing agent and is used in the clean-up and refurbishment of buildings contaminated with asbestos. It is also used for the restoration of historical documents. Furthermore, it helps to support healthy joints and bones, and has many other uses. However, in spite of these numerous applications, not all of the many and various functional properties of gelatine have been exhaustively researched. The highly versatile history of gelatine has shown that its future has in fact just begun.

1.2

The Development of the Gelatine Industry

This chapter will give an overview of the development of the industry over more than 200 years from small local manufacturing through growth periods to global players. Because of the limited space available in this book, very small operations and companies of little importance or significance for the general development of the industry or which disappeared rapidly have been ignored. Company names have been abbreviated.

1.2.1

Period 1800–1865

In this early period, gelatine was produced for edible purposes solely on a private level or by small businesses on a semi-commercial scale. But some small glue manufacturers already existed and saw the possibility of changing their production to the manufacture of gelatine.

France

The first production of gelatine on an industrial scale by the company *Coignet* was reported in 1818 for their plant in Barabon-sur-Rhône (see Section 1.1). Soon after, they acquired further small glue and gelatine plants in France and Belgium and also started exporting. In 1839, the business of *Weishardt* started what was most likely the first glue manufacturing facility in the south of France.

Belgium/England

In the following years, small companies started in Belgium and most likely also in Great Britain. However, no details are known.

Germany

In 1840, the first German gelatine plant of O. Lindenbauer was established, but during the next 25 years only three more were built, including the company *Creutz*, which subsequently existed for more than 100 years as an independent small gelatine company.

There is no information about the size of production available from those times, but it is very likely that even the best and largest plants did not produce more than 10 000 kg per month.

The raw materials used in those times were hide pieces, but also bones collected from butchers and residues from those businesses making combs and buttons from bone were used. Most of the process development was transferred from France to other countries. The product made had the form of thick gelatine plates, like those of chocolate.

After the invention of the use of gelatine for the photographic process in several steps between 1839 and 1856, the best qualities of edible gelatine were chosen for this application. The general interest in gelatine production also became

obvious, and it must have been profitable because soon more and more gelatine companies were founded.

1.2.2

Period 1866–1900

France

The existence of four more glue and gelatine plants in France in 1875 is reported. These also supplied products to Germany. In 1891, E. Rousselot founded the company *Rousselot* which manufactured glue, and he acquired two additional glue plants in France in 1894 and 1900. His gelatine production is confirmed for 1909 but may have started earlier. These were the roots for today's second largest gelatine manufacturer in the world.

Belgium

Efficient, well-known manufacturers must have existed, because purchases from this region are reported by German companies. In 1895, a plant processing Indian bone was built (*Société Anonyme de Vilvorde*) next to an existing plant (*Société Anonyme de Grimbergen*). Both establishments merged in 1911 and are the roots of today's company *PB Gelatines*.

Great Britain

The company *W. Oldroyd* started gelatine production in Widnes – which was later an important gelatine site, and *B. Young* changed his production in London from glue to gelatine. About 1900, *C. Simeons*, the son of a German gelatine manufacturer, came to England and founded the companies *C. Simeons* and the *British Gelatine Works* in Luton to manufacture photographic gelatine. The Luton plant later (1920) became part of *British Glues & Chemicals* and afterwards part of the *Croda* company.

United States

Several gelatine plants were established during this time. In 1890, *C. Knox* founded *Knox Gelatine*, but no details are available about production. In 1888, some 92 glue plants existed in the United States, but it is not known to what extent they also produced gelatine.

One of those glue plants was owned by *Peter Cooper*, who had purchased a glue plant in 1820 in New York City. He invented several pieces of labor-saving equipment for manufacturing gelatine, and in 1845 he obtained the first American patent for his process.

Germany

Gelatine manufacturing became very popular during this time, and a total of 16 plants are reported by 1900. Some were based on modified glue plants, and others started when tanneries decided to upgrade the value of their by-product hide splits and pieces instead of selling or dumping them.

The following were the roots of today's GELITA AG, the world's largest manufacturer of gelatine. In 1867, A. Schmitt started his gelatine production in Schweinfurt, and in 1872 C. Heinrichs founded a gelatine plant in Höchst, which was then merged in 1889 with the Schmitt company to form the first DGF. In 1880, the brothers Paul and Heinrich Koepff, who ran a tannery, founded a gelatine and glue plant in Göppingen. Their relative, Jacob Koepff, founded a gelatine plant in Süßen in 1889. In 1888 H. Stoess established the *Heidelberger Gelatine-Fabrik Stoess* in Ziegelhausen (close to some large tanneries) and soon specialized in the production of photographic gelatine.

The glue plant of *Caesar & Ewald* was founded in 1886 because several tanneries were in the neighborhood. Mr. Ewald was a businessman and Mr. Caesar had experience in tanning. In 1906 they changed from glue to gelatine plates. Today they are still a major manufacturer of edible leaf gelatine.

The other plants founded during this period had disappeared by this time.

The production of photographic gelatine increased rapidly after 1880, and included exported material. During this period, about 100 tons/annum of photographic gelatine was exported from Germany to the United States, mainly to Eastman Kodak.

Only for Germany are best-estimated production figures (all kinds) available:

1880	approx. 200 tons
1890	approx. 400 tons
1900	approx. 1200 tons.

During this period, the gelatine plates produced became thinner, and the description "leaf gelatine" was created. The thinnest leaves have proven to be of the best quality – a rule which is still valid today. In this period the milling of plates and leaves was also started for the manufacture of powder gelatine.

Local fresh bones, partly degreased with solvents, and hide splits and pieces were the raw materials used during this period. However, calf heads and legs were also common. The manufacture of ossein started in Germany after the first attempts in France.

Regarding the location for a gelatine plant, some basic requirements had to be fulfilled:

1. Nearby raw material supply, at that time mainly tanneries.
Long transport routes for material comprising 80% water was expensive, as it is today, especially as the raw material degraded rapidly during long periods of transport.
2. Adequate availability of fresh water wells for groundwater, springs, or good quality river water.
3. Location away from housing areas because of the odor of the raw materials and from the plant.
4. Close to a river or the sea shore, primarily for disposal of the effluent, but also to transport raw materials and final products.
5. For fuel for firing the boilers, the availability of wood and coal.

6. A location close to forests was also an advantage because of the requirements for the drying of the gelatine. A forest cleans the air of dust and also has a moderating effect on the climate. This was important because at that time no air conditioning for drying the air was available. Because of this, it is reported that the gelatine quality in winter months was superior of that of summer months. Some companies even manufactured only during winter.

1.2.3

Period 1901–1914

France

This was a period of rapid growth for the gelatine industry. In France, both *Coignet* and *Rousselot* developed their businesses very successfully. In 1901 *Rousselot* acquired the plant in Camp-Major near Marseille; after this they built the plant in Angoulême near Bordeaux, and in 1913 the construction of the plant in Isle-sur-Sorgue near Avignon was commissioned. And they also acquired an ossein plant and a glue and gelatine plant in Belgium. Angoulême and Isle-sur-Sorgue are still major manufacturing plants of *Rousselot* today.

In 1908, *La Société des Colles et Gélatines Francaises* was founded to manufacture hide gelatine and glue in two plants. One was destroyed during the war and was rebuilt in 1922 in Attichy to manufacture bone gelatine; it also specialized in the manufacture of hard shell capsule gelatine. The *Compagnie des Gélatines Francaises* (CGF) also became an important supplier of photographic gelatine. In 1971, the Attichy plant was purchased by *Rousselot*. It was shut down in 1981 after complete know-how transfer because of over-capacity within the *Rousselot* group.

Belgium

It is also surprising to see the development of the glue and gelatine industry in a small country like Belgium during this period. Eleven manufacturing companies existed at places around Vilvorde and Ghent, which are still the locations for large gelatine plants. So they must have been successful in their export business.

Germany

Four new companies went into operation. The Koepff brothers split their business into the *Göppinger Gelatine-Fabrik Paul Koepff* and the company *Koepff & Söhne* in Heilbronn, which in 1964 became part of Agfa AG. Also of importance was the foundation of the *Chem. Fabrik Calbe* which, after World War 2, became the major manufacturer of gelatine in East Germany until its liquidation in 1991. In 1911 the Göppingen company of Paul Koepff and the *DGF* company in Höchst merged, *DGF* thus becoming the largest manufacturer in Germany.

Because of the technology transfer, the production methods of the gelatine plants became more and more similar. The French companies had by this time lost their leading position. The business in gelatine and glue was quite profitable, and a lot of money was invested in expansion and modernization of the plants. In 1912/13, *DGF* built the most modern and largest gelatine plant in Europe and most likely in the world. In 1914/15, they produced 614 tons of leaf gelatine, of which 258 were for photographic purposes.

Great Britain

In England, a new company, *Cleveland Products*, was established in 1907 to manufacture gelatine from ossein. This company was also merged in 1920 into *British Glues and Chemicals* along with four other companies.

The Netherlands

The Dutch company *Lijm and Gelatine Fabrik Delft*, which was established in 1885 and started the production of bone glue in 1887, partly moved into gelatine production in 1911.

Australia/New Zealand

Until 1913, there was no gelatine production in the Pacific area. In that year, C. Davis, who had formed the *New Zealand Glue Company* in Auckland in 1889, changed another hide glue plant, which he had bought in Christchurch in 1909, into gelatine manufacturing, and *Davis Gelatin* was founded. The technology used was imported from England. The business progressed rapidly, and sales were soon extended to both Canada and Australia, so that it became necessary to import large quantities of raw materials from Australia.

United States

At the same time, the granulated gelatine of *Kind Gelatine* in Camden NJ, a company founded in 1908 by M. Kind, became very popular in the United States. Most of it was sold to the ice cream industry. Kind had learned how to make gelatine in his family business in Czechoslovakia.

In the same year the first gelatine was manufactured by the *American Glue Company* in their plant in Peabody MA. The Boston area was at that time very popular for its tanning industry, and Peabody was called "Leather City". Eastman Kodak soon became the principal customer for this plant. Some technical exchange was initiated to produce high-quality photographic gelatine. Some time before this, George Eastman almost went bankrupt when batch after batch of his photographic glass plates produced poor results because of inferior gelatine from one of his suppliers. In 1930 the Peabody plant was purchased by Eastman Kodak and renamed *Eastman Gelatine* to ensure access to the high quality gelatine from this plant. At this time, close cooperation between the photographic companies and their gelatine suppliers started. The emulsion recipes and the gelatine used fitted like a key in a lock. For this reason *Eastman Kodak* and *Stoess* also intensified their business relationship.

During this period, the use of imported bone from overseas started in Europe because the local raw material supply of bone and hides was not sufficient and quality problems were experienced.

In 1910/11 more than 23 000 tons of bone were exported from India to Belgium, and in 1913/14 this increased to 34 000 tons. In the same year 16 000 tons were exported from India to France and 10 000 tons to the United States. However, Brazil and Argentina also started to export bone to France, Germany and the United States.

The best estimates for the total production of edible and photographic gelatine in 1910 are approx. 2000 tons each in France and Belgium. In 1913, production in Germany was most likely about 3500 tons.

In 1913, the total gelatine production in the US is reported to have been approx. 5000 tons.

1.2.4

Period 1915–1918

The First World War had a very negative impact on overall gelatine production.

Europe

Raw material imports decreased, utilities were scarce, and production decreased in Germany in 1918 to about 1/3 of normal. The plants in Belgium also stopped production during the war. But in France, the *Coignet* plant in Isle-sur-Sorgue expanded, and very soon (in 1918) took advantage of the market demand. Mainly, the market for photographic gelatine was growing, which was related to the importance of the military use of the photography. However, quite apart from the war, there was still export business during this period.

United States

In the United States, *Knox* acquired an interest in the *Kind* gelatine plant in Camden NJ, because he saw his business mainly in marketing and less in production. Because of the cutting off of imports of ossein from Europe during the war, an ossein plant was built in Everett MA, which was in operation until the late 1940s.

Australia/New Zealand

In 1917, the first gelatine plant in Australia was established in a suburb of Sydney by the New Zealand-based *Davis Gelatine*. M. Davis wrote in his book on company history that the presence of many tanneries in this area and the plentiful supply of pure, fresh water in the sand beds beneath the property were the most important factors involved in selecting the location.

1.2.5

Period 1919–1939

Shortly after the end of the war, the gelatine industry recovered rapidly and expanded worldwide.

France

In France, *Rousselot* in 1920 acquired a further gelatine plant in Strasbourg and in 1931 the plants in Angoulême and Isle-sur-Sorgue; at the same time the business became a public company. Also in 1931, *Rousselot* started the production of photographic gelatine. A further step in their expansion was the foundation of a gelatine plant in 1936 in Clifford, England. However, during this period, France lost its leading position in the market, with a production of only approx. 4000–5000 tons in 1938.

Belgium

Substantial changes took place here. All companies expanded and, following a fusion, the company *Gélatines Hasselt & Vilvorde* was established, which had had a production of approx. 4000 tons before the war. At that time, Belgium was most probably the largest gelatine manufacturing country in Europe, with more than 6000 tons/annum.

In 1919, a bone-degreasing operation based on petroleum was established in Vilvorde, and in 1932 the name of *Pont Brûlé Etablissements Duché* was changed to *Pont Brûlé*.

Germany

Of course, Germany suffered most from the war. However, good personal contacts helped to regain and even increase some export business afterwards. The war had created severe supply problems for the *Eastman Kodak Corp.*, which had been supplied by *Stoess* and *DGF*. To develop this business further because of the good quality of the *Stoess* gelatine, the two companies founded a joint venture in 1921. This resulted in the *Odin* gelatine plant being built in Eberbach for the exclusive delivery of products for 20 years to the various plants of *Eastman Kodak*. In 1939, however, the plant was closed down because of the war.

DGF on the other hand had made a contract with *Agfa* to supply them with gelatine. In the same period, two new gelatine plants were built in Germany, but many others disappeared. From a total of 26 plants built since 1840, only 11 remained in 1934 because of the worldwide economic crisis in 1929/33. But the industry recovered again from approx. 1000 tons in 1919 and reached a peak in production in 1938 with approx. 5000 tons. However, margins were extremely low.

In 1929/31, the production of *Stoess* was moved from the Heidelberg plant to a new plant in Eberbach approx. 30 km away because of the need to expand.

Because of the growing demand for bone gelatine, *Ewald*, in 1928, built a plant for the manufacture of ossein and also started the production of photographic gelatine, which ceased in 1960.

Great Britain

The foundation of *British Glues and Chemicals* in 1920 was an important step, which consolidated the business of five gelatine companies.

Beside this, five more gelatine plants were established, of which that built in 1937/38 by *Leiner* in Treforest, Wales later became a very important factory. The

total production increased from 2400 tons in 1930 to 7000 tons in 1935, but the use of gelatine in England exceeded domestic production by approx. 3000 tons/ annum.

United States

Production showed rapid growth during this period. Thirteen plants manufactured more than 10 000 tons of edible gelatine in 1937, and a further approx. 3000 tons of edible gelatine was imported. For 1930, imports of approx. 600 tons of photographic gelatine from Germany were documented.

During this period, the use of pigskin as a raw material was started by the company *Swift* in Chicago, a meat packing company, as was the gelatine plant of *United Chemical and Organic Products (UCOPCO)* in Calumet City/Chicago, part of *Wilson & Co.*, another meat packer. This plant later became *Dynagel* and part of *DGF Stoess*. Also *Grayslake Gelatin*, which was founded in 1919, used pigskin as the sole raw material. This company ceased its production in 1982 because of the energy crisis. Eastman Kodak had had its own gelatine plant in Peabody since 1930 and built a further one in Rochester NY because of growing demand and quality problems with some purchased gelatines. The plant in Peabody still exists; the one in Rochester was closed in 1984.

AGFA in Germany later produced also its own gelatine, in common with *Konica* and *Fuji* in Japan.

In 1919 a gelatine plant was founded in Woburn, by five tanneries in that area. The first major customer was the owner of the *Jell-O* table jelly business. Production in 1920 was approx. 100 tons, and in 1921 it was approx. 300 tons. In 1922, a five-year contract was signed to supply 500 tons per year. The total production of that plant in 1924 was up to 1000 tons. In 1925, the *Postum Cereal Company*, later to be known as *General Foods*, purchased the *Jell-O* brand. Because of the high demand for gelatine for table jellies and to ensure a steady supply, *General Foods* acquired *Atlantic Gelatin* in Woburn in 1930, which then became the largest gelatine plant in the world after the war with about 10 000 tons/annum.

Kind Gelatine, Camden was also of great importance, as was the gelatine plant *Keystone* in *Dubuque IA*, founded by *American Agricultural Chemical*, which owned two more small plants.

Peter Cooper owned a gelatine plant (*US Gelatin*) in Oak Creek, using pigskin raw material. This was acquired in the mid 1970s by *Rousselot*. The raw material at that time was imported ossein.

Japan

The production trials for gelatine in Japan were started in 1926 by the company *Nitta Belt*. Local hide glue production had become important for the *Nitta* company after world war one because of import restrictions for many goods. As in many other countries, the production of glue started to be shifted into higher quality gelatine because, after the war, western products like ice cream, marshmallows, and jellies increased in popularity also in Japan. In 1930, a gold embargo was imposed, and the price of imported gelatine increased rapidly. *Nitta*

therefore started to produce gelatine on a regular basis in their Yao factory. Soon, several other companies followed suit. In 1932, *Nihon-Hikaku (Nippi)* evaluated the gelatine production based on hide splits in their Tokyo plant. In 1940 they built a new gelatine factory in Fujinomiya for photographic bone gelatine in close technical cooperation with Fuji. Because of growing demand, the Ministry of Commerce and Industry had, in 1933, decided to offer cash incentives for the domestic production of photographic film, which supported the foundation of Japanese photo manufacturers. These companies also started to search for close cooperation with domestic gelatine manufacturers. In 1934, *Rokuo-sya (Konica)* manufactured about 1000 kg per day together with *Yasu Photo Chem.* In 1937 a public grant was given to the Sanshine Chemical Institute because of the work of a researcher, G. Kobayashi, who had been working on photographic gelatine since 1920, to build a plant for photographic gelatine in *Takarazuka*, which, after the war, became part of the *Konica* company. The plant went into operation in 1939. Also, Fuji was involved during this period in investments in the *Japan Chemical Industries* to make gelatine in the factory, which became known, after 1941, as *Fuji Film Kawakami* when they acquired ownership. But this plant was closed in the 1950s. One of the reasons for the increasing photographic gelatine production was also the war between Japan and China in 1937, which made imports very difficult.

Australia/New Zealand

The *Davis* plants in New Zealand and Australia were also expanded during this period, and many overseas sales offices were established. During the 1930s, *Davis* supplied about 40% of the Canadian edible gelatine requirements and 55% of South Africa's.

South America

In the early 1920s, the first gelatine plant in South America was established in Brazil north of Sao Paulo by a British meat packer called *Angelo*. But the business went bankrupt after a few years. Until the 1970s, slaughter was predominantly done in the south of Brazil, which was therefore also the location of the tanneries. But it took another 20 years before a second and very successful round of gelatine production started in South America.

All the plants in the industry modernized on a step-by-step basis. Stainless steel started to play an important role in the equipment. Also, new equipment for jellifying the gelatine solution was invented to replace manual work in the production of gelatine leaves, which were still very common in Europe.

More and more plants changed from expensive hide raw material, which was in short supply after the war, to bones, which were imported at very low cost from India, Brazil, and Argentina.

In 1929/30, France imported approx. 11 000 tons from India, Belgium more than 50 000, Germany approx. 8000, the United States 11 000, and Japan 4000. In addition to this, the United States imported on average approx. 40 000 tons/ annum from Argentina in the period 1924/29.

1.2.6

Period 1940–1948

The Second World War affected the whole European gelatine industry tremendously. Several plants were more or less completely destroyed and were not rebuilt. Others, which were less damaged, re-started with different products and reduced production. During the war, what production there was concentrated on photographic gelatine because of its military importance, most of the other plants in Continental Europe having closed down.

France

In 1947, *Rousselot* started to export gelatine again, and in 1948 *DGF* in Germany followed with photographic gelatine and in 1950 with edible gelatine.

Germany

In 1939 the cooperation between Eastman Kodak and Stoess was discontinued and the *Odin* plant stopped production. Very little production remained.

Great Britain

In Treforest (Wales), a new plant was built by *Leiner* to manufacture hide gelatine. In 1943 they expanded the plant to produce bone gelatine based on imported bone from India and Pakistan, where they later installed their own bone mills.

United States

Production in the gelatine industry expanded strongly during this period because of the missing imports from Europe. In 1948/49, over-capacity was first reported, and in 1948 *Atlantic Gelatine* exported approx. 500 tons of photographic gelatine to Russia. In 1945, *Hormel*, a large meat packing company, established a gelatine plant in Austin MN based on pigskin from their own slaughtering plant. The gelatine plant was located in the same building. At that time, *Hormel* was the third meat packer to enter the gelatine business.

Japan

In Japan, the government reorganized the location of gelatine and glue plants to spread them over different regions and to ensure a reasonable size of the businesses (130 companies were merged into 9). In 1941, *Miyagi Chemical Industries* started to make gelatine from whale bones, and Fuji Film acquired the gelatine plant of *Japan Chemical Industries*. In 1944, *Konishiroku* (*Konica*) bought the San-shine Chemical Research Institute and changed its name to *Sanyo Military Use Photographic Gelatine Co.*, changing it again in 1948 to *Takarazuka Gelatine*. In 1945 *Nitta Belt* segregated its activities and established *Nitta Glue & Gelatin*.

Spain

In 1947 in Spain, a company named *Junca* started to manufacture hide glue in a little town close to Girona where many tanneries were located, because of a sur-

plus of water supply. Because Spain was relatively isolated at that time, it took about 20 years to develop into a regular daily gelatine production based on hides. Not far away, in Girona, another glue manufacturer, *Pagans*, founded in 1942, had a business based on bone. In 1948 their daily production of gelatine based on imported ossein was about 200 kg per day.

South America

The companies *Sairsa*, *Rodrigues Pinto*, and *Rebiere* were founded in the early 1940s in Brazil to manufacture glue and some gelatine. *Sairsa* and *Rebiere* had already been part of a tannery businesses and *Rodrigues Pinto* was also built close to a tanning facility. All were located within a radius of about 100–300 km north west of São Paulo. But as the companies grew in production they were forced to source their raw material hundreds of kilometers away because the tanneries had moved with the cattle herds further north. *Rebiere* is still an independent family business, *Sairsa* became a part of *DGF Stoess* and *Rodrigues Pinto* was acquired by General Brands, then Nabisco and today Kraft General Foods.

Just after the war, the American *Stauffer Chemicals* completed a new gelatine plant in Buenos Aires to serve the local market. In 1965 *Rousselot* became a shareholder in this company.

1.2.7

Period 1949–1972

France

After the war, *Coignet* and *Rousselot* were dominant in the French gelatine industry. The *Weishardt* company was of less importance until the 1960s. But then they expanded and started to export larger quantities of pigskin gelatine, mainly to Germany. Nevertheless, by the end of the war, *Weishardt* had serious cash flow problems and *Rousselot* acquired 30% of the shares in the company.

One of the shareholders in the *Coignet* business, which had six plants for glue, gelatine, and bone degreasing, was at this time the large industrial company *Ugine Kuhlmann*, and this company acquired the business completely in 1965.

Rousselot developed its business further with its four French plants for ossein and gelatine. In 1962, the gelatine plant in Ghent was acquired from *Union Chimique Belgium*. In 1964, the ownership in *Rousselot* was 75% the *Rousselot* family and 25% the large French St. Gobain corporation, a leader in the chemical industry. In 1965, *Rousselot* acquired a shareholding in the Argentinian *Stauffer* company to have better access to the South American markets. In 1968 the glue, gelatine, and raw material businesses of *Rousselot* and *Ugine Kuhlman* merged, *Rousselot* retaining a 66% majority.

Belgium

After the war, six plants remained in Belgium. The two largest in Ghent and Vilvoorde are still important manufacturing sites.

In 1958, the ownership of the Vilvorde plant changed to *Pont Brûlé*, the majority share of that company being acquired in 1964 by *Produits Chimiques de Tessenderlo*, a large chemical group which was itself mainly in the ownership of a French government-controlled company. In 1972, the gelatine-related activities were split off and became *PB Gelatines*. In 1972, the Vilvorde plant made its first attempt to move from bone and cow hides to pigskin.

The plant of *Hasselt & Vilvorde*, also a major producer of leaf gelatine for household purposes, was closed in 1971 after acquisition by *Rousselot*, and the plant of *TMB (Tannerie & Maroquinerie Belges)* in Zaventem was closed in 1978. Another plant in Zaventem (*Colles et Gélatines Zaventem*) was acquired by *Pont Brûlé* in 1970 and closed after a short time.

Germany

The partition of Germany after the war placed three of its 11 companies in East Germany. Two of these plants did not start up again, and only the *Chemische Fabrik Calbe* became a state-owned company to supply the German Democratic Republic (DDR), other East European countries, and to some extent also Russia, mainly with photographic gelatine based on hides and bone. In addition, some pigskin use followed in the 1980s. After Germany's reunification, the company went bankrupt in 1992 because *DGF Stoess* were not able to acquire the plant under acceptable terms.

DGF repaired the Göppingen plant and started to expand soon afterwards. In 1973, a brand new plant had double the capacity of the previous one. The Eberbach plant of *Stoess* was also modernized and expanded in the years 1966/67. In 1965, *Stoess* acquired the *DGF* shares, combined the activities in the market, and merged the two companies in 1972. By this time the *DGF Stoess* group was again a worldwide player in photographic, pharmaceutical, and edible gelatine.

In the Eberbach plant, a large, modern semi-automatic drier for leaf gelatine was installed in 1967 after several less successful trials in the Göppingen plant several years before.

The *Koepff* plant in Heilbronn (result of the business split of the *Koepff* brothers in 1904) was also repaired and expanded, but on a step-by-step basis mainly with money from their main customer *Agfa*, who bought shares in the company. It is reported that in 1964 the shareholding of *Agfa* reached 75%. Thus, the company was renamed, and the name *Agfa* appeared for the first time in the new name.

After 1965, the *Chemische Werke Pfeffer* in Memmingen changed their production from glue to gelatine. But in 1974 the plant was closed by the regulatory bodies because of environmental problems.

In 1969 the *Reinert* family, a large trader of edible gelatine, acquired the small gelatine plant *Herold* (a *DGF* plant before the war) and built a new pigskin gelatine plant there in the 1970s.

In 1951, the glue plant of *Ratjen* in Nienburg also started a gelatine production, which was soon expanded, and the plant was modernized. In 1965, the glue and gelatine businesses were separated, and a new company *Nienburger Gelatine* was

formed. Both businesses were acquired by the pharmaceutical company Schering in 1969, which was mainly interested in the glue business and had no expertise in the gelatine field. Thus, in the early 1970s, they started to look for a potential buyer.

The *Ewald* company ceased the production of photographic gelatine around 1960 and concentrated more on leaf gelatine for households, bakeries, and catering. In 1971 the conversion of the raw material from hide splits and bone to pig-skin started.

Great Britain

British Glues developed very successfully and in 1964 was the largest gelatine manufacturer in Europe. Part of their success was the establishment of modern bone degreasing plants in England, Austria, and the Netherlands for domestic bone. This gave them some quality advantages in photographic gelatine compared with the imported Indian bone. From 1949 through 1958, all plants were completely modernized. In 1968 *Croda* acquired *British Glues*, and the latter name disappeared. *Croda* was founded in 1925 as a chemical company to manufacture raw materials for the cosmetic and chemical industries. General chemicals and dyes, emulsifiers, and fat derivatives followed. The gelatine acquisition was carried out to add a further important pillar to the portfolio shortly after the company went public and had sufficient funds available.

Leiner also expanded the plant in Treforest, mainly based on imported bone. In 1956, a new plant in Canada was built, but this shut down again after a short period because of a lack of raw material. Most of the equipment was shipped to Brazil (Cotia/Sao Paulo), where a new *Leiner* company, *Cobrige-Compania Brasileira de Gelatinas*, started production in 1959. Also in this period, *Leiner* founded a gelatine production enterprise in India (today *Shaw Wallace/Narmada*). In 1961, *Leiner* became the largest bone gelatine manufacturer in the world. After 1959, *Leiner* tried to manufacture pigskin gelatine; this proved to be a fiasco and forced the company into bankruptcy in 1980.

The small *Rousselot* plant in Clifford was not of importance at that time, and the same was true of *Gelatine Products* in Runcorn, the former Cheshire Glue Co., which was acquired in 1991 by *DGF Stoess*.

The war had changed the position of Great Britain in the world market completely. In the 1930s, imports had been approx. 2500 tons/annum and exports approx. 250 tons/annum. In the 1960s, imports dropped to approx. 600 tons/annum and exports increased to approx. 2500 tons/annum.

The Netherlands/Switzerland

The *Delft* company in the Netherlands changed from glue to gelatine, and production increased slowly to about 1000 tons/annum.

In Switzerland, the company *Geistlich* started to produce a small amount of gelatine after being a traditional glue manufacturer since 1909.

The *Winterthur* plant in Switzerland was liquidated in 1971.

Sweden

In 1967, the KemaNord Group, a large chemical manufacturer, acquired the *Stids-vigs & Hälsingborgs Limfabriker*, a company which had been producing about 1000 tons/annum of edible gelatine from hides and bone since 1957. A new plant (*Ex-traco*) was built in 1971 with the target of producing 3000 tons/annum, mainly based on pigskin. In 1976 the target was exceeded, but the distance to the raw material sources, and hence the transportation costs for frozen pigskin, created financial problems.

Italy

In this period, a small plant, *Barbero* in Sta. Vittoria d'Alba, was founded, but it went bankrupt in 1968 and was acquired by F. Vezza. It then became *Italgelatine* with about 1000 tons/annum production after some investment.

In Torino the company *Fermonte* produced approx. 700 tons/annum of photographic gelatine. *Fermonte* was owned by the photographic company Ferrania Spa, which itself was owned by 3M. The *Fermonte* plant was sold in 1973 to the third Italian gelatine manufacturer during this period, *Lapi*, with its plant in Empoli, near Pisa, which had a production of approx. 700 tons/annum at that time.

Spain

In 1960, the owners of *Pagans* decided to focus completely on gelatine and divested themselves of their other businesses. In 1967, they expanded their degreasing and demineralization capacity and brought up their production to 1200 tons/annum, but they ran into severe financial problems in paying for this investment.

The other manufacturer, *Junca*, erected a new plant in the outskirts of the town in 1953/54. At the end of the 1960s the production of leaf gelatine was also started for the domestic market only. The first gelatine exports of this company were made in the early 1970s to Egypt and to the USA.

Eastern Europe

There are some indications that in those years very small technical gelatine production facilities existed in Yugoslavia, Czechoslovakia, Poland, and Romania. Most of these disappeared in the years following because of inferior technology and their small size.

Russia

No details about the foundation of the Russian gelatine industry are known. However, it can be assumed that some plants did exist during this period, founded before the war. Total production of about 5000 tons/annum was reported for the end of the 1960s.

United States

Because of the lack of imports during the war and the growing use in all applications, the gelatine industry expanded rapidly. In 1949, *Atlantic Gelatin* manufactured approx. 10 000 tons/annum. The fairly unrestricted access to fresh pigskin

impelled the industry to make their plants much larger. However, only one new plant was built in this period, the new pigskin gelatine plant of *Kind & Knox* in Sioux City IA in 1966. In 1937, a total of 13 plants produced approx. 10 000 tons/ annum; in 1953 it was approx. 25 000 tons, but in 1974 only approx. 19 000 tons/ annum were produced by 11 plants because imports had resumed. From 1971 to 1974 production had to be reduced because of an oversupply situation.

In 1972 *Lipton*, a *Unilever* company, acquired *Kind & Knox*, with their plants in Sioux City and Camden, from the Knox family. Their main business target was the retail market, in which the “Knox Sparkling Gelatin” packs for households played a dominant role. Therefore they sold the Camden plant in the middle of the 70s to Peter Cooper.

In the same period the gelatine plant in Dubuque became *Keystone Gelatin* and the gelatine plant in Calumet City became the *Gelatin Division of Wilson*, a large meat packer. In 1978 the *Rousselot* company bought *US Gelatin* with its plants in Oak Creek WI and Camden NY from Peter Cooper and continued international expansion.

Canada

A large Canadian integrated meat products company, *Canada Packers*, built a gelatine plant in Toronto in the 1950s mainly based on their own pigskin. In 1970 it was expanded to make 1500 tons. For a brief period it also manufactured some hide gelatine.

Australia/New Zealand/South Africa

The plants in Australia and New Zealand were further modernized and expanded, and in 1970 the first semi-automatic continuous extraction process was constructed in Botany, Sydney.

Because of the limited raw material sources in Australia and New Zealand, all kinds of raw materials besides pigskin were used – sheep legs, dried hide splits and pieces, wet hides, hairy material, but no ossein.

In 1951, *Davis* acquired 70% of the shares of the small gelatine company *Gelatex* in South Africa, which then became *Davis Gelatine Industries*. In 1971, the remaining 30% were purchased and the plant modernized and expanded.

Japan

In 1954, *Fuji Film* decided to curtail their own gelatine production, close their Kawakami gelatine plant, and concentrate on the purchase of gelatine from outside but in close technical cooperation with their Japanese suppliers.

In 1955, *Nippi* doubled their production by means of a large modernization and expansion program.

In 1957, *Tadera Glue* changed its name and *Asahi Gelatine* was founded to produce high-grade glue. In 1960 it became a cooperative factory of *Nippi* and entered a technical and sales agreement. In 1971 the factory was rebuilt and expanded and the production of acid gelatine started.

In 1960, *Nitta Glue and Gelatin* changed its name to *Nitta Gelatine*.

In 1968, *Yamaguchi Trading* and *Nitta* established a JV company, *Hikone Gelatin*. Their gelatine was exclusively marketed by *Nitta*.

Because of its dependence on imported raw material, *Nitta* started, in 1970, to make ossein with a partner in Thailand, and *Takarazuka Gelatin* did the same in 1973 with a partner in India.

Gelatine production of all types in Japan was reported in 1966 to be 3600 tons; in 1974 the confirmed figure was 6,600 tons.

But Japan was still dependent on gelatine imports for the photographic industry. So was it not surprising to see an import duty of 20% for edible and pharmaceutical gelatine but only 3.5% for photographic gelatine.

Mexico

In 1959, Mexican investors, under the leadership of A. Olazábal, founded *Industrias Coloidales* approx. 2700 m above sea level in Toluca, close to Mexico City. This was later modernized with the assistance of *PB Gelatines*. The production was based on pigskin. Some time later Olazábal left the company. Since 1990, the company has been known as *Coloidales Duché* and is controlled by a group of French investors. This is a result of certain banking turbulences.

In 1968, A. Olazábal founded a further gelatine plant, *Panamericana de Grenatina*, also in the Toluca area and approx. 8 km from his old plant. The reasons were the weather conditions and the water availability. At the beginning, the plant processed 100% pigskin; however, during the 1970s and 1980s, hide and bone processes were developed for cost reasons.

Also in the 1960s, *Grenatina Diamante* was founded in Leon in the North of Mexico in the predominantly tanning area. The plant was and still is of little importance outside Mexico. The same is true for *Grenatina Regia*.

However, probably the first gelatine plant in Mexico was *Progresa*, founded in the 1950s in Leon. This small plant still exists. Because of the importance of the table jelly market, Mexico has developed a relatively large gelatine production.

Brazil

In 1965, *Leiner* continued their world-wide expansion and founded a gelatine plant in Cotia, a suburb of Sao Paulo, a location which was also close to slaughterhouses and tanneries.

At this time, another gelatine plant was built in the South of Brazil in Estancia Velha by *Inbragel*. This was later taken over by *Leiner do Brazil*.

Colombia

In 1930, E. Minski and I. Gilinski founded a tannery in Colombia. In the late 1960s and early 1970s, two gelatine plants were built, one in Baranquilla (*Gelatinas de Colombia-Gelco*) by Minski and Gilinski and the other in Manizales (*Progel*) by Nabisco. For the latter plant, *Davis* provided the production know-how and owned a 30% stake in the company.

India

In 1948, the company *Rallis* was founded to make chemicals. Most probably late in the 1960s, their affiliated company *PPI* (*Protein Products of India* – at first a large ossein manufacturer) started to become a gelatine manufacturer based on *Rousselot* technology after *Rousselot* acquired a 14% share holding in 1969. In 1983, when the use of Indian bone became more and more questionable, *Rousselot* sold its share, and *PPI* was renamed *Rallis*.

Since 1961, *Leiner* has had a small production plant in India, the company *Leiner-Knit Gelatine* in Jabalpur. The partners previously owned tanneries in that area. Some years later, the large industrial group *Shaw Wallace* became a partner, and the plant was modernized and expanded and became *Shaw Leiner*. After several financial irregularities in that operation, all the English employees, including Mr. Leiner, had to leave the company in 1970. Leiner lost his shareholding completely in 1978 and the company became *Shaw Wallace Gelatines*.

Further, *Raymond Glues & Chemicals* in Baroda was founded in 1964. An ossein plant was built, followed by a gelatine plant.

But besides this relatively small production in gelatine itself, the Indian companies became more and more important as suppliers of crushed bone or ossein for the world's gelatine industry. However, in the 1950s, the import of crushed bone was restricted because, when unloading a vessel in France (Dunkirk), several dock workers were infected with anthrax and died. The same happened a few years later in Hamburg. This created an increased preference for the more sanitized ossein. The accidents also created a public discussion about the source of such bone material (animals that had not been slaughtered but simply died), and as a result it was used more for photographic gelatine – at least until the industry realized that Indian bones are not the best source for high-quality inert photographic gelatine.

Korea

In 1963, *Sammi* was established for the purpose of producing and distributing edible and pharmaceutical gelatine. The raw material at that time was most likely hide split, because many tanneries were located in Korea. This privately owned plant still exists today.

The most important events in this period were the following:

1. *Rousselot* and *Leiner* started to become real international companies with production sites overseas.
2. Large industrial groups entered the gelatine business for different reasons, so several private ownerships disappeared.
3. The importance of safe and secure raw material supplies was recognized because of the growing output of the industry. Local sourcing became more and more difficult. Several companies invested in affiliated businesses domestically and abroad to collect raw materials and also to install the first pre-treatments like degreasing and demineralization of the bone material.

4. Pigskin was used in Europe by many companies as an additional or alternative raw material, mainly for edible gelatine.
5. The demand for photographic gelatine showed a constant growth potential, but the main driving force in the markets in the years after 1960 was the sharply rising demand for pharmaceutical capsule gelatine, including microcapsules. In Europe, fruit gummies became very popular, and with the dairy industry a new market was created.

1.2.8

Period 1973–1993

France

In 1973, the name *Rousselot-Kuhlmann* changed again and the company became *Rousselot* by merging with its raw-material-collecting company *Soporga* and the acquired *Compagnie des Gélatines Francaises*. In 1977, the owner family of *Rousselot* had tremendous fears about the intention of the Socialist Party to nationalize important French businesses. As a result, they decided to sell the business. Because of the first oil crisis, the petroleum industry was looking into alternative businesses, and one of the major projects was to make protein from crude oil by bio-fermentation. Thus, there was general interest in proteins at that time. A potential buyer was found quickly – *British Petroleum*. However, the French government intervened and presented an alternative buyer, *ATO-Chemie*, a subsidiary company of *ELF-Aquitaine* and *TOTAL*. In 1985, the name changed again because of a restructuring of the businesses of *ELF* and the newly founded state-owned *Sanofi* company. *Rousselot* became a part of *Mero-Rousselot-Satia (MRS)*, with a large portfolio of other products including other hydrocolloids. The next name change happened in 1988, and *MRS* became *Sanofi-Bio-Industries (SBI)* in the sole ownership of *Sanofi*. In a restructuring program, *Rousselot* closed the plants in Attichy (France) in 1981 and Clifford (England) in 1980, because they decided to concentrate all investment in their Camp-Major and Isle-sur-Sorgue plants. In 1975 the total production of *Rousselot* in France and Belgium was approx. 20 000 tons/annum, but further expansion was undertaken and in 1985 the total production was approx. 25 000 tons. In 1989, the Dubuque plant of *Keystone Gelatin* was acquired, and in 1990 the Argentinian plant of *Stauffer* was completely taken over. This expansion program was completed with the acquisition of the *Pagans* plant in Spain in 1991.

During this period, *Weishardt* expanded further and was reported to produce approx. 3500 tons in 1982. Export businesses were developed, and since 1981 the company has been trying, unsuccessfully, to produce photographic gelatine.

Belgium

In 1981, the last production of limed bone gelatine was made in the Vilvorde plant of *PB Gelatines*. All this production was moved to the acquired plant in

Nienburg, Germany. The plant became mainly a pigskin gelatine plant apart from some remaining acid bovine bone production. Between 1987 and 1993, substantial investment was made in Vilvorde in the bone-degreasing unit and the gelatine plant, and the capacity now exceeds 9000 tons/annum. Also, the Ghent plant of *Rousselot* (manufacturing mainly pigskin gelatine) was further modernized and expanded to produce 10 000 tons/annum.

Germany

In 1973, *DGF Stoess* acquired more than 25% of the shares of the largest bone collector in Germany, *Scheidemandel*, to safeguard the raw material supply for future expansion. At the same time, the site of the *Pfeffer* plant in Memmingen was acquired, which had previously been shut down by the authorities. On this site, the most modern bone degreasing plant in the industry was established, followed, in 1977, by an acidulation plant. After further purchases of *Scheidemandel* shares, their gelatine plant in Minden was integrated by *DGF Stoess* in 1981 and completely modernized, and the production portfolio changed from hide to pigskin gelatine. Together with *Scheidemandel*, a new raw material collection company, *Rohage*, was founded, because, after several shortages in supply, it had become more and more obvious that a secure raw material supply at reasonable prices was the most important key to the success of gelatine companies. In 1990, *DGF Stoess* tried to acquire the *Gelatinefabrik Calbe* in the former East Germany, but, because of previous environmental problems with the soil, the negotiations failed and the plant went into receivership. In 1978, *DGF Stoess* decided to expand outside of Germany. It acquired a minority shareholding in the Australian *Davis* group and started a 50/50 joint venture with *Davis* in the USA by acquiring the old gelatine plant from *Wilson* in Calumet City and building a brand new pigskin gelatine plant (*Dynagel*). Soon, further acquisitions followed – in 1983 in Brazil (*Sairsa*), in 1991 in Great Britain (*Gelatine Products*) and Sweden (*Extraco*), and in 1992 again in the United States (*Kind & Knox*). With a worldwide production of approx. 36 000 tons/annum in 1993, the difference to the *Rousselot* group had become insignificant. In 1979, the production of hydrolyzed gelatine in a separate plant in Eberbach was started. To expand these activities, a smaller operation for hydrolyzed gelatine was acquired in Finland (*Lappro*) in 1989, but the growing lack of hide splits in that area during this time forced its closure in 1998.

After the Schering group had realized that gelatine production did not fit into their business interests, they sold the plant to *PB Gelatines* in 1975, and over time the production portfolio moved more and more from hide gelatine to bone gelatine.

Great Britain

The *Leiner* production was continuously increased from approx. 6000 tons/annum in 1973. In 1979 it was in the region of 8000 tons/annum. *Leiner* had tried to make pigskin gelatine for many years because of the high cost of the imported bone and the growing demand for high grade gelatine of this type.

However, because of poor technical investments, lack of know-how and the need to import the pigskin, the company encountered financial difficulties and went into receivership in 1980 despite the fact that the Welsh Development Agency had earlier invested 2 million pounds in subsidies. The whole international *Leiner* group was split into separate pieces and put up for sale. A management buy-out by five managers followed, *Leiner Gelatin* was founded, and a further 1 million pounds in subsidies were provided. These, however, disappeared somehow and were subject to a parliamentary investigation. The whole site was reduced, with some bone gelatine production remaining, but the next bankruptcy took place in 1985. At this point, the plant was acquired, and the company became *PB Gelatines UK*.

Croda upgraded their plants in Widnes and Luton and implemented a new process to use chrome shavings from the leather industry to make low-grade gelatine. With more than 5000 tons/annum being produced, *Croda* became an important manufacturer of mainly photographic and pharmaceutical gelatine.

As mentioned before, *Rousselot* closed their plant in Clifford in 1980 because of lack of size and some environmental problems.

Gelatine Products had gone through a costly modernization program in the late 1980s and had established itself successfully on the market for edible hide gelatine in Great Britain. It had previously been in the ownership of a large British food company which had run into financial problems and was forced to sell off several of its companies. *DGF Stoess* took this opportunity to buy the company and to become, together with the imports of pigskin gelatine from Germany and Sweden, the leading food gelatine supplier in Great Britain.

Sweden

After the first difficult years, *Extraco* became a successful manufacturer of high quality pigskin gelatine and expanded its capacity continuously (in 1987 a quantity of 5000 tons/annum was reached, in 1989 7000 tons, and in 2001 12 000 tons), but it always had problems getting enough raw material from within short distances because it did not have its own raw-material-collecting company. After German reunification, it went into a contract manufacturing agreement with *DGF Stoess* under which they got German pigskin and sold the manufactured gelatine back. This way, a close cooperation started, and when their parent company (*Nobel Industries*) was forced for financial reasons to sell *Extraco* together with 15 other businesses, *DGF Stoess* acquired them in 1991. The combination with the raw material organization of *DGF Stoess* secured their raw material supply for future expansion.

Italy

At this time, *Italgelatine* expanded their plant to approx. 3000 tons/annum capacity and started to use pigskin, as many of the Italian tanneries had been closed by the authorities because of pollution by their waste water. As a result, hide splits became in short supply.

Spain

In 1975, *Pagans* was acquired by the Belgian DeSmeet group, one of their equipment suppliers, as they could not pay their bills. DeSmeet decided to start the production of pigskin gelatine and to move the plant out of town. In 1986 the new plant was inaugurated, and in 1991 the business was sold to *Rousselot*. Also, *Junca* started to change away from hide splits to pigskin because the breeding of pigs increased constantly in Spain and generated additional raw material for the gelatine industry. Besides this change, *Junca* also started to make hydrolyzed gelatine in liquid and spray-dried form.

Eastern Europe

At this time, there were three small plants in Czechoslovakia, of which one, founded in 1982, was acquired in 1995 by *Weishardt* and became *Gelima*. There were three plants in Poland and one in Romania. In Poland, several attempts had been made to increase gelatine production by building new plants with state subsidies, but most of the money mysteriously disappeared, and, after a large corruption scandal (in the press at least), one of the persons responsible was sent to prison. *Lapi*, an Italian manufacturer, invested in the Romanian plant unsuccessfully and the plant was closed.

Russia

In the 1980s, five plants existed, with a total production of approx. 6000 tons/ annum. However, they never showed up on international markets. The main site was *Kazan*, which accounted for 50% and was the center for photographic gelatine next door to the largest Russian plant for the manufacturing of photographic films and paper.

United States

In the United States, the business of *US Gelatin* was bought by *Rousselot* with the two production sites in Oak Creek WI and Camden NJ. In 1980, the Camden plant was closed and the production transferred to Oak Creek, which was also closed in 1985. Thus, the name *US Gelatine* disappeared from the market. Further restructuring took place in the United States. In 1979, *Hormel* started up a new gelatine plant in Davenport IA and the Austin MN plant was closed. As well as standard gelatine, they also started to make hydrolyzed gelatine.

At the same time, Lipton decided to build a new bone gelatine plant, which started up in 1978, and was directly connected to their pigskin plant in Sioux City IA. During the 1980s *DGF Stoess* had tried a few times to convince Lipton about a joint venture or to sell their business, but without success. However, suddenly, in 1991, Unilever decided to concentrate on their consumer business and to sell *Kind & Knox*, which made mainly gelatine for “industrial use”. After an auction process, which lasted many months, the business was sold to *DGF Stoess*, not so much because of the highest offer, but because of the best business concept. After this acquisition, *DGF Stoess* became equal in size to *Rousselot*, with about an 18% share of the world market.

Canada

In 1990, *Canada Packers* sold their gelatine plant in Toronto to *Nitta*, and it was named *Cangel*.

Australia/New Zealand/South Africa

In 1983, the *Davis* holding company was acquired by the food company *Fielder Gillespie* and lost its independence. A few years later, the new company was again taken over by *Goodman*, and in 1987 *Goodman Fielder* acquired a 60% stake in *Leiner do Brazil* and the company *Leiner Davis* was formed. The remaining part of this business was then bought in 1992, including the new Argentinian plant. In 1991, the Australian plant in the Sydney area had to be closed because of environmental problems, and a new plant for hide gelatine was built in Queensland by transferring much of the dismantled equipment. Because of many technical problems, it took until 1995 for the first production batch to emerge from this plant.

Japan

In 1974, *Nihon-Hikaku* became *Nippi*, and established an affiliated company in India to produce ossein. *Nitta* did the same in 1975 by establishing *Kerala Chemicals and Proteins (KCP)*. In 1978, the glue plant of *Koei Chemicals* was changed to gelatine production, with technical and business cooperation with *Nitta*, which also sells their gelatine. In 1983, *Asahi Gelatine* also started to make alkaline gelatine and, in 1986, collagen powder gelatine. In 1987, a second production line was added.

In 1988, *Takarazuka Gelatin* changed its name to *Konica Gelatin*. *Nitta* acquired a gelatine plant in Canada (*Cangel*) from *Canada Packers*.

In 1980, the total gelatine production in Japan surpassed 10 000 tons for the first time, reaching 15 000 tons in 1990.

Mexico

After being mainly a pigskin gelatine producer, *Duché* changed their production in 1992 for cost reasons to acid hide processing, and finally, in 2002, they started to manufacture alkaline-treated hide gelatine, which is their main product today.

Brazil

After the bankruptcy of *Leiner* in Great Britain, the Brazilian operation was taken over by the management and some investors under the leadership of H. Cobelo.

In 1983, the plant of *Inbragel* in Estancia Velha in the South of Brazil was acquired, and in 1985 the new Maringá plant was established. The attempt to produce bone gelatine in Maceio failed. The plant started up in 1986 and was shut down in 1989. The Cotia gelatine plant was also closed in 1989, but the Maringá plant expanded.

In 1983, *DGF Stoess* expanded to South America and acquired a 50% shareholding in the *Sairsa* hide gelatine plant in Mococa, north west of São Paulo, an attempt at a shareholding in *Leiner do Brasil* some years before having failed. The

plant was renamed *Sairsa-Gelita* and was completely modernized with German know-how and technology.

Ecuador

In 1981, Nabisco founded a plant (*Gelec*) in Ecuador with partner *Davis Australia* (33%) to secure the supply for their jelly business in the Andean area. It was and still is a very small plant producing about 800–1000 tons/annum, which has always had problems securing its raw materials.

Argentina

Rousselot acquired the *Stauffer* plant completely and started a modernization program. In 1987, the construction of a new plant was started in Santa Fe (*Leiner Santafesina de Gelatinas*) owned 40% by the Brazilian Leiner group and 60% by *Goodman Fielder* (*Davis*). In 1991 *Goodman Fielder* acquired 100% of the shares, and it became *Leiner Davis Argentina* with a production of approx. 2000 tons/annum.

India

In 1973 *Takarazuka Gelatin* formed a joint venture with *India Gelatin & Chemicals* to manufacture ossein. In 1975, *Kerala Chemicals & Protein (KCPL)* was founded with the shareholders Kerala State (26%), Nitta Gelatin (25%) and Mitsubishi Corp. (10%). The rest of the shares were public. Their business was to make ossein and pre-treated limed ossein – an intermediate for bone gelatine production exclusively for *Nitta*.

Korea

Over the years, the production of *Sammi* has been increased from approx. 500 tons/annum to more than 2000 tons/annum today of mainly hide gelatine, but some pigskin gelatine is also manufactured. In 1980, the plant of *Kyunggi* was established to make hide gelatine. With the technical assistance of *Nitta*, the plant was modernized in the late 1980s and is now called *Highgel*. In 1988, a large manufacturer of capsules in Korea, *Su-Heung Capsule Co.*, decided to start their own gelatine operation (*Geltech*) to secure a steady supply of hide gelatine. At that time Korea was a good place to make hide gelatine because many tannery businesses had moved out of Europe for environmental reasons and this business now boomed in Korea. But now Korea is experiencing a shortage of raw material because many tanneries have meanwhile moved to China.

China

There is very little documented information about the Chinese gelatine industry during this period. Some notes were provided by the industry association about the state-owned industry, but names and places of plants were represented in different ways at different times, mainly when China decided to change the way all names were to be written in English. There was also a mix-up between gelatine and glue. The best estimation in 1982 was a total production of 2000 tons/annum

in approx. 30 locations. The plants always sourced their raw material locally because of the totally fragmented slaughtering business, and they sold their products also in very limited area around the plants.

However, this has changed completely over the past 15 years. During this period, the industry has become more and more international through acquisitions by the leading companies. A clear tendency to move more to pigskin and less to

Table 1.1 Gelatine production in the different areas in 1974 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	25	0	15	0	3	0	43	33.1%
Beef hide	17	3	5	5	8	5	43	33.1%
Bones	20	9	11	0	4	0	44	33.8%
Total	62	12	31	5	15	5	130	

Table 1.2 Gelatine production in the different areas in 1986 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	37	1	22	0	12	0	72	39.3%
Beef hide	10	2	6	17	9	6	50	27.3%
Bones	25	10	10	1	15	0	61	33.3%
Total	72	13	38	18	36	6	183	

Table 1.3 Gelatine production in the different areas in 1993 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	47	1	23	4	4	0	79	37.3%
Beef hide	16	3	2	29	6	4	60	28.3%
Bones	30	8	11	0	24	0	73	34.4%
Total	93	12	36	33	34	4	212	

bovine raw material could be seen. The necessary investments in environmental activities, effluent plants, and odor and noise protection increased everywhere, at least when a local production was purchased by a big gelatine maker. All activities related to raw material sourcing were allocated a higher priority because the growth of the industry generated more competition in the raw material markets with their limited size.

1.2.9

Period 1994–2005

France

In 1995, Sanofi decided to concentrate their business completely on pharmaceuticals and to sell *Sanofi-Bio-Industry*, of which gelatine was only a part. The buyer was a German chemical industry group (SKW Trostberg). The result was the next name change, to *Systems-Bio-Industries*, which helped to keep the abbreviation (*SBI*) alive. But this was not kept for long, because in 1998 the company was again renamed *SKW-Biosystems*, directly linked to the German parent company of the group (DEGUSSA); but the headquarters remained in France and they also kept the traditional name *Rousselot Gelatine* for their products. Suddenly, the number one and two of the world in gelatine were in German ownership, and this made competition even stronger. Finally, in 2002, this business was acquired by the Dutch Sobel Group, a company active in meat packing, rendering, and capsule manufacturing. The fifth name change in 12 years then took place, and the company was named *Rousselot* again. However, their business activities were also subject to many changes. In 1996, they became the first company to move into China, establishing a joint venture in *Kaiping* with a local producer to make bone gelatine. In 2000, *Rousselot's* total production was a little over 45 000 tons. In 2003, a further step followed with the acquisition of a 70% share in a pigskin gelatine plant (*Sanfan*) in Wenzhou. In 2003 they decided to shut down their operation in the Netherlands (*Delft*), which had been previously acquired by Sobel. And in 2004 the traditional photographic gelatine production plant in Camp-Major was shut down because of the declining demand for photographic gelatine.

In the same period, the *Weishardt* group expanded further and doubled their production of pigskin gelatine in France.

Belgium

Because of the BSE discussion in Europe, all bovine material was banned from the *PB Gelatines* plants in 2001. In 2003, the former *Leiner Davis* plants in Argentina and in the United States were acquired by *PB Gelatines*, which ranked them third in the world market.

Germany

DGF Stoess continued to modernize and expand their German plants. In 2000, the gelatine plant of *AGFA* in Heilbronn, the previous *Koepff* plant, was acquired from *AGFA*, based on a long-term exclusive supply agreement. After the bank-

ruptcy of AGFA Germany in 2005 and the declining demand for photographic gelatine in general, the plant was shut down in 2006. In 2002, approx. 75% of the business of *Leiner Davis Gelatin* (Mexico, Brazil, Australia, New Zealand, and South Africa) was acquired, and *DGF Stoess* became, by a substantial margin, the world's largest gelatine manufacturer, with a worldwide network of production sites. This process was completed in 2006 when the company established itself in China. In 2005 the company decided to change its name and to make their product brand *GELITA* also the company name, not only for the parent company in Germany but also for all their gelatine plants around the world.

Because of the changing demand for gelatine and the reduced availability of hide splits, the production of pigskin gelatine was implemented in 2001 in the Nienburg plant of *PB Gelatines* after a large expansion program which brought the capacity of this plant up to more than 5000 tons/annum. This plant also became an important manufacturer of hydrolyzed gelatine.

Great Britain

The BSE crisis had hit the gelatine industry around the world but of course the one in Great Britain most. Even gelatine based on imported raw material but made in Great Britain could not be sold any more for edible and pharmaceutical applications. As a result the DGF Stoess plant *Gelatine Products* was shut down in 2000, the Luton factory of *Croda* in 2002, and their Widnes plant in 2004. And with these actions, two well-known gelatine manufacturers disappeared from the map, and one of the important gelatine manufacturing countries in history became insignificant, with just one plant (*PB Gelatines*) left. The gelatine market in Great Britain survived the BSE crisis without huge problems, but the industry did not.

The Netherlands/Switzerland

Because of very stringent and costly environmental requirements, *Geistlich* decided that their small plant could not carry this burden, and they closed it in 2001; thus, the last gelatine production in Switzerland disappeared.

In 1997 a glue manufacturer in the Netherlands (Trommelen) started producing edible gelatine in a new plant (*Trobas Gelatine*), with considerable growth expected.

In a further consolidation step, *Rousselot* decided to shut down their Delft gelatine plant and sell the equipment to China.

In 2002, *DGF Stoess* started production in a new pigskin gelatine plant in the Netherlands, based on an innovative and completely new raw material concept linked to new technologies.

Currently, a new pigskin gelatine plant is under construction funded by private investors close to the German border.

Sweden

After a further production increase in 1995, *Extraco* became the largest pigskin gelatine plant in the world.

Italy

Italgelatine expanded further, reaching more than 6000 tons/annum, and changed in 2003 completely from hide gelatine to pigskin gelatine. *Lapi* started production of fish gelatine.

Spain

Both existing plants of *Junca* and *Rousselot* were further expanded and *Junca* started to make fish and poultry gelatine.

Eastern Europe

After the acquisition of the hide and bone gelatine plant of *Gelima*, *Weishardt* started a modernization program, and recently the production was changed to pigskin gelatine, because even in Eastern Europe quality hide splits are in short supply. The bone degreasing operation (installed in 1992) was shut down earlier.

Russia

Some years after the fall of the iron curtain and the implementation of more free trade, the Russian gelatine industry collapsed almost completely. Only small fragments in Russia, Belarus, and the Ukraine are left, with a total production of only approx. 1000 tons/annum. First, products containing gelatine were imported, and now, after the installation of local plants to manufacture those products, the gelatine required is imported.

United States

In 1997, *DGF Stoess* added a complete second bone gelatine plant to the existing one and made Sioux City the world's largest single-site gelatine manufacturing facility. In 2003, *Kind & Knox* and *Dynagel*, both owned by *DGF Stoess* changed their names in the market to *GELITA USA* after the remaining 50% of the *Dyna-gel* shares were purchased from *Goodman Fielder* in 1998. Because of the declining demand for bone gelatine in general and for photographic applications in particular, the old production plant for bone gelatine was shut down in 2005.

In 1997 the *Hormel* plant in Davenport was sold to *Goodman Fielder (Davis)*, and in 2003 it was acquired by *PB Gelatines*.

In 2004 *Nitta* founded *Nitta Gelatine USA* and started to build a new pigskin gelatine plant in North Carolina, which was commissioned in 2006.

Canada

The capacity of *Cangel* was doubled in the 1990s to approx. 3000 tons/annum, and the company name was changed again to *Nitta Gelatin Canada*. The location of the plant is still one of the most critical ones of the whole industry for environmental reasons, right in the middle of the city of Toronto.

In 2005, *Weishardt* started to build a new pigskin gelatine facility in Montreal, Canada.

Australia/New Zealand/South Africa

After 1995, the new *Davis* plant in Queensland reached its planned production in stepwise fashion. In 2002, *DGF Stoess* acquired all the plants in this area after the acquisition of the main businesses of *Leiner Davis Gelatin* and started a modernization program.

Japan

From 1984 through 1997, *Nippi* modernized most of their production, which is located in the center of a town. In 1995, *Asahi* started to manufacture hydrolyzed gelatine, which had become more and more interesting for the Japanese market. The company *Miyagi Chemicals* was renamed *Jellice* in 2003. *Nitta* announced the construction of a new pigskin gelatine plant in the United States in 2004.

Mexico

In 1994, the *Panamericana de Grenatina* was sold to *Leiner Davis Gelatin* and in 2002 it became part of *DGF Stoess*, and a complete modernization program was started, which made the plant the largest facility in Mexico.

In 1996 the *Pilsa* company established a strategic alliance with *Rousselot*. Their production is exclusively the alkaline processing of hides.

Brazil

In 1994, the capacity of *Sairsa-Gelita* was doubled and the company name was changed to *Sargel*. Over the years *DGF Stoess* increased its shareholding, and in 2002 it achieved 100% ownership. In 1995 *Rebiere* built a new plant in the western part of Brazil, in Presidente Epitácio, with a capacity of approx. 5000 tons/ annum, and, in parallel, the Amparo plant was modernized and expanded after the glue production was discontinued. The *Kraft* plant was also upgraded to make up to 2500 tons/annum. Their production is still completely used internally for their table jellies.

In 1998, the previous owners of the *Leiner do Brasil* business, H. Cobelo and his four partners, founded a pigskin gelatine plant (*GelNex*) in the South of Brazil, where the breeding of pigs is concentrated. In 2005 he followed this by building a new hide gelatine plant in the mid-west of Brazil. The current production of the two plants is about 5000 tons/annum, with an installed capacity of about 7000 tons/annum.

In 1998, the *Estancia Velha* plant of *Leiner Davis* also started to manufacture pigskin gelatine, and in 2002 the Brazilian plants of *Leiner Davis* became part of *DGF Stoess*. A further expansion program was started, and the operations of these plants and the *Sargel* operation were restructured.

Colombia

In 2001, the Australian *Goodman Fielder Group (Davis)* sold their 30% shares in the Colombian (*Progel*) businesses, which they had acquired in 1967 from *Nabisco*, to the Minski & Gilinski families, who now own both plants in Colombia.

The current capacity in Colombia is approx. 6000 tons/annum if enough raw material can be imported, mainly from Brazil.

Argentina

In 2003, the *Leiner Davis* plant in Santa Fe was acquired by *PB Gelatines* when *Goodman Fielder* sold the remaining parts of their gelatine business after the major purchases of their operations by *DGF Stoess*.

India

In 1999, *KPCL (Nitta)* expanded their activities with a new bone gelatine plant. *KPCL* thus became the second largest supplier of ossein in India, producing more than 6000 tons/annum, and also started to deliver product to other gelatine companies. The current gelatine plant has a capacity of approx. 2000 tons/annum, and a minimum of 50% of the production is purchased under a contract by *Nitta*. In the mid-1990s, the Sandesara group, a leading tea company, decided to sell their tea business and invest in gelatine. With technical know-how from *Croda*, a first gelatine operation (*Sterling*) was established, and in 1998 their first gelatine products appeared on the market. Since then, several further production lines have been established and its current production is reported to be in the range of 11 000 tons/annum. Within a short period of time they became the most important gelatine exporter in India. Another small ossein and gelatine manufacturer was established during this period by a slaughterhouse and meat packer as an integrated operation (*Rohilkhand Chemicals & Proteins*) with a production of less than 2000 tons/annum and serving mainly the domestic market. In 1997, the Mirani family, owner of an ossein business since 1973 together with Konica Gelatine (*India Gelatin and Chemicals*), decided to build up a gelatine plant with financial and technical cooperation of the Japanese companies Nichimen and *Konica Gelatin*. Being a small operation, the business was strongly hit by the closure of their main customer, *Konica Gelatin*, in 2002. In 2000, *Shaw Wallace* decided to change the name of their gelatine company to *Narmada Gelatines* because the company had been up for sale for many years, not only because it did not fit in with the other businesses of *Shaw Wallace* (mainly liquor) but also because of the many problems associated with the company itself. In 2003/2004 the operation was temporarily shut down by the authorities because of environmental problems (river pollution). *Raymon Gelatin* also planned to double their production during the last few years and to enter the international markets for photographic and pharmaceutical gelatine with the technical and commercial assistance from Germany, but the attempts failed.

Korea

All plants are running, but most of the time with somewhat reduced production because of a shortage of raw material.

Taiwan

Prior to 1996 there were three small mainly pigs skin gelatine manufacturers in Taiwan. *Kuang Ming*, *Taiwan Gelatine* and *Oriental Gelatine*. In 1996 the *China Syn-*

thetic Rubber Corporation set up a new plant with a capacity of approx. 2000 tons/ annum in the Southern part of Taiwan. Nobody really understood this decision. Because of the limited raw material availability in Taiwan, this new plant forced the closure of the other three manufacturers but it also drove the raw material cost up dramatically. And the raw material supply is still the biggest concern, which has forced this plant constantly to reduce production. In 2005, the plant was acquired by the Japanese *Jellice* gelatine company.

China

As mentioned before, *Rousselot* went into China in 1996 to *Kaiping* (25% of the shares are still owned by a Chinese partner) and in 2003 to *Wenzhou* with a 70% shareholding. Since the beginning, production in *Kaiping* has more than doubled to 6000 tons/ annum. And they did the same with the other plant, which now has a capacity of approx. 4000 tons. In 2005, *GELITA* followed and became involved in three production plants with a total capacity of approx. 8000 tons/ annum. Besides these plants, five other fully Chinese-owned plants exist with a total production of approx. 4500 tons/ annum of bone gelatine and approx. 5000 tons/ annum of hide and pigskin gelatine. There may well be some more smaller plants, sourcing and selling only locally. Thus, for 2006, the total gelatine production will be in

Table 1.4 Gelatine production in the different areas in 1994 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	48	1	28	4	6	0	87	38.8%
Beef hide	15	3	2	30	6	4	60	26.8%
Bones	32	6	14	0	25	0	77	34.4%
Total	95	10	44	34	37	4	224	

Table 1.5 Gelatine production in the different areas in 2000 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	70	0	31	3	3	0	107	41.5%
Beef hide	16	3	10	32	7	7	75	29.1%
Bones	32	1	16	0	28	0	77	29.8%
Total	118	4	57	35	38	6	258	

Table 1.6 Gelatine production in the different areas in 2005 (thousands of tons).

Raw material	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa	Total	Share
Pigskin	81	1	36	5	14	0	137	44.9%
Beef hide	11	4	10	47	6	7	85	27.9%
Bones	27	2	15	0	39	0	83	27.2%
Total	119	7	61	52	59	7	305	

Table 1.7 Annual world gelatine production of all grades by areas in 1974–2005 (thousands of tons).

Year	Total production	Western Europe	Eastern Europe & Russia	NAFTA	South America	Asia	Oceania & Africa
2005	305	119	7	61	52	59	7
2004	290	119	6	62	48	49	6
2003	278	118	5	60	43	46	6
2002	276	117	4	61	43	45	6
2001	264	117	4	58	39	40	6
2000	258	118	4	57	35	38	6
1999	252	111	7	54	38	36	6
1998	253	113	7	55	38	34	6
1997	248	110	8	52	35	38	5
1996	232	102	9	51	31	34	5
1995	226	101	10	46	30	35	4
1994	224	95	10	44	34	37	4
1993	212	93	12	36	33	34	4
1992	206	91	12	39	27	33	4
1991	200	90	13	37	24	32	4
1990	193	83	10	35	21	38	6
1989	190	81	12	36	20	35	6
1988	185	78	13	36	19	33	6
1988	185	79	13	35	19	33	6
1987	186	77	13	37	17	36	6
1986	183	72	13	38	18	36	6
1974	130	62	12	31	5	15	5

the range of approx. 25 000 tons. This explosion in production was necessitated by the fast-growing use of gelatine for hard and soft shell capsules and by the introduction of gelatine-based fruit gummies to the Chinese market, bringing a further increase in demand. Import restrictions and high import duties keep the market closed and protect domestic production. The photographic gelatine used in China is of very minor significance.

In this period, the change from hide and bone gelatine to pigskin gelatine continued mainly in Western Europe because of BSE fears and the declining demand for photographic gelatine. Because of increasingly stringent environmental requirements, the tanning industry has moved away from Western Europe to Russia and China. But technology changes in the worldwide tanning industry (tanning of the complete hide before splitting) have also reduced the availability of gelatine raw material in general. The availability of raw material has become the major concern of the industry, because this could limit the chances for further growth. Companies for which gelatine was not considered a core business sold these holdings to gelatine experts, thus increasing market growth of the market leaders.

The BSE crisis hit the industry worldwide despite the fact that scientific information had been produced, at a very early stage, showing that the gelatine production process would render the product safe even if infected animal material had inadvertently entered the production process. The authorities in many countries were very reluctant to lift all the implemented bans and restrictions for different gelatine types or gelatine-containing products like capsules. However, despite intense competition, this crisis has also improved the solidarity of the industry around the world and resulted in several millions of euros being spent jointly on scientific studies and publications.

Today, the industry consists of 90 production plants in 30 countries.

References

Specific References for Section 1.1

- 1 Chemie in unserer Zeit 2/96, p. 6.
- 2 Hilary Wilson, Egyptian Food and Drink, Aylesbury 1988, p. 42.
- 3 Tode S, The GELITA Story, Verlag Hanseatischer Merkur, 2003, p. 26.
- 4 Podczeck F, Jones BE, Pharmaceutical Capsules, Pharmaceutical Press 2004, p 13.
- 5 Koepf W, Die Entwicklung und Bedeutung der deutschen Gelatineindustrie, Dipl.-Arb., 1934.
- 6 Saddler J M, Horsey P J, The new generation gelatine, Anaesthesia. 1937 sep.; 42(9):998–1004.

General References for Section 1.2

- Diploma thesis of Werner Koepff, 1934, on the historical development of the German gelatine industry.
- Summery of information gathered by Horst Kühnel, DGF Stoess in 1982.
- Davis History by Malcolm C. Davis, 1993.
- The Gelita Story, 2003, Verlag Hanseatischer Merkur.
- J. Alexander, Glue and Gelatine, The Chemical Catalog Comp., New York, 1923.
- L. Thiele, Die Fabrikation von Leim und Gelatine, Max Jäneke Verlag, Leipzig, 1907 und 1922.
- E. Sauer, Chemie und Fabrikation der tierischen Leime und der Gelatine, Springer Verlag Heidelberg, 1958.
- Gerngross-Goebel, Chemie und Technologie der Leim- und Gelatinefabrikation, Th. Steinkopf Verlag, Dresden und Leipzig, 1933.
- Internet company information of the gelatine industry associations.

2

From Collagen to Gelatine

2.1

Basic Chemical/Physical Principles and Technological Properties

Gelatine is a fascinating example of just how multifunctional nature can be. The essential constituent of gelatine is protein. The protein content is between 85 and 92%, the remainder being mineral salts and any moisture still left after drying. Gelatine is produced by the partial hydrolysis of native collagen. Collagen is the most frequently occurring protein class in both animals and humans. In contrast to spherical globular proteins, collagen is composed of linear, fiber-like structures (see Fig. 2.1).

2.1.1

Basic Chemical/Physical Principles

Collagen is not a uniform substance, but is rather a family of proteins. To date, some 27 different types of collagen have been identified. Type I collagen occurs widely, primarily in connective tissue such as skin, bone, and tendons. Type II collagen occurs practically exclusively in cartilage tissue. Type III collagen is strongly dependent on age: very young skin can contain up to 50%, but in the course of time this is reduced to 5 to 10%. The other collagen types are present in very low amounts only and are mostly organ-specific.

2.1.1.1 Chemical Composition and Molecular Structure of Collagen

Like all other proteins, collagen exhibits primary, secondary, and tertiary structural elements. Collagen also has a quaternary structure similar to other complex oligomeric proteins which are characterized by having multiple polypeptide chains or subunits.

The primary structure of type I animal collagen as used in the manufacture of gelatine comprises some 1014 amino acids that are linked in the form of a chain with a molecular weight of approximately 100 000 g mol⁻¹. These so-called alpha-chains comprise 334 repetitive units of the general sequence glycine-X-Y. Only at the N- and C-terminal ends are there short chains comprising some 15–26 amino acids that do not conform to this structure.

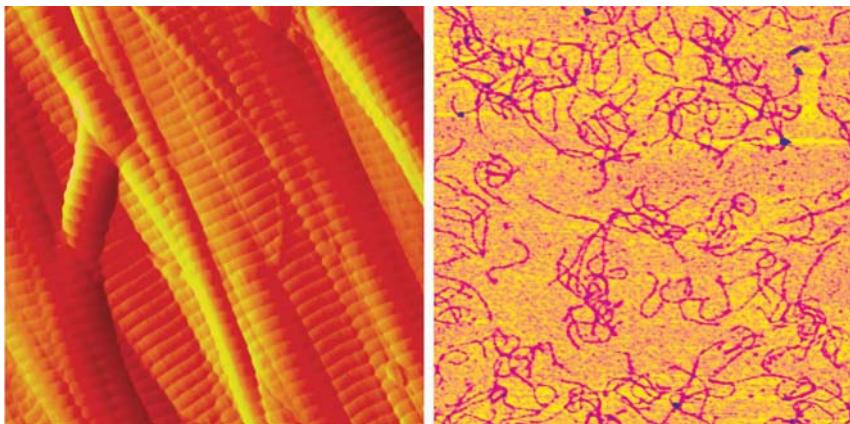


Fig. 2.1 Collagen is comprised of linear, fiber-like structures. Left: Rat tail tendon collagen. Right: Kangaroo tail collagen (Source: Leibniz Research Center for Medicine and Biosciences, Borstel, Germany).

Glycine alone constitutes approximately 33% of the amino acid component, proline and hydroxyproline together about 22%. Proline frequently occurs in the X-position and hydroxyproline almost always in the Y-position. The remaining 45% are distributed over the X- and Y-positions, certain combinations being preferred for steric and electrostatic reasons.

Proline and hydroxyproline are responsible for the unique secondary structure of collagen. These amino acids limit the rotation of the polypeptide backbone and thus contribute to the stability of the triple helix. The hydroxyl group of hydroxyproline plays an important role in stabilizing the triple helix of collagen. Collagen polypeptides lacking hydroxyproline fold into triple-helical conformations at low temperatures, but these are not stable at body temperature.

Type I collagen is composed of three alpha-chains of which two are identical (alpha 1) and one slightly different (alpha 2) (primary structure). Each alpha chain is coiled into a left-handed helix with about three amino acids per turn (secondary structure). The three alpha chains are then twisted around each other into a right-handed super-helix to form a rigid rope-like structure (tertiary structure, see Fig. 2.2).

These triple-helical elements represent the basic building blocks of the collagen tissue. They are some 300 nm in length and have a diameter of 1.5 nm. Because of the charge distribution, these basic structures are staggered by about one quarter of their length (quaternary structure). Four to eight collagen molecules in cross-section constitute the basic unit to form so-called collagen fibrils. The entire structure is stabilized and reinforced by cross-links in the form of covalent bonds. Many of these collagen fibrils are then further cross-linked to form the basic structure for tissues such as skin and bone.

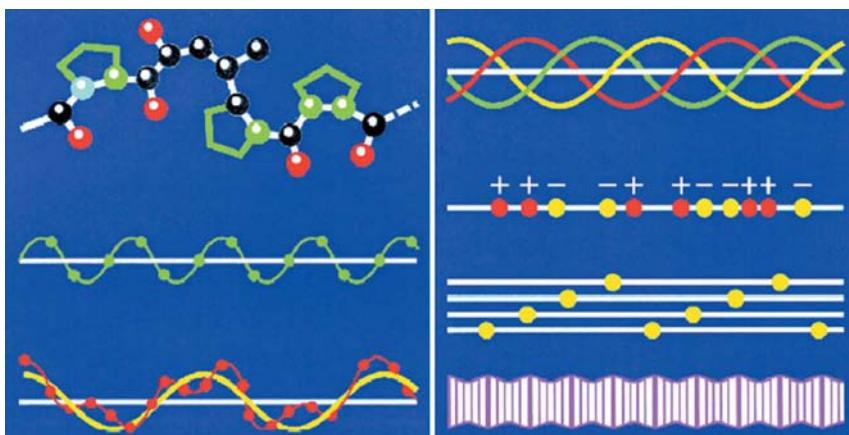


Fig. 2.2 From the primary structure through the quaternary structure.
The steps in collagen formation.

Collagen is made up of 20 amino acids. Of the nine amino acids designated as essential for the human body, very little methionine is present and tryptophan is completely absent. The traces of cysteine occasionally found in hide and skin gelatine probably originate from the type III collagen in the raw material, as type I collagen contains no cysteine.

Typical for collagen, and hence for gelatine, are the modified amino acids 3-hydroxyproline (1 amino acid residue/1000), 4-hydroxyproline (92 amino acid residues/1000), and 5-hydroxylsine (6 amino acid residues). These occur primarily in collagen – this fact enables the gelatine content in the final product to be determined. The hydroxyproline content, for example, is particularly important for the gelling effect (see also Section 2.2.7).

Collagens also contain carbohydrate units, either the monosaccharide galactose or the disaccharide glucosylgalactose, linked to hydroxylsine residues via the hydroxyl functional group of the amino acid. The extent of glycosylation and the ratio of mono/disaccharide vary depending on collagen type and physiological status. The function of the carbohydrate units is not yet fully understood, but their influence on the lateral packing of collagen molecules into fibrils and the diameter of these fibrils is under discussion.

2.1.1.2 The Conditioning Process and its Effects on the Amino Acid Composition of Gelatine

Collagen obtained from very young animals is soluble in warm water. However, it loses this property with increasing age. This is because labile structures are continuously converted into extremely stable, cross-linked ones. At the same time, its ability to bind water decreases; this is what causes wrinkles in the skin of the elderly.

In the manufacture of gelatine, treatment of the animal raw material with dilute acid or alkali results in partial cleavage of these cross-links; the structure is broken down to such an extent that “warm water-soluble collagen”, i.e. gelatine, is formed. This chemical hydrolysis can be supplemented or even replaced by the use of enzymes. Special enzymes known as collagenases are required for such a process as most of the protein-cleaving enzymes do not attack the water-insoluble collagen of skin and bone as they do in the case of gelatine. Only highly specific protein-cleaving collagenases are capable of breaking down the native collagen structure.

This type of chemical or biochemical denaturation and hydrolysis is known as “the conditioning process” within the gelatine industry. In the subsequent extraction step, i.e. the melting out of gelatine from the raw material, an additional thermal hydrolysis step takes place. This reduces the molecular weight still further (see also Section 2.2.5).

In native collagen, the acidic amino acids glutamic and aspartic acids occur to the extent of about 35% in the amidated form of glutamine and asparagine respectively (see Table 2.1). In the case of alkaline-conditioned type B (basic) gelatine, both asparagine and glutamine are almost completely converted to aspartic and glutamic acids respectively. The amino acid composition of collagen and an acid-conditioned type A (acid) gelatine hardly differ. This explains the different iso-electric points (IEP) typical of types A and B gelatine. The IEP is the pH at which a gelatine molecule is neutral in charge. For gelatine of type A, this corresponds to collagen at about pH 8–9 and for type B at pH 4.8–5.5.

2.1.1.3 The Conditioning Process and its Effect on the Molecular Weight Distribution of Gelatine

In converting collagen to gelatine, the effects of acid or alkali as well as thermal energy create different types of collagen fragments. In addition to the high molecular weight oligomers of the alpha subunits, intact and partially hydrolyzed alpha-chains occur. This gives rise to a mixture comprising different molecular weights.

The goal of the gelatine manufacturer is to carry out a controlled partial hydrolysis of the cross-links and peptide bonds of the original collagen structure and to obtain the ideal molecular weight distribution of gelatine for the application envisaged. The viscosity of a gelatine solution, for example, correlates relatively well with the proportion of high molecular weight components. Current research has indicated that the fraction in the molecular weight region around 100 000 g mol⁻¹ is of significance for the gelling power of any particular type of gelatine. Gelatine of high gelling power normally has a high average molecular weight, and gelatine of lower gelling power a lower value.

The molecular weight distribution is determined by the type and intensity of the hydrolysis procedure used (see Fig. 2.3). In the case of alkaline-conditioned high-Bloom gelatine (Type B), the major part of the molecular weight fractions is in the region of 100 000 g mol⁻¹; this corresponds to the alpha-chain. Acid-conditioned gelatine (Type A), on the other hand, does not have such a pronounced peak, but rather a wider distribution.

Table 2.1 Amino acid composition of gelatines and collagen, residues per 1000 residues.

Amino Acid	Gelatine Type A	Gelatine Type B	Type 1 collagen (cattle)
Alanine	112	117	114
Arginine	49	48	51
Asparagine	16	0	16
Aspartic acid	29	46	29
Cysteine	—	—	—
Glutamic acid	48	72	48
Glutamine	25	0	25
Glycine	330	335	332
Histidine	4	4.2	4.4
Hydroxyproline	91	93	104
Hydroxylsine	6.4	4.3	5.4
Isoleucine	10	11	11
Leucine	24	24.3	24
Lysine	27	28	28
Methionine	3.6	3.9	5.7
Phenylalanine	14	14	13
Proline	132	124	115
Serine	35	33	35
Threonine	18	18	17
Tryptophan	—	—	—
Tyrosine	2.6	1.2	4.4
Valine	26	22	22

Source: Rose, P. I., Gelatine in Encyclopedia of Polymer Science and Engineering, Volume 3, Wiley & Sons (1987), p. 488–513.

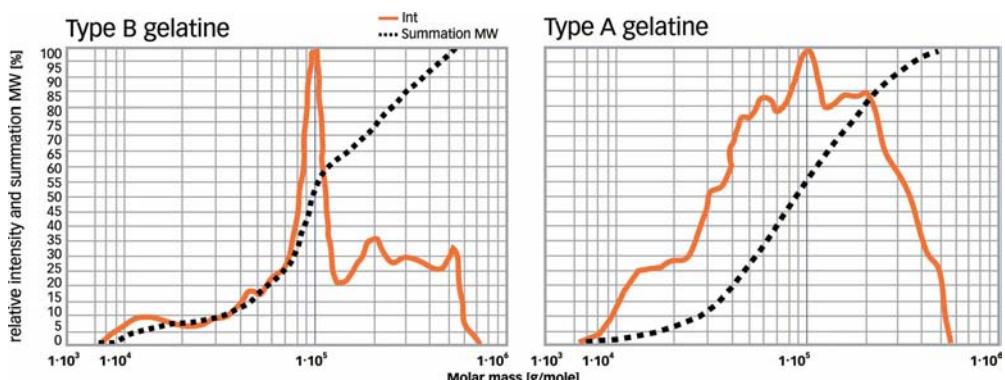


Fig. 2.3 Typical molecular weight distribution of high-quality type A and type B gelatines is like a finger print of the production process used.

The molecular weight distribution that can be currently determined analytically in both types of gelatine starts below 10 000 g mol⁻¹ and ends at over 400 000 g mol⁻¹. The high molecular weight fractions are known as micro-gels. The polydispersity, i.e. the quotient of weight average molecular weight (M_w) and number average molecular weight (M_n), of gelatine always has a value over 2 because of its polydisperse molecular weight distribution.

During the processing of gelatine, further hydrolysis of peptides occurs. This changes the molecular weight spectrum of the product. In general, gelatine of higher gelling power or of very high viscosity is broken down to a greater extent. This is because the less gelling types have already been subjected to relatively high temperatures over an extended period of time during manufacturing.

Breakdown is largely dependent on the three factors temperature, time, and pH (see Fig. 2.4). High temperatures and long periods of exposure to heat accelerate the process. The same effect is obtained when the process conditions are more acidic or more alkaline than during hydrolysis.

It is known from the literature that acid treatment of collagen tissue initiates hydrolysis of specific acid-labile peptide bonds within the helical part of the collagen molecule, leading to degradation of the protein. Thus, users of gelatine should avoid drastic process conditions that accelerate the breakdown of the gela-

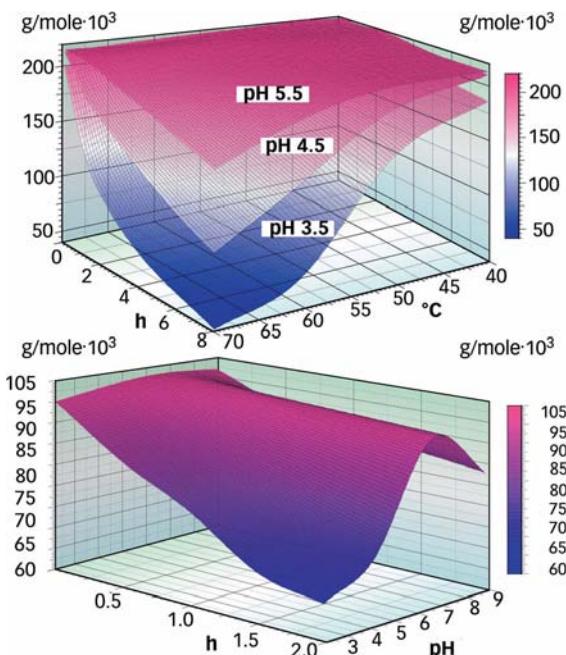


Fig. 2.4 Hydrolysis of gelatine as a function of temperature, time and pH measured by mean molecular weight. Top: type B gelatine. Bottom: type A gelatine at 65 °C.

tine (i.e. lower the quality in terms of gelling power, viscosity, and all other physical and organoleptic properties) (see also Section 3.1.2).

2.1.2

Technologically Important Properties and Characteristics of Gelatine

Gelatine forms colloidal solutions with water; in physical chemistry in fact, these are regarded as “ideal colloidal solutions”. Technologically, gelatine is thus a hydrocolloid. Apart from gelatine, pectin, caraganeen, gum arabic, xanthan, guar gum, and locust bean gum, to name just some of the most important, are also members of this class of products (see also Section 3.1.1). Hydrocolloids are used in the food industry, not so much for their nutritional value but more for their multifunctionality. However, a single hydrocolloid is incapable of fulfilling all the desired or known functions. Gelatine is no exception; but, in comparison with other hydrocolloids, it is much more multifunctional. This means that the user can often utilize many other ancillary functions in addition to its main function (see Table 2.2).

In addition, gelatine possesses other positive nutritional and physiological properties, and these are frequently of advantage when it comes to marketing (see Section 3.2.5).

The physical-chemical behavior of gelatine is principally determined by the amino acid sequence of its molecules, the resulting spatial structure, the molecular mass distribution, as well as milieu conditions such as pH, ionic strength, and reaction with other components.

The functional properties of gelatine can be divided into two groups. The first has properties that are associated with gelling, e.g., gel strength, gelling time, setting and melting temperature and viscosity. The second group relates to the surface behavior of the gelatine. These properties are, e.g., the formation and stabilization of foams and emulsions, its adhesive properties, and its dissolution behavior.

The most important properties – and these are typical of gelatine – are:

Properties associated with gelling:

Gel formation

Texturizing

Thickening

Water binding

Surface effects:

Emulsion formation and stabilization

Protective colloid function

Foam formation and stabilization

Film formation

Adhesion/cohesion

Table 2.2 The multifunctionality of gelatine, e.g., in the production of foodstuffs.

Application	Gelatine type	Concentration	Principal function	Secondary function
Desserts	200–260 Bloom	1.5–3.0%	Gel formation	Texture, transparency, brilliance
Fruit gummies	200–280 Bloom	6.0–10.0%	Gel formation	Texture, elasticity, transparency, brilliance
Marshmallows	160–260 Bloom	1.0–3.0%	Foam formation	Foam stabilizer, gel formation
Nougat	180–220 Bloom	1.5–3.0%	Foam formation	Foam stabilizer, gel formation
Pastilles	160–220 Bloom	1.0–2.0%	Binding agent	Texture, improvement of melting properties in the mouth, prevents disintegration
Caramels	140–200 Bloom	0.5–2.5%	Emulsifier, foam stabilizer	Chewability
Yogurt	220–260 Bloom	0.2–1.0%	Syneresis stabilizer	Texture, creaminess
Foamed milk dessert	180–240 Bloom	0.3–3.0%	Foam formation	Texture, stabilization
Jellied milk dessert	180–240 Bloom	1.0–2.0%	Gel formation	Texture, creaminess
Sandwich spread (without meat)	240–280 Bloom	0.3–1.5%	Emulsion stabilizer	Texture, creaminess
Meat and sausages	220–260 Bloom	0.5–2.0%	Emulsion stabilizer	Water binder
Broths and canned meats	220–260 Bloom	0.5–2.0%	Binding agent	Texture, sliceability

2.1.2.1 Gel Formation, Viscosity, and Texture

Gel formation, viscosity, and texture are very much related properties determined mainly by the structure, molecular size, and temperature of the system.

Gelatine is a mixture of polymer chains of different lengths. Thus, real solutions are not formed; instead, colloidal solutions or sols are formed. On cooling, these sols convert to gels, and on warming they revert to sols. This theoretically unlimited reversibility of the gelling process is by far the most important technological property of gelatine. Many other hydrocolloids such as alginates, carra-

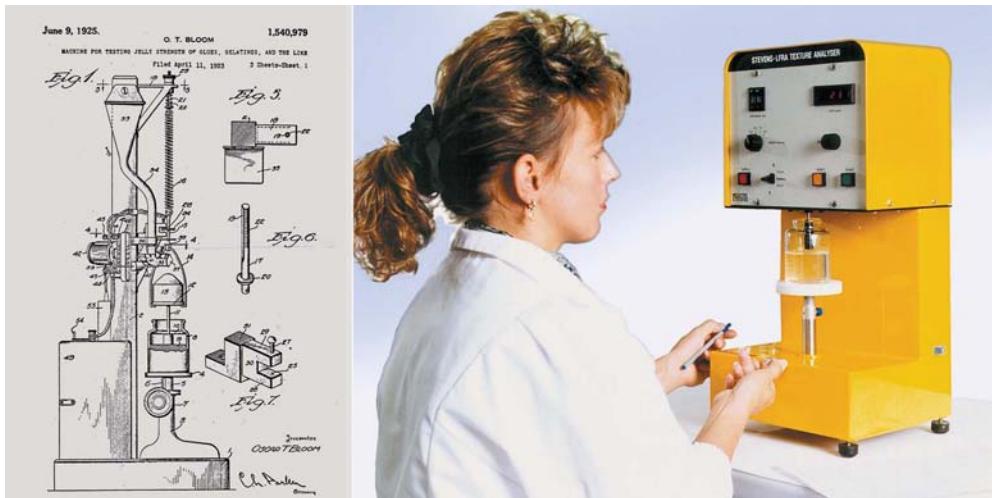


Fig. 2.5 The measurement of the gel strength is still the most important quality parameter for gelatine. Left: the original equipment in the patent application of O. Bloom from 1925. Right: a modern, semi-automatic instrument.

ganeens, or pectins also gel. However, this is by chemical reaction that may be irreversible or reversible to a limited extent only.

2.1.2.2 Gel Strength/Bloom Value

The analytical measure of gelling power is the Bloom value. The process for measuring the parameter is named after the American scientist Oscar T. Bloom, who developed a “Machine for Testing the Jelly Strength of Glues, Gelatines, and the Like” (see Fig. 2.5), which was patented on June 9, 1925 (US Patent No. 1 540 979). The Bloom value is the weight in grams that is required for a specified plunger to depress the surface of a standard, thermostatted gel to a defined depth under standard conditions (see also Section 2.3).

The Bloom values of commercial gelatine types are within the range 50–300 Bloom. Gelatine of high Bloom has characteristically higher melting and gelling points and shorter gelling times in the final product, and is lighter in color and more neutral in odor and taste. The stronger gelling power also means that smaller amounts of gelatine are required to bring about the desired gel firmness in the finished product.

This can be illustrated mathematically and shows a good degree of correlation. The calculation is based on the fact that, in a pure aqueous solution, the product of gelatine concentration times and the square root of the Bloom value is constant for gelatine produced by any one method:

$$C_1 \times B_1^{1/2} = C_2 \times B_2^{1/2}$$

or

$$C_2 = C_1(B_1/B_2)^{1/2}$$

According to this formula, a manufacturer of products containing gelatine, by changing, e.g., from 250 to 280 Bloom, can reduce the specific gelatine concentration from 8 to 7.7%. However, he still obtains the same degree of gel firmness. These calculated values provide him with an initial rough indication only. Sensory and other analytical tests are also necessary, as all the other ingredients of the formulation can influence the behavior of the gelatine and hence the degree of dependence of gel firmness on the concentration.

Alternatively, using a constant concentration of higher Bloom gelatine in the formulation, a harder, less rubber-like texture can be produced. The food industry refers to such products as having "a short bite".

2.1.2.3 The Kinetics of Gel Formation

All the hydrodynamic properties of gelatine are dependent on its molecular weight distribution. The only difference between gel formation and viscosity is the temperature at which the system is observed. This is easy to explain, as the viscosity determines the mobility of the molecules in the liquid, whereas the gel firmness primarily describes the structure formed by intermolecular hydrogen bonds (see Fig. 2.6). If a gelatine solution is cooled, the mobile molecules aggregate to small clusters; these continuously grow and subsequently form a gel. In this case, hydrophobic and electrostatic interactions also exert some influence. Thus, there is a continuous transition between these two properties of gelatine.

Gel formation and viscosity, however, do not have a linear relationship with each other. Bloom value and the standard viscosity as specified by the gelatine manufacturer are single-point measurements which cannot be used to draw conclusions regarding the kinetics of gel formation, primarily because the different molecular weight fractions also play a role. Thus, the gel strength is mainly dependent on the proportion of fractions having a molecular weight of approx. $100\,000 \text{ g mol}^{-1}$, whereas the viscosity is primarily a function of those in the

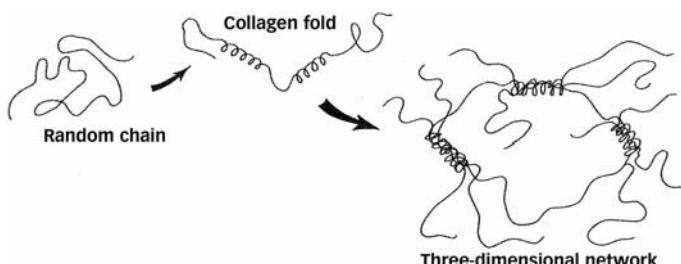


Fig. 2.6 Model of gel formation (from sol to gel upon cooling).

molecular weight range of 200 000 to over 400 000 g mol⁻¹. For this reason, depending on the method of manufacture, gelatines of the same Bloom value can have quite different viscosities.

2.1.2.4 The Rheology of a Gelatine Solution

In order to determine the visco-elastic behavior of a specific type of gelatine during gelation, an oscillating rheometer must be used. This enables the viscosity and the elastic properties to be measured simultaneously as a function of time and temperature. Ideally, the viscosity is represented by the so-called viscosity or loss modulus G'' and the elastic properties by storage modulus G' . Based on the conditions of Bloom measurement and utilizing the storage modulus G' over a period of 17 h, gel firmness as measured by the Bloom gelometer can be assessed.

During gelation, there is a geometric point where the loss modulus G'' (viscous part) and the storage modulus G' (elastic part) are in equilibrium. This crossover point of G' and G'' on the cooling curve is defined as the temperature of the sol-gel transition, i.e. the gelation point. On the heating curve, in contrast, this crossover point represents the gel-sol transition temperature or gel melting point.

The cooling and heating curves are never congruent; they show a clear degree of hysteresis, and the melting process is at a higher energy level (see Fig. 2.7). Using an empirical rule of thumb, the temperature difference between the melt-

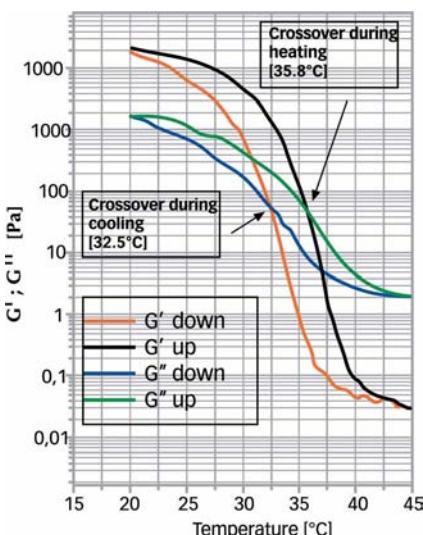


Fig. 2.7 Cooling and heating curves of a gelatine solution. The crossover point of the cooling curve represents the gelation point. The crossover point of the heating curve is defined as the melting point.

ing and setting points in a pure aqueous gelatine solution of 5–25% is approximately 5 °C.

In summary, the rheological behavior of aqueous gelatine solutions can be described as follows:

A dilute gelatine solution is a Newtonian fluid showing purely viscous behavior, but cooling initiates structural changes. These are represented by the formation of hydrophilic and hydrophobic interactions between the gelatine molecules. In this initial phase the system can be described as a solution (see Fig. 2.8).

Upon further cooling, the structure-forming process continues as the temperature decreases until the phase transition point is reached. At this point, interactions, some of which are much more stable, are formed, and gelling starts.

If the temperature continues to fall, a permanent gel is formed. This gel is visco-elastic in nature. The system now has the nature of a solid; this phase transition is known as sol-gel transition.

2.1.2.5 From Gelatine/Water to Complex Systems

From the point of view of technical applications, however, the rheological model is of limited significance. In industrial practice, phase transitions of gelatine/water systems depend strongly on the type of gelatine, the ratio of water to gelatine, the temperature, and a number of other parameters.

In general, sol/gel transitions can be evaluated within a temperature range of about 5–60 °C, and the gelatine concentration can vary between 0.5 and 50% (depending on the quality of the gelatine). But, for practical applications, it

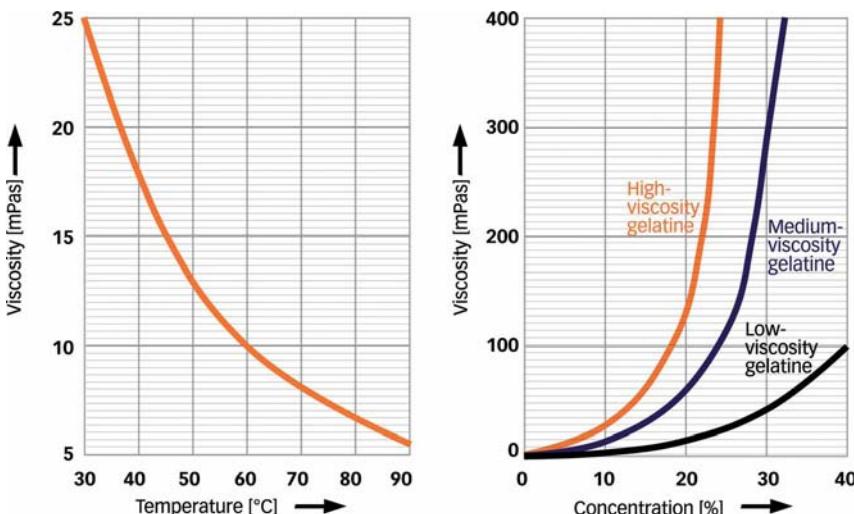


Fig. 2.8 The viscosity of a gelatine/water system and its dependence on quality, temperature and concentration.

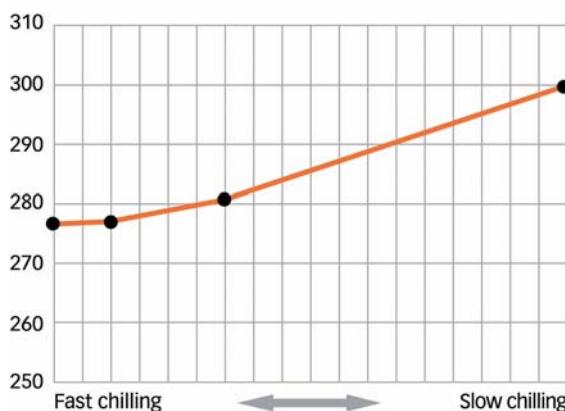
Bloom

Fig. 2.9 Influence of cooling rate on gel strength of a 6.67% gelatine gel.

should be kept in mind that the setting and melting performance of the gelatine-containing final product is strongly influenced by the nature and the quantity of the other ingredients.

Another example of deviations in the setting performance of complex formulations is their thermal and mechanical “history”. If, during the processing of a solution containing gelatine, it is cooled too quickly, rheological parameters like setting and melting temperatures are not comparable with well-defined laboratory results.

Because of the rapid increase in viscosity, the system has too little time to approach equilibrium (characterized by an optimal three-dimensional structure) by forming a stable network by hydrogen bonds. Thus, for rapid cooling, the measured gel strengths are lower than those that would normally be expected of the gelatine grade used (see Fig. 2.9).

Because of the poor alignment of the gelatine molecules brought about by rapid cooling, deviations in gel strength of 10–15% can be observed.

The same is true when dissolving gelatine: solutions prepared at temperatures below 50 °C have a rheological performance that is different from that of solutions produced at higher temperatures, indicating a kind of pre-structure at lower temperatures (see Section 3.1.2).

Furthermore, each additional component changes the behavior of the entire system.

In a pure gelatine/water system, sol-gel transition takes place within a very narrow temperature range. The complex viscosity increases rapidly within a few Celsius degrees (see Fig. 2.10).

If, for example, in the case of fruit gummies, the standard ingredients are added consecutively, the curve becomes flatter. The viscosity increases over a

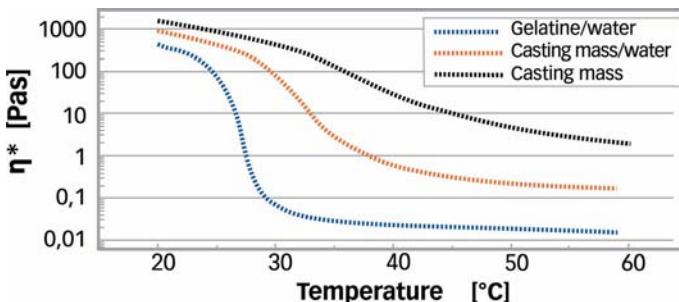


Fig. 2.10 Development of the complex viscosity of fruit gummie formulations on cooling as a function of composition.

wide temperature range, depending on the nature of the components added. The final firmness of the product is only achieved after a longer period of time.

Rheologically, upon cooling, the gelatine in a high-solids system containing little water is not, or is only very slowly, capable of forming and stabilizing the three-dimensional network characteristic of a sol-gel transition. Gel formation in this case takes place over a wide temperature range and is also strongly inhibited by the additional components. At the same time – because of the reduced amount of water – the setting point is increased, for example, from 28 °C for the pure gelatine/water system to 45 °C for the casting solution used for fruit gummies (see Fig. 2.11).

The impact of all these factors on real systems can only be assessed by practical experiments. In practice, this can be achieved quickly and successfully with modern analytical methods coupled with comprehensive background knowledge of gelatine.

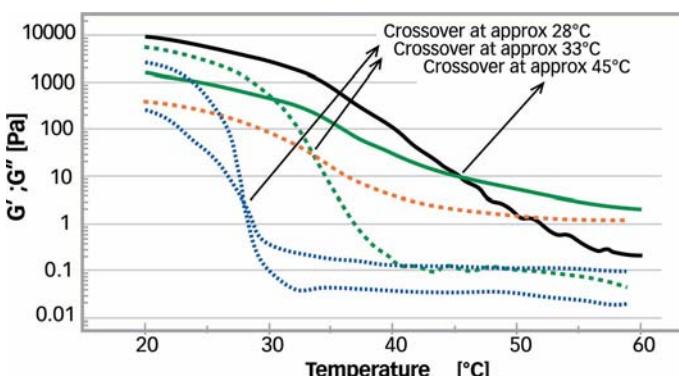


Fig. 2.11 Development of G' and G'' of fruit gummie formulations as a function of mix.

2.1.2.6 Surface Properties

The surface properties of gelatine are based on the facts that the gelatine side chains, like those of all proteins, have charged groups and that certain parts of the collagen sequence contain either hydrophilic or hydrophobic amino acids (see Table 2.3).

Both hydrophobic and hydrophilic parts tend to migrate toward surfaces, hence reducing the surface tension of aqueous solutions. At the same time, gelatine has several properties that protect and stabilize the surfaces formed. This multifunctional property of gelatine is utilized in the production and stabilization of foams and emulsions.

The ability to form and stabilize foams depends on the molecular structure of the substance in question. Basically, it must possess surface-active characteristics, for only in this way is it possible to cause a product to foam by reducing the surface tension at the liquid/air interface. In order to prevent the rapid collapsing of such a foam, an increase in viscosity of the continuous phase is essential. In the ideal case, the foaming agent will stiffen the entire product, thus completely stabilizing the foam structure.

Emulsifiers are soluble substances that enable other substances that nature normally keeps apart to be brought together. If such an emulsifier is added

Table 2.3 Hydrophilic and hydrophobic amino acids in gelatine.

Amino Acid	Hydrophilic	Hydrophobic	Information
Alanine		+	Aliphatic, non-polar side chain
Arginine	+		Basic
Asparagine	+		Weak polar side chain
Aspartic acid	+		Acid
Glutamine	+		Weak polar side chain
Glutamic acid	+		Acid
Glycine		+	Aliphatic, non-polar side chain
Histidine	+		Basic
Hydroxyproline		+	Weak polar side chain
Hydroxylsine	+		Basic
Isoleucine		+	Non-polar side chain
Leucine		+	Non-polar side chain
Lysine	+		Basic
Methionine		+	Aliphatic, weak polar side chain
Phenylalanine		+	Aromatic, non-polar side chain
Proline		+	Non-polar side chain
Serine	+		Weak polar side chain
Threonine	+		Weak polar side chain
Tyrosine	+		Aromatic, weak polar side chain
Valine		+	Non-polar side chain

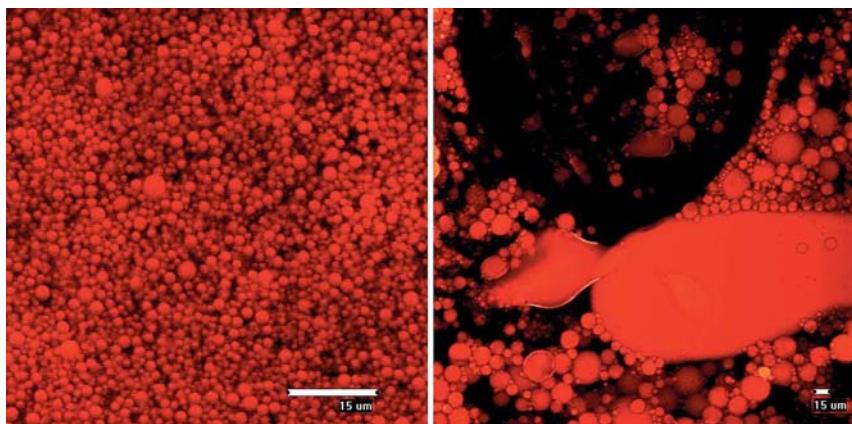


Fig. 2.12 Stable emulsion with gelatine (left) and “broken” emulsion without gelatine (right). Source: DIL (Deutsches Institut für Lebensmitteltechnik e. V.) Quakenbrück, Germany.

in low amounts to a dispersion of an oily phase in an aqueous phase, its molecules tend to gather at the interface between the two phases. The emulsifier then covers the individual oil droplets with an extremely thin film. If these films have the same electrical charge, they repel each other, hence essentially preventing the formation of larger drops. However, high mechanical stress and high temperatures tend to destroy the fine emulsion film and hence the emulsion itself. This emulsion “breakdown” can be prevented by providing it with additional stability (see Fig. 2.12).

The stabilizer used should increase the viscosity of the emulsion, create a particularly stable protective sheath around the droplets, or prevent the latter from becoming electrically neutralized. This last-named property is also known as the “protective colloid effect” of the stabilizer (see Section 2.1.2.8).

If now the requirement profile of a whipping agent, emulsifier, or stabilizer is compared with the functional properties of gelatine, it can be seen that gelatine possesses the necessary functions for all three application areas to a very high degree.

Gelatine decreases the surface tension of aqueous systems and forms the required identically charged film around the components of the dispersed phase, which can be additionally strengthened by gel formation. Important criteria in selecting a suitable gelatine type are hence the distribution of charge (IEP, see Section 2.1.2.7) and the gel firmness of the gelatine employed, because the higher the gel firmness, and hence the Bloom value, the firmer is the the gel-like protective sheath around the oil droplets or air bubbles at the same temperature and concentration.

Moreover, gelatine stabilizes an oil/water emulsion or foam even without gelling, because it increases the viscosity of the aqueous phase. However, the viscos-

ity of a gelatine solution is strongly dependent on the conditioning process used. Type A gelatine produced using the acid process has only half the viscosity of type B gelatine of identical firmness produced by classical alkaline conditioning. Type B gelatine of higher viscosity is thus frequently advantageous in a production process which requires stabilization of emulsions.

2.1.2.7 Amphoteric Behavior/Isoelectric Point

The isoelectric point (IEP) – the electric zero – is of fundamental importance in the surface activity effects of gelatine. Because of the method of determining this parameter, it is also known as the isoionic point. Theoretically, there is a slight difference between the two; in practice, however, they can be regarded as being identical.

If the pH of a milieu around the gelatine corresponds to the IEP, gelatine is neutral in charge (see Fig. 2.13). If the pH is higher it is negatively charged, and if it is lower the gelatine is positively charged. In gelatine solutions of pH approx. 5.0 to 9.0, alkaline-conditioned gelatine is hence negatively charged and acid-conditioned gelatine positively. Below pH 5.0 all types of gelatine are thus positively charged and over pH 9.0 all are negative.

At its IEP, a protein molecule, because of its neutral charge, has a so-called “random coil structure”. Should, however, the pH of the matrix shift away from the IEP, the charge on the molecule, in this case gelatine, will also be changed. Charges are then released and the molecule unfolds. This structural change influences the surface-active effect of gelatine in a positive way.

Depending on the pH of the solution to be whipped or emulsified and the state of charge of its components, either type A or type B gelatine has proven to be particularly suitable. In some cases gelatine mixtures are deliberately used in order to combine the specific qualities of both types.

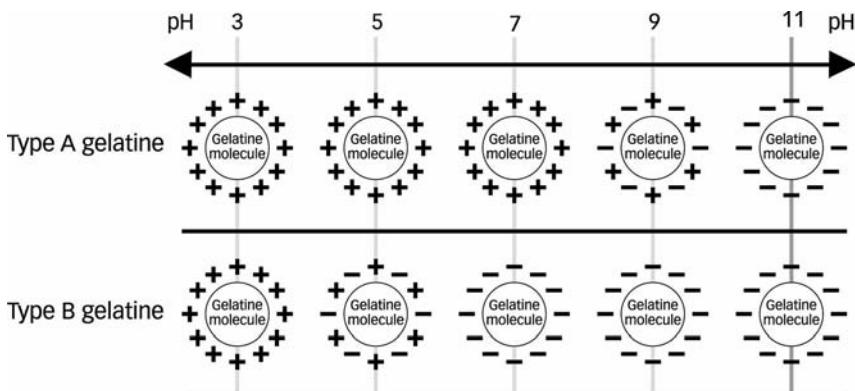


Fig. 2.13 Charge distribution pattern of type A and B gelatines in aqueous solutions of different pH.

For further processing it is important to know that, in the case of low concentrations of gelatine, turbidity and loss of firmness can occur if the pH of a particular product corresponds exactly to the IEP. The IEP also affects the compatibility of gelatine with other hydrocolloids. Thus, apart from the other components, the pH of the final product is an important criterion for the selection of the optimal type of gelatine.

2.1.2.8 Protective Colloid Function

Gelatine is a very effective protective colloid. It prevents the aggregation of crystals and particles and hence stabilizes heterogeneous suspensions and dispersions. In the case of photographic emulsions as coated onto photographic carrier material such as film or paper, gelatine acts not only as a carrier and binding agent for the light-sensitive coating, it also functions as a protective colloid. The same function is also utilized in the ice cream industry; here the addition of gelatine enhances the formation of very fine crystals, thus preventing coarse crystallization of the lactose in the mixture.

Just how effective gelatine is in comparison to other hydrocolloids in stabilizing disperse systems is demonstrated by the calculation of the gold number according to Zsigmondy. This method describes how much (in mg) protective colloid is required to prevent the agglomeration of 10 mL of red formalin gold solution as brought about by 1 mL of a 10% saline solution.

Such a task can be accomplished using only 0.0001 mg of gelatine, whereas 0.02 mg of gum arabic or 0.05 mg of starch are required. Gelatine is thus by far the best protective hydrocolloid of those currently available.

2.1.2.9 Adhesion Properties

The adhesive characteristics of gelatine are probably the longest known and used of its surface-active properties; this particular property has been known for some 8000 years. Today, for example, cereal bars with low water contents are produced by adding gelatine hydrolysate as a binding agent (see Fig. 2.14). In this application, the binding power between the particles to be bound is utilized by the gela-



Fig. 2.14 Cereal bars with low water and low sugar content are produced with gelatine or gelatine hydrolysate as a binding agent.

tine solution. Physically, this compound effect of the binding agent is based on adhesion and cohesion.

Cohesion is due to the interaction between the molecules within a substance. Adhesion on the other hand is due to the interaction between the molecules of the various components of a system.

Highly concentrated gelatine solutions are capable of fully covering the surface contours of the particles to be affixed to each other and, as a result, adhesion forces are built up. In this condition, however, its own cohesive power is extremely low. Once the gelatine solution has been evenly distributed over the surfaces to be joined, it starts to gel on cooling while retaining its form. This process increases the cohesion of the binding layer considerably, thus producing the desired adhesive effect. The adhesive power of gelatine is thus directly dependent on the viscosity of the solution being used in the application and less on its gelling power. If more liquid is available for dissolution, a medium-Bloom gelatine is recommended.

2.1.3

Basic Principles for Selecting a Suitable Type of Gelatine

Apart from its principal functional properties, gelatine has other characteristics that are important for the production process of the final product. These can be adjusted or brought about by blending and include parameters such as pH, salt content, and particle size distribution.

The combination of properties that is most suitable for a particular production process or application cannot be predicted with any degree of accuracy. Thus, the user should select the most suitable gelatine type for his product and process in cooperation with the application experts of the gelatine manufacturer. Because of the complex reactions involved, such a close exchange of experience and cooperation with raw materials experts, product developers, and production specialists is highly recommended.

2.1.4

Chemically Modified Gelatines

Chemically modified gelatines are primarily used in technical areas such as photography and cosmetics but also in the pharmaceutical industry for the production of capsules and blood plasma substitutes. The flocculation reaction used in the clarification of wine is also based on a natural chemical modification of the clarifying gelatine used. The gelatine is cross-linked by the tannins that occur naturally in wine; as a result, the gelatine is hardened and loses its solubility irreversibly.

Generally, gelatine can be modified via its amino, carboxyl, and hydroxyl groups. Most modifications, however, are via lysine, hydroxylysine, and the amino groups of the N-terminal amino acid. These can be modified in the neutral to slightly alkaline range without the gelatine becoming strongly hydrolyzed and

Table 2.4 Overview of possible chemical modifications.

Functional group	Modification/reagent	Reagent example
Amino group –NH ₂	Organic acid halides/acid anhydrides Aryl-substituted reagents Activated organic halogen compounds Carbamoylation Reaction with double bonds Epoxides Guanidylation	Succinic acid anhydride Phthalic acid anhydride Phenylisothiocyanates Benzyl bromide Biphenylhalomethane Cyanates Maleimides Glycidyl ether O-methylisourea
Carboxyl group –COOH	Methylation of carboxyl groups Reaction with carbodiimides	Methanolic sulfuric acid Carbodiimides
Hydroxyl group –OH	Acetylation	Acetic acid anhydride

Source: A.G. Wards, A. Courts: "The Science and Technology of Gelatin", Academic Press, London, New York, San Francisco, 1977.

degrading. The chlorides and anhydrides of carboxylic acids, sulfonyl chlorides, isocyanates, and epoxides are normally used for the reaction.

Several examples of modifications with the various groups are shown in Table 2.4.

The property profile of a particular gelatine can be significantly altered through chemical modification. For example, by modifying the lysine group with succinic acid anhydride, a gelatine type characterized by improved swelling in water (among other properties) is obtained.

Biodegradable, non-toxic, and non-irritating detergents suitable for use in cosmetics are other examples. These are produced by reacting hydrolyzed gelatine with long-chain fatty acid chlorides (see also Sections 3.2.8 and 3.2.9).

Modification using poly-functional compounds such as dialdehydes, poly-epoxides, and poly-isocyanates – chemicals that can react with several of the side groups of gelatine – leads to cross-linking of the gelatine (see Fig. 2.15).

Depending on the degree of cross-linking, products can be obtained that are capable of withstanding boiling water. The melting point of the gel is increased, the swelling ability decreased, and resistance to mechanical stress improved.

The degree of cross-linking is dependent on a number of different parameters, e.g., the type of gelatine, the reaction temperature, the reaction duration, the pH, and the cross-linker used. A number of classical cross-linkers for gelatine are listed below:

Metallic cross-linkers: Al³⁺, Cr³⁺, Fe³⁺, Ce³⁺, La³⁺, Zr⁴⁺.

Organic cross-linkers: Aldehydes, ketones (e.g., formaldehyde, glyoxal), epoxides, isocyanates, and carbodiimides.

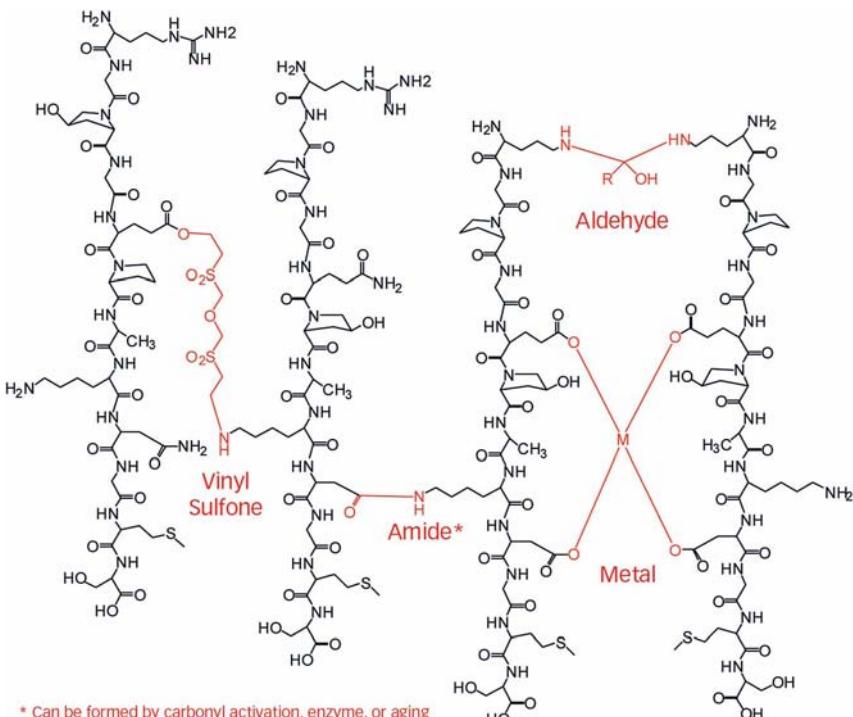


Fig. 2.15 Structure of cross-linked gelatines with different agents.

Reaction with reactive derivatives of acrylic and methacrylic acids enables “macromers” with polymerizable side chains to be produced. In a second reaction step, namely polymerization initiated by radicals, irradiation, or redox reactions, the modified gelatines thus obtained can be converted into derivatives resistant to organic solvents and boiling water. In contrast to conventional gelatine cross-linking, this method enables precise control of product properties to be achieved, because the modification and the cross-linking are separate processes. Polymerizable gelatines are used, for example, for the microencapsulation of fragrances or as coatings for packaging materials.

Another type of modification is based on a biological process. The addition of the enzyme transglutaminase reconnects parts of the linear collagen chains that are broken. The result is increasing viscosity and a gel that melts less and less on being heated to 100 °C. However, the firmness of the gel increases only slightly. This effect is used in several countries in meat processing to produce luncheon meat or similar products.

More detailed information on the special properties of modified gelatines can be found in the relevant application chapters of this book.

2.2

Manufacture of Gelatine: Theory and Practice

The gelatine industry, by investing heavily in technology, plant, and equipment, has been able to continuously develop its products and open it up to new application areas. Today, manufacturers can select processes to optimize the properties of the gelatine to be produced. The manufacturing process selected depends on the one hand on the raw material but also on the envisaged application of the gelatine produced. At the same time, apart from savings in terms of energy and process water to an extent of some 25% over the past 10 years alone, both the consistency of quality and the yields obtained have been substantially increased.

In the large-scale manufacture of gelatine (see Fig. 2.16), the primary raw material used, for reasons of availability and attainable product quality, is the collagen found in cattle and pigs. Raw materials from fish and poultry are very new and are mostly processed to satisfy the wishes of specific religious consumer groups. They currently occupy niche markets only. Even if the raw materials are different in nature, they all have one thing in common: they originate from animals that, after being subjected to stringent controls, have been approved for human consumption.

2.2.1

The Raw Material “Ossein”

In slaughterhouses and meat processing plants, not only fresh meat but also fresh bone material is obtained.

A small portion of the bone material obtained is supplied, like the meat, to butchers for sale as soup bones. However, the major part of this valuable source of collagen goes to gelatine manufacturers. The process is a rapid one and is carried out under strictly hygienic conditions. At the manufacturers, the bone material is gently chipped to a cube size of about 0.5 cm and degreased by washing for 30 min with hot water (85–90 °C) under strong mechanical agitation. This process completely removes any residual flesh and bone skin that may still be attached. Subsequently, the chipped bone is dried with hot air in continuous driers and then sieved and sorted according to particle size. The various chip grades are then further processed separately. During this process, fat (used in the chemical industry and in many countries by animal feed producers), meat, and bone meal are produced as by-products, the latter being used in Europe and North America mainly as fertilizer.

2.2.1.1 Maceration

The bone chips that have been released for further processing to gelatine are treated with dilute (4–6%) hydrochloric acid in a counter-current process in a battery of tanks for about a week at ca. 10–20 °C. During this period, the calcium phosphate and calcium carbonate, which are bound to the bone material and provide it with its firmness, are converted into their soluble forms and are later

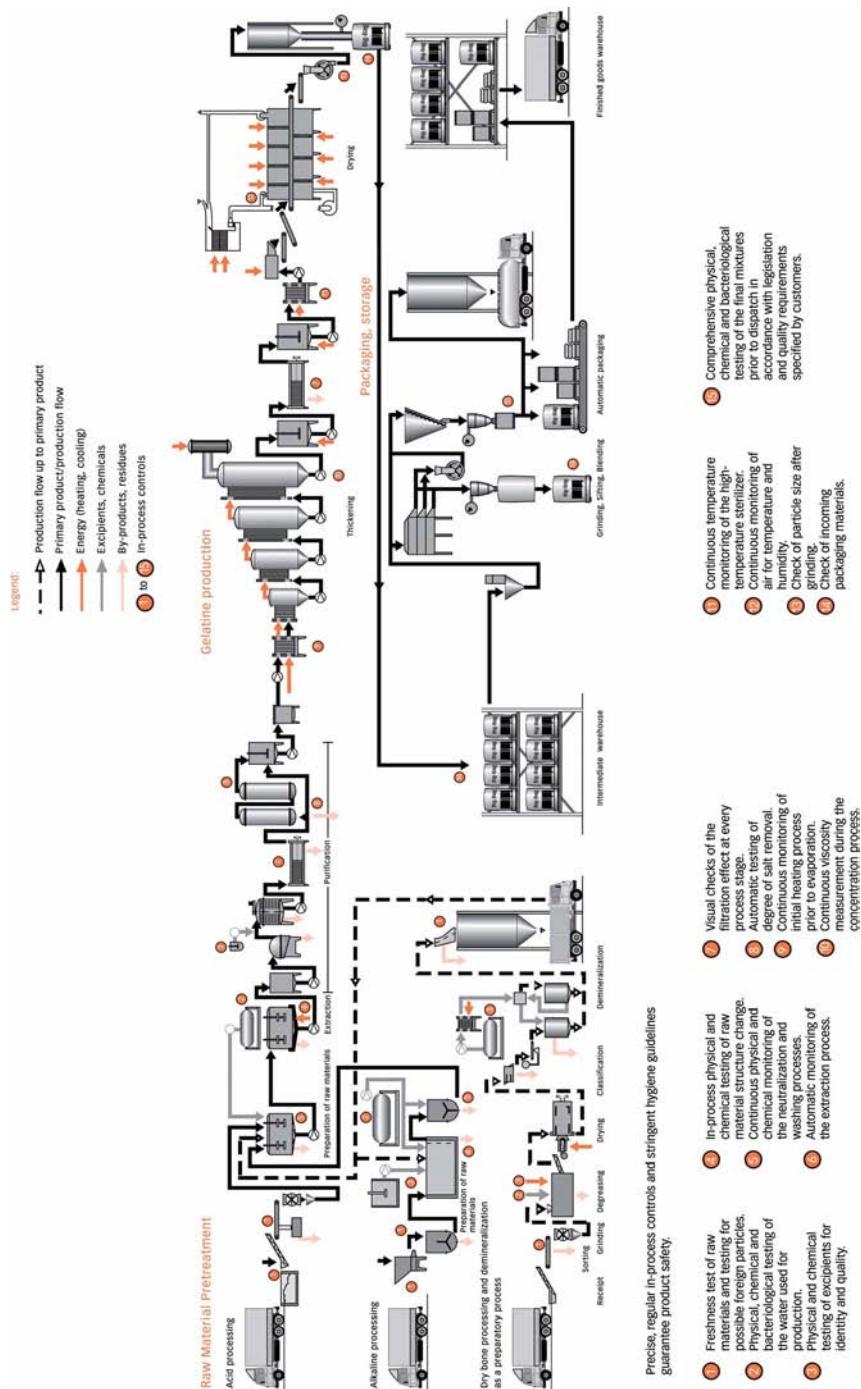


Fig. 2.16 Schematic of a modern industrial manufacturing process for different types of gelatine. In-process controls guarantee reliable and consistent quality.



Fig. 2.17 At first glance, ossein particles still look like crushed bones. The term “ossein” is a combination of the French “os” for bone and “ein” for protein.

separated by precipitation. This process of demineralization is known as maceration. On completion of the maceration, all that is left is the proteinaceous structural framework of the bone – the actual raw material or “ossein” that is used for the production of gelatine (see Fig. 2.17). The term “ossein” originates from French and is a combination of “os” for bone and “ein” for protein.

Maceration takes place using a counter-current process (see Fig. 2.18). Here, the freshly chipped and degreased bone material is initially treated with an already salt-rich acid solution. In the final process step, the substantially demineralized bone is then treated with fresh acid. This counter-current scheme increases the overall efficiency of the maceration process considerably and prevents unwanted warming and foaming.

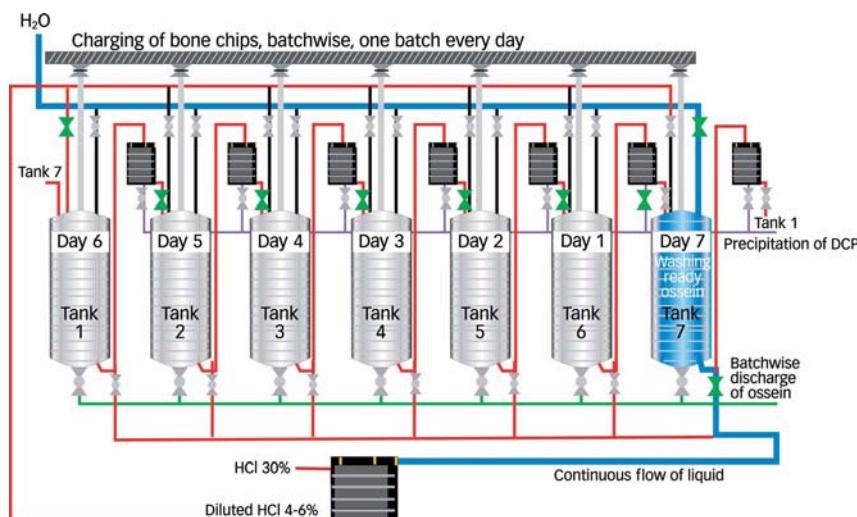
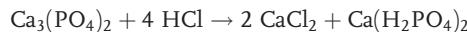


Fig. 2.18 Counter-current acidulation process for the demineralization of bone for the production of “ossein.”



Fig. 2.19 Dicalcium phosphate – a by-product of ossein-production – is used as a fertilizer in agriculture.

Upon adding milk of lime to the saturated acid solution in a separate apparatus, dicalcium phosphate is precipitated. $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaHPO}_4 + 2\text{H}_2\text{O}$

This material, after removal of water by centrifugation or filter presses followed by drying, is used by the agricultural industry as a mineral supplement for animal feed or as a fertilizer (see Fig. 2.19).

2.2.1.2 Pressure Hydrolysis

In recent years, individual manufacturers have introduced a process for the manufacture of gelatine from raw bone that functions without the need for maceration. This process, known as “pressure hydrolysis”, is an improved version of the traditional process for manufacturing bone glue. The bone chip material is treated batchwise in autoclaves in an aqueous medium under extraction conditions at about 140 °C for over 20 min. During this process, the collagenous protein is dissolved in a stepwise manner. The result is gelatine with a strong color, taste, and odor that exhibits a very low gelling power; these characteristics limit its applicability considerably.

As a result of the process conditions of pressure hydrolysis, the extraction process follows a basic rule: the smaller the particle size the shorter the process. Finely ground bone chips can be converted into gelatine exhibiting excellent gelling power and good sensory properties within minutes and is well suited for continuous extraction processing (see also Section 2.2.6). Appropriate systems have been submitted for patenting (Swedish Patent No. SE 9300912 and French No. FR 625412). However, no industrial process has so far been developed.

2.2.2

The Raw Material “Hide Split”

The second major source of collagen for the manufacture of gelatine is fresh cattle hide. The thickness of the hide depends on the climate where the cattle are

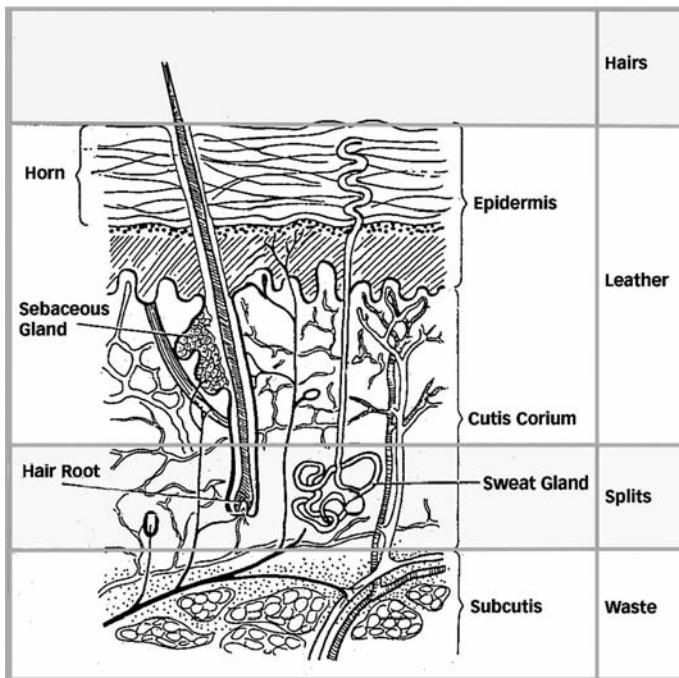


Fig. 2.20 The central layer of the cattle hide (“split”) is an excellent source of collagen for the manufacture of gelatine.

raised. The warmer the climate, the thinner is the hide. The external side of this material contains less collagen and is almost exclusively used for the manufacture of leather. The meat side is made up of fatty tissue, which is expertly removed. The central layer, however, is practically pure collagen, and is thus an excellent raw material for the manufacture of gelatine (see Fig. 2.20).

After pretreatment with alkali, a process that swells the hide and enables it to be dehaired, the hide is cut into three separate layers using horizontal cutters. This process gave rise to the designation “split” used throughout the industry. This “split”, which, depending on the age of the animal, can be up to 4 m^2 in size, is first cut into hand-sized pieces in cutting machines in the gelatine factory and immediately conditioned with acid or alkali. In principle, pieces of hide that have not been subjected to the splitting process can also be processed, but they will also need a dehauling stage using alkali/sulfide solution before being processed by the gelatine manufacturer. Their low collagen content reduces the yield considerably and consequently lowers the operating efficiency and productivity.

The size reduction of the hides is fundamental for good conditioning. The alkaline and acid treatments are more uniform and the extraction is facilitated.

2.2.3

The Raw Material Pigskin

Pigskin, first used for the manufacture of gelatine in the 1930s, is today's most important raw material for gelatine worldwide. Some 3–4 kg of processable skin is obtained from every pig slaughtered.

The pigskin is first separated from the layer of fat during meat processing, and then, if it is not required for processing into sausages or luncheon meat, is transported (cooled or frozen) to the gelatine factory (see Fig. 2.21). The cooling process prevents microbial degradation and oxidation of any fat remaining in the skin during transport.

The fatty tissue of pigskin also contains collagenous protein that can be used by the manufacturer for the production of gelatine after the fat has been melted out in the form of "greaves". However, because of the turbidity caused by emulsified fat, a special process using special equipment is required.



Fig. 2.21 The removal of pigskin, today's most important raw material for gelatine worldwide, from the fat layer is often still done by hand. However, machines are being increasingly used.

In countries such as China that have a huge pigskin leather industry, the pigskin is split as described above for cattle hide and then further processed to gelatine.

2.2.4 Conditioning

The collagen contained in animal connective tissue dissolves very slowly, even in boiling water. This is because of the cross-linked nature of the collagen. Thus, prior to extraction, gentle chemical treatment is necessary to break down these cross-links. The type and degree of cross-linking is dependent on the age of the animal (see Section 2.1). The gelatine manufacturer must therefore adjust the process parameters for conditioning as well as the subsequent extraction conditions precisely to the raw material being processed to be able to obtain gelatine with the desired properties (see Table 2.5).

In principle, the cross-links could be cleaved by a process of slow “cooking”, a method used for centuries in the preparation of aspic. However, subjecting the material to longer periods of higher temperature tends to negatively influence all the parameters that affect quality. Thus, gentle chemical cleavage produces a much better quality of gelatine. For this reason, only highly dilute acids and alkalis are used. In this way, the chains of the collagen protein remain essentially intact, but the cross-links are cleaved. In this case, only partial hydrolysis has taken place.

For older animals, more intense alkaline treatment is preferred, while for younger ones a short period of conditioning with very dilute acid is all that is necessary. Pigskin, because of its rather high fat content, is principally suited for digestion with acid to prevent the saponification that would otherwise occur. Any gelatine produced with such material would, however, be unusable for most

Table 2.5 Raw material conditioning.

Raw material type	Raw material conditioning	
	Acid	Alkali
Bones	x	X
Cattle hide splits	x	X
Pigskin splits	x	X
Pigskin	x	
Fish skin	x	
Poultry skin	x	
Poultry feet	x	

applications for sensory and visual reasons. However, all other raw materials used in the production of gelatine can also be processed using the acid method. This also applies to hide splits which, during the swelling and dehairing process, are subjected to alkaline treatment; this is the equivalent of brief alkaline conditioning.

Apart from acids and alkalis, enzymes, or a combination of enzymes and chemicals, are also used for cleaving the cross-links. Special collagenases are required for such a process, however, as conventional proteinases are not able to digest native collagen. Thus, gelatine, but not collagen, can be digested in the human body.

This shows just how variable today's production processes, and the resulting types of gelatine obtained, are. The manufacturer can thus select the production process in accordance with the required properties of the gelatine to be produced. Within a certain scope, therefore, "customized" gelatine can be produced for specific applications.

2.2.4.1 Alkaline Pretreatment "Conditioning" for Type B Gelatine

In the alkaline process, both the chopped split material (see Fig. 2.22) and the ossein prepared from bone are treated with alkali in tanks or pits up to 125 m³ in volume, with or without agitation.

Depending on the concentrations and temperatures used, the conditioning process takes from a few days, for example, with a 1% sodium hydroxide solution at 20 °C to four months with supersaturated milk of lime. Agitation always speeds up the conditioning process.

The quality of the gelatine with respect to the Bloom and viscosity can be a result of the relationship between concentration of sodium hydroxide, temperature, and duration of conditioning. Stronger conditioning normally results in higher viscosity.



Fig. 2.22 Cut hide splits ready for extraction of type B gelatine.

Although the process with milk of lime would appear to be somewhat inefficient at first glance, it has a number of technological advantages: because of the low solubility of the calcium hydroxide, a constant degree of relatively weak alkalinity is maintained even when the solution is super-saturated. During the treatment, a process that lasts several months, the non-protein substances such as mucopolysaccharides and sulfur-containing compounds as well as non-collagenous proteins, especially albumin and globulin, which are always contained in the raw material, are reliably dissolved out. This results in the raw material being effectively purified. At the same time, the relatively mild calcium hydroxide helps to balance out certain differences in the raw materials. This applies to the age of the animals, the particle size of the bone chips, and the thickness of the hide pieces. In this way, undesired yield losses can be avoided. If treatment with alkali is excessive, the collagen becomes soluble in cold water. Therefore, as the raw materials are being washed, collagen will dissolve in the aqueous phase and hence contribute to lower yields.

During the alkaline treatment process, the solution is constantly enriched with dissolved non-collagenous protein and other substances, and it is therefore repeatedly changed over the months, at first daily and later on a weekly basis. Subsequently, the treated material is washed free of alkali and neutralized by the addition of acid. Most of the neutral salts produced during this process are then essentially removed by numerous washings.

2.2.4.2 Acid Pretreatment for Type A Gelatine

The breeding methods used today mean that pigs are approximately five to seven months old when they are slaughtered. As a consequence, the collagen of their skin is relatively weakly cross-linked. All that is then required to ensure the warm-water solubility of the collagen is to soak the hand-sized pieces (see Fig. 2.23) for up to 24 h, for example in 2–4% dilute sulfuric or hydrochloric acid at room temperature (see Fig. 2.24).

At the same time, because of the mechanical agitation involved, this process separates off most of the fat, which floats to the surface and is hence easy to remove. The fat content of pigskin, carefully separated from the bacon fat, is 30% or so; in comparison, the protein content is only about 20%.



Fig. 2.23 Piece of fresh pigskin for type A gelatine.



Fig. 2.24 Large, insulated acidulation and extraction tank for gelatine.

Phosphoric and organic acids are also suitable for this processing step, but they are more expensive and tend to influence the odor and taste of the final product negatively.

If bovine hide splits are conditioned with acid, the manufacturer normally allows the acid to react over a period of 48–72 h. It must be noted, however, that, subsequent to acid conditioning, extraction must be carried out in an acid medium too.

After the treatment with acid, the gelatine manufacturer raises the pH to about 2–4 by adding alkali. Most of the salts formed are then washed out over a period of 24 h using frequent changes of water.

The ratio of gel firmness to viscosity during subsequent extraction is regulated by the pH and the extraction time/temperatures used (see Fig. 2.25).

Both parameters, however, exert an influence on the speed of extraction. The manufacturer must therefore find the optimal ratio between the desired rapid extraction and undesired chemical/thermal hydrolysis of the gelatine already melted out (see Fig. 2.26).

2.2.5

Traditional Extraction (Batch Process)

The gelatine is extracted from the pre-treated raw material using different processes. The traditional method is to use drinking quality water at different temperatures in a multi-stage batch process. The gelatine is dissolved out in stages at temperatures between 50 and about 100 °C, the raw material being dissolved from the outside to the inside. The actual time for each of the steps ranges from four to seven hours. During the extraction process the material is agitated very

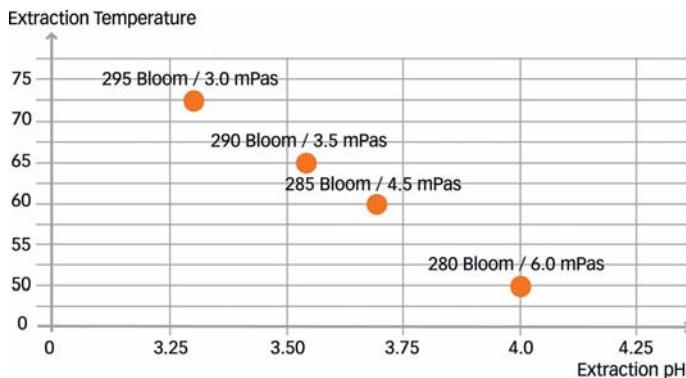


Fig. 2.25 Relationship between gel firmness and viscosity as a function of extraction temperature and pH over the same time.

gently, if at all, so that any residual fat does not form a fine emulsion, which would be impossible to remove at a later stage.

After each extraction stage a 3–7% gelatine solution is obtained. Its gelling power decreases as temperature increases with each subsequent extraction step. During the extraction phase of 18–36 h, unavoidable and progressive thermohydrolysis takes place, i.e. the polypeptide chains are cleaved (see Fig. 2.27).

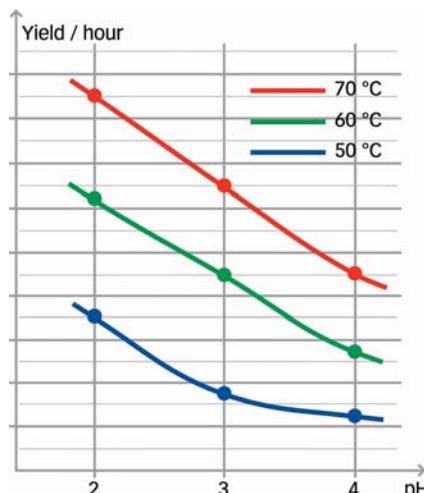


Fig. 2.26 Trend of the quantity of extracted gelatine as a function of extraction pH and temperature.

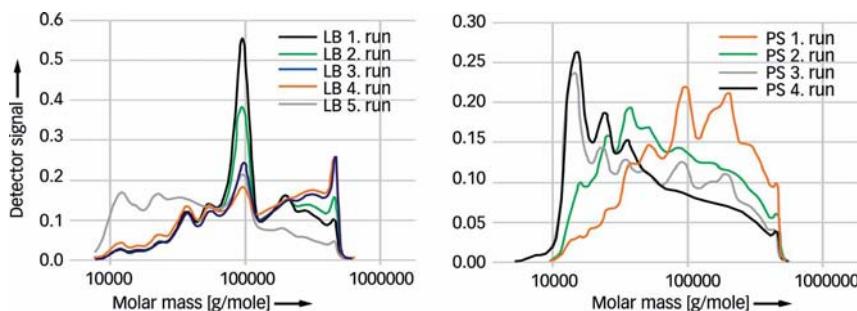


Fig. 2.27 Molecular weight distribution of gelatine from different extraction runs: type B gelatine (limed bone) left and type A gelatine (pigskin) right.

The coloration of the gelatine on the other hand increases with increasing reaction time due to the Maillard Reaction between protein and traces of carbohydrate in the raw material (see Fig. 2.28).

Other chemical reasons for the increase in color intensity have not yet been precisely clarified. Addition of legally approved oxidizing or reducing bleaching agents such as hydrogen peroxide or sulfur dioxide can render the product lighter in color.

If, during a batch process of type B gelatine, extraction takes place under slightly alkaline conditions, gelatine of high viscosity can be obtained. This viscosity, however, tends to be lost if the gelatine is later processed at acid pH (see also Section 2.1).



Fig. 2.28 Increasing color of the extracted gelatine, depending on the extraction step. (first extraction top right.)

Where the alkaline pretreatment process is used, very little residue is left in the extractor, practically all foreign protein having been almost completely dissolved during the conditioning process. Manufacturers of photographic emulsions use alkaline-conditioned gelatine almost exclusively; this is because of the high purity specifications required. In the case of the acid extraction of pigskin, on the other hand, some 5% of undissolved non-collagenous protein and porcine fats remain as by-products.

2.2.6

Continuous Extraction

Alternatively, bovine hide gelatine can be produced using a continuous process, where the gelatine is extracted at low pH (between 2 and 3). In this procedure, pretreated raw material is continuously fed to the extractor water using a counter-current process.

Thus, there are always raw materials from the various extraction phases in the reactor at the same time. This means that different types of gelatine are extracted in parallel, but these are mixed in the extractor. Because of the low pH, the extraction speed increases rapidly, the fundamental condition for a continuous process.

The result is a uniform gelatine with respect to its analytical data: the Bloom value is high, the viscosity low, and the color light. These parameters are very close to those required by users of pigskin gelatine in the food industry. This is therefore a preferred alternative to pigskin gelatine if the latter is not desired (for example for religious reasons). If the manufacturer reheats the material left in the bottom of the extractor, which is several meters high, at the end of the process, he additionally obtains, in the case of a continuous process, very low-Bloom gelatine.

The continuous process also requires the bottom of the extractor to be purged periodically; in this way, insoluble parts of the raw material can be eliminated.

Another extraction process for gelatine is the semi-continuous process. In this case, starting material is added to the extractor batchwise and is then extensively extracted with water. Increasing the temperature continuously intensifies the extraction; this enables gelatine from the center of the raw material pieces to be obtained which is more difficult. During this process, the different gelatines are consecutively withdrawn from the extractor; each extract becomes weaker in terms of Bloom strength over time and, as in the batch process, increases in color.

The result is high-Bloom, light-color gelatine at the beginning of the extraction process and low-Bloom, strong-color at the end.

As in the case of “Pressure Hydrolysis” (see Section 2.2.1.2), the continuous process can be additionally modified by reducing the particle size of the raw material even further and by reducing the pH and increasing the temperature. The gelatine can then be extracted within minutes (see Fig. 2.29).

Theoretically, all the gelatine can be obtained, in high quality, at a temperature of around 50 °C. For this to be possible, each individual raw material particle

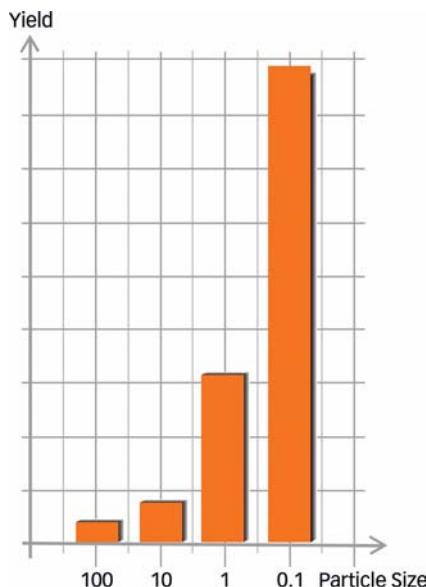


Fig. 2.29 The quantity of extracted gelatine per unit of time is extremely dependent on the raw material particle size.

must have a practically identical partially hydrolyzed collagen structure and the interior of each particle must be as homogeneous as possible. In practice, however, acid and alkali have a more intensive effect on the outside of the particles than on the center. In addition, the difference in the thickness of the pieces of material and the different ages of the source animals also exert a considerable influence. If the manufacturer optimizes the treatment of the material for the interior of the pieces, the exterior parts will be too strongly hydrolyzed and the yield will be lower. Thus, the lower degree of digestion of the interior must be compensated for by a higher extraction temperature.

If the extraction process is to be optimized, the design of the extraction vessels used (see Fig. 2.30) should be precisely adapted to the process. If this is done, however, the producer cannot, using the same vessel, change from a batch to a continuous process or vice versa.

2.2.7

Production of Fish and Fowl Gelatine

Fish gelatine is normally extracted from fish skin and can be conditioned using both acid and alkali. The skins can be obtained either from fish processors that work in conjunction with fish farms or from fishing vessels that carry out filleting at sea. However, the fish skins should be cleaned thoroughly in order to remove any fat that may still be present.

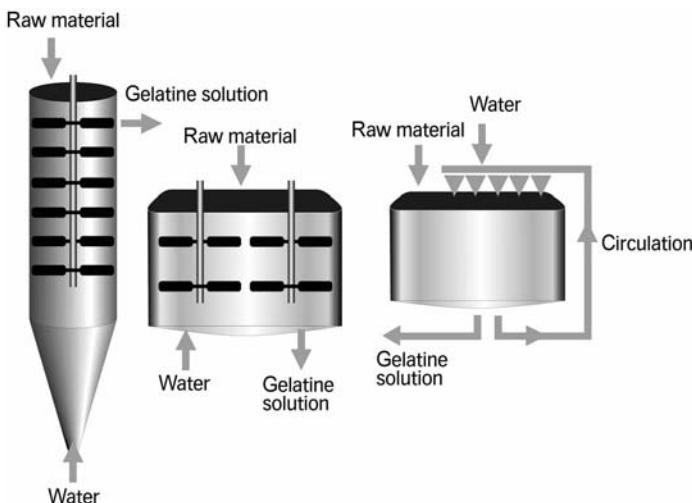


Fig. 2.30 Different types of gelatine extraction tanks. Left: continuous counter-current process. Center: batch process with stirrers. Right: semi-continuous process with circulation.

The skins are frozen and transported to the gelatine factory. There they are thawed, washed several times, and treated with mineral or organic acids over a period of 24 h. Occasionally, a pretreatment stage with milk of lime is carried out first to bind any residual fat (European Patent No. EP 0436266 and US Patent No. US 6368656).

Gelatine produced from fish taken from the cold water of the North Atlantic region contains considerably less proline and hydroxyproline (see Table 2.6). This, in spite of the high molecular weight, reduces the gelling power of the gelatine produced. This serves to demonstrate anew just how complex the mechanism of gelatine gelling really is.

However, these gelatines characteristically exhibit good film formation and have good emulsifying properties. As a result, the main application areas are almost exclusively the embedding of oil-based vitamins using spray-drying techniques.

In contrast, the gelatine produced from fish taken from warmer waters has good gelling properties; it is in fact very similar in nature to the more common types of gelatine and is frequently used in the food and pharmaceutical industries. However, the user must note that these types of gelatine tend to have technological properties, e.g. stability of viscosity, that are dependent on the species of the fish from which the raw material is processed. As a consequence, gelatine produced from the skin of a tuna fish has different properties from that of a Nile perch or Tilapia.

At present, fish gelatine is considerably more expensive than gelatine that is produced traditionally. This is mainly because of the high cost of transport and

Table 2.6 Comparison of the amino acid composition of Type I cattle hide collagen and fish skin collagen (rounded residues per 1000 residues).

Name	Hide ^[a]	Codfish ^[b]	Sturgeon ^[b]
Alanine	114	105	119
Arginine	51	63	52
Asparagine	16		
Aspartic acid	29	42	48
Cysteine			
Glutamic acid	48	77	71
Glutamine	25		
Glycine	332	332	337
Histidine	4	12	5
Hydroxyproline	104	41	82
Hydroxylsine	5	8	14
Isoleucine	11	17	11
Leucine	24	30	18
Lysine	28	33	22
Methionine	6	21	9
Phenylalanine	13	14	14
Proline	115	90	102
Serine	35	61	50
Threonine	17	26	29
Tryptophan			
Tyrosine	4	5	2
Valine	22	25	18

^a Rose, P. I.: Gelatine in Encyclopedia of Polymer Science and Engineering, Vol. 7, Wiley, London, 1987, p. 488–513.

^b Gross, J.: Comparative biochemistry of collagen, Comparative biochemistry, Vol. 5, Academic Press, New York, 1963, 307–346.

the low concentration of collagen in the fish skin. It is thus difficult to achieve efficient utilization of production plants. Although fish bone is fundamentally suited for the production of gelatine, the industry, after much research, has, for economic reasons, decided in principle against its use. Although fish gelatine is also a foodstuff, different countries have different regulations regarding declarations, e.g. due to its associated allergenic potential.

Poultry gelatine is also obtained from fresh skin and bone material. As the birds involved are normally young when slaughtered, the material can be pre-treated using the acid process. Because of the processing of the fats and other by-products, however, processing is optimally carried out in facilities that primarily process pigskin (see Fig. 2.31).

The poultry skins contain a lot of fat and the concentration of collagen is low; it is thus preferable to use other material such as feet. The poultry bone is normally



Fig. 2.31 A modern gelatine production plant.

not demineralized before conditioning, and during the extraction the concentration of salts is high. Thus, a precipitation step after extraction is necessary. Other steps like ultrafiltration and deionization remove excess salts.

However, because of the relatively high costs involved, gelatine produced in this manner will remain a niche product at least in the medium term; this is mainly because the skin obtained from poultry is a coveted raw material for other food applications.

2.2.8

Processing the Extracted Gelatine

After the extraction process, the gelatine solution obtained has to be subjected to intensive purification. The processes used are quite varied, and producers tend to have their own combination of methods and apparatus based on experience. Only a small selection of the possible process steps used will be described.

2.2.8.1 Filtration and Clarification

Initially, sometimes continuous high-performance separators are used to divide the gelatine solution into three phases; this separates out undissolved solids and fats from the aqueous gelatine solution. This technical grade fat is repurified and used mostly by the chemical industry for further processing or saponification. In many countries, the fat obtained during pigskin processing is used in the animal feed industry. In the processing of pigskin, the quantity of fat obtained is greater than that of the gelatine produced; it thus becomes an important and valuable by-product. In the case of hide split and ossein, however, fat represents a much smaller portion, and it thus becomes more of an undesired by-product.



Fig. 2.32 Modern centrifugal alluvial filter equipment. Several subsequent filtration steps ensure the produced gelatine is pure.

On exiting from the separators or other steps of pre-clarification, e.g., fine sieving, the gelatine solution still does not have the required clarity. It is thus subjected to a number of additional filtration steps (see Fig. 2.32).

Mostly, this purification process begins with centrifugal pre-coated alluvial filtration, where turbidity-causing substances are filtered out by diatomaceous earth or perlite. However, filtration through pressed cellulose cakes is also widely used. This is mostly followed by multi-stage fine filtration using cellulose sheet filters as employed, e.g. in the beverage industry. The diatomaceous earth or perlite layers and the filter sheets are used until a certain pressure differential is observed; they are then discarded. The cellulose filters, however, can be recycled.

For certain low molecular weight types of gelatine, the manufacturer can use modern membrane microfiltration techniques (see Fig. 2.33) instead of centrifuges and filters.

With pore sizes of about 1 micron, most linear gelatine molecules can pass through the membranes, while globular fat particles or solids are held back. In the case of high molecular weight grades, more of the gelatine is held back in the retained volume. Hence, it is not a suitable process for this particular application.

2.2.8.2 Deionization

As a result of conditioning and neutralization, the gelatine solution, in spite of numerous washing steps, still contains considerable amounts of mineral salts. The ash content of such gelatine is in the order of two to three percent and hence frequently exceeds the limit prescribed by most pharmacopeias and food regulations, which specify less than two percent. Many users in the pharmaceutical industry in fact require an ash level of under 1% for certain applications. For special



Fig. 2.33 Membrane microfiltration plant for the filtration of low molecular weight gelatine.

photographic layers, practically “salt-free” gelatine is required, i.e. with contents of certain cations of just a few parts per million.

The dissolved salts exert an influence on most of the physical properties of gelatine – these worsen with increasing salt content – as well as on the sensory parameters. Sometimes, however, only certain salts are undesirable. For example, if gelatine of high sulfate content is dissolved in drinking water containing much calcium, the final dried product may demonstrate turbidity caused by calcium sulfate or precipitates of other insoluble salts.

In order to avoid such undesired effects, the dilute gelatine solution is passed through ion exchangers (see Fig. 2.34).

These remove cations or anions specifically or, using the so-called mixed bed procedure, the solution can be completely deionized in one step. The former method has the advantage that the final mineral salt composition can be adjusted to the application envisaged.

Ultrafiltration is also a suitable technique for desalting gelatine. Here, in addition to the concentration effect on the dilute gelatine solution, the salts are removed. Nanofiltration with a pore size of approximately 0.005 microns is another



Fig. 2.34 Ion exchangers in large columns specifically remove cations or anions or deionize the gelatine solution completely.

possibility. Because of the low throughput, however, it is only practical when the mineral salts are to be partially removed.

2.2.8.3 Concentration

The purified and demineralized gelatine solution consists of over 95% water. This water now has to be almost completely removed. Only dried gelatine with its normal residual water content of 10–12% has an unlimited shelf life from the microbiological point of view. In addition, dilute gelatine solutions can neither be stored nor transported easily.

As a rule, concentration takes place in a multi-stage vacuum system using plate, circulatory, or thin-layer evaporators. In this way, in a one-step process at about 52 °C or in a multi-step process between 50 and 100 °C, the water is gently evaporated. Subsequently it is condensed, with energy recovery, and then reprocessed and reused.

Membrane filtration such as ultrafiltration, attractive because of its energy and thermal advantages, is also widely used in practice. Using pore sizes of about 0.05 microns, high degrees of separation of water and mineral salts are possible. One disadvantage, however, is that small molecules of gelatine are also able to pass through the membrane. This in turn lowers the gelatine yield and means that the permeate has to be reprocessed. Thus, the pore size of the membrane used is dependent on the type of gelatine to be concentrated.

The final concentration is adjusted via the evaporator, the size of which, however, is considerably smaller than it would be without ultrafiltration. Depending on the type of gelatine, concentrations of up to 50% can be achieved. Basically, the gelatine manufacturer wishes to obtain a highly concentrated solution at the end of this step in order to save the energy required for drying at a later stage,

this being about 10 times that required for removal of the water with a multi-effect evaporator.

Because of the heat applied during the evaporation process, traces of globulin or albumin contained in the solution may be denatured and consequently precipitated. This necessitates an additional filtration step to ensure a crystal clear gelatine solution.

2.2.8.4 Final Sterilization

In the next production step, the highly concentrated and filtered gelatine solutions are sterilized.

For this important step, both indirect sterilization via plate heat exchangers and direct steam sterilization are used (Fig. 2.35).

Both methods are microbiologically safe to a very high degree. Use of the plate heat exchanger means that up to 95% of the heat energy can be recovered. Energy used for direct vaporization, however, cannot be recovered; the process, however, is gentler on the product (see Fig. 2.36).

2.2.8.5 Drying Process for Granulated Gelatine

Subsequent to final sterilization, the gelatine solution is chilled using a scraped surface heat exchanger. During this process, the highly concentrated solution gels and is extruded in the form of “noodles” that are fed onto the conveyor belt of a drier (see Fig. 2.37).

During this drying process, the residual water is gently removed using filtered, de-humidified, and microbiologically clean air.

Because of its low melting point, gelatine cannot be dried using direct warm air; thus, initially, the relative humidity of the drying air is 10–15%. The temperature of the air is initially about 30 °C, and this is gradually increased according to the degree of dryness of the gelatine; in this way, the ability of the air to absorb

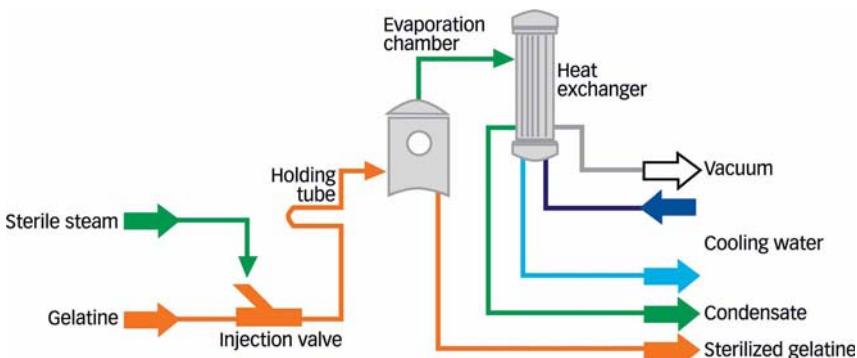


Fig. 2.35 Sterilization by direct steam injection is the most common technology in the gelatine industry. It has widely replaced indirect sterilization by plate heat exchangers.

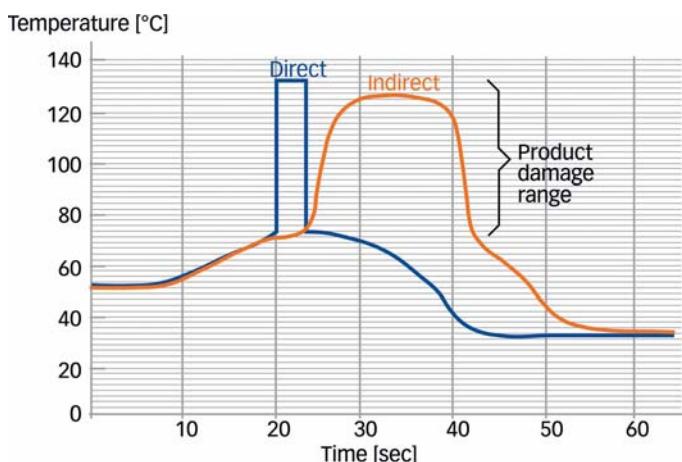


Fig. 2.36 Direct steam injection sterilization is more gentle on the product.

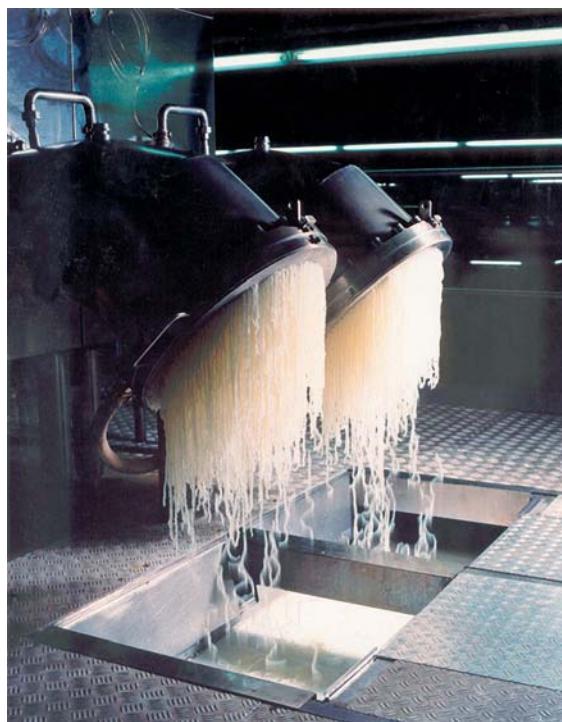


Fig. 2.37 After chilling the highly concentrated solution, the gelatine is extruded from the heat exchanger in the shape of “noodles”, which are then fed onto the conveyor belt of the drier.

water increases. By the end of the process, the air, at about 60 °C, has a high humidity. The gelatine leaves the drier in the form of a “woven carpet” of noodles with a water content of about 10%. However, before being ready for intermediate storage, the noodle bed is crushed and milled to a very coarse grist size.

2.2.8.6 Standardization and Packaging of Granulated Gelatine

At the end of a production run, homogeneous batches of gelatine of up to 10 tons and above are obtained. These differ according to the raw materials used, the manufacturing process employed, and other treatment steps involved. For special applications, factors such as the nature of the raw materials (e.g. the species of animals, age, and type of feed used) have to be taken into account. However, in order to ensure that gelatine of consistent and uniform quality is available for further processing by the customer, it is standardized prior to delivery (see Fig. 2.38).

This is performed by blending the various batches based on the physical, chemical, and, if relevant, photographic data of the individual batches obtained during analysis. Using such standardized procedures, completely uniform blends of any required size are possible.

Part of the standardization procedure also includes grinding and sieving; this is because the coarse granulate obtained after drying is often not optimal for further processing by the customer.

Table 2.7 lists the particle sizes for commercially available types of gelatine.

However, these standard types contain particles that are not necessarily uniform in size; it simply means that all particles are guaranteed to be smaller than the indicated limit. Thus, very fine particles or “fines” are also included, even if the great majority of particles are very close to the given limit. In addition to these



Fig. 2.38 The necessary blends of various gelatine batches to ensure consistent and reproducible quality are based on the physical, chemical and, if relevant, photographic data. Intensive computer support is required.

Table 2.7 Typical particle sizes of commercially available gelatine blends.

Particle size to	Corresponds to	Degree of grinding
0.1 mm	140 mesh	Powder form
0.5 mm	35 mesh	Fine mesh
0.8 mm	20 mesh	Standard mesh
2.5 or 3.5 mm	6–8 mesh	Coarse mesh
10 mm	3/8 inch	Very coarse mesh

simple grit sizes, gelatine grades with the “fines” removed by sieving are also available.

The gelatine granulate is packaged in paper envelopes in amounts of 10–15 g for retail sales to households. For small businesses, amounts of 1, 5, and 10 kg are packaged in cartons and plastic bags or plastic containers. Industrial customers receive their deliveries in bags containing 25 or 50 kg or in Big Bags (Super Sacks) containing 500 to 1000 kg (see Fig. 2.39). These large-scale users can also obtain their gelatine in bulk delivered by silo truck; this is then stored in their own silos until required for further processing.

2.2.9

Manufacture of Leaf Gelatine

Whereas powder gelatine is ready for dispatch after drying, standardization, grinding, and packaging into bags, leaf gelatine, the preferred type for use in households, bakeries, and catering establishments, is produced according to a special process. This gives the gelatine leaves their characteristic form and pattern (see Fig. 2.40).



Fig. 2.39 Semi-automatic blending and packaging stations for granulated gelatine.



Fig. 2.40 Leaf gelatine is the preferred type for use in households, bakeries and catering businesses.

To produce leaf gelatine, the manufacturer dissolves a granulated gelatine which has been tested and standardized. To prevent the occurrence of air bubbles during this process, a specific vacuum is applied. Subsequently, the concentrated solution is poured as a film onto a cooled, highly-polished stainless steel drum. The gel film is cut lengthwise according to specifications and placed onto a continuous nylon conveyor net. The net then runs through a drying tunnel of up to 100 m in length that, because of the drying principle used and the pretreatment of the air used for drying, acts in the same way as a powder dryer. During the drying process, the network pattern of the nylon net is transferred to the individual leaves. At the end of this process, the gelatine strips are cut into appropriate lengths, packaged to prescribed retail and wholesale sizes (see Fig. 2.41), and, after quality testing, delivered to the customer.

Alternatively, the manufacturer can produce a wide, uncut foil that can later be cut into individual leaves.

In the case of leaf gelatine, the leaf thickness and hence the weight of the individual leaves is set according to the type of gelatine being processed (see Table 2.8). Thus, any particular leaf of gelatine dissolved in a given amount of fluid results in the same gelling power, independent of whether “high-Bloom” or “low-Bloom” gelatine is used in the leaf manufacturing process. This principle is valid



Fig. 2.41 Automatic counting and packaging line for leaf gelatine.

Table 2.8

Number of leaves per kg	Bloom of gelatine
600	240
500	210
400	170
300	140
200	100



Fig. 2.42 Leaf gelatine is manufactured mainly by 2 companies but sold under many OEM brands. The gelling power of one leaf is always the same, regardless of the brand.

for both major worldwide manufacturers and hence for all the brands available on the market (see Fig. 2.42).

In comparison to leaf gelatine, the dosage of powder gelatine is more difficult to control. This is because, in order to achieve equivalent gelling properties, the amount of gelatine used in the solution has to be constantly varied according to the gelling power of the starting gelatine, a factor usually unknown to the user. This, however, is also a somewhat complex measuring procedure because of the small quantities often involved. For this reason, leaf gelatine is an attractive solution for small operations and households (see Fig. 2.43).

2.2.10

Instant Gelatine

Instant gelatine is produced using two distinct physical production processes. These result in two different gelatine types. The first type is, from the purely chemical point of view, a protein without additives; the other is a product that is frequently produced by drying gelatine together with carbohydrates such as sugar,



Fig. 2.43 Due to the simplicity of dosing, leaf gelatine is ideal for the small amounts processed in households.

starch, or maltodextrin. Both types, however, have a common characteristic: in contrast to normal gelatine, they can be directly processed under cold conditions.

The unique properties of instant gelatine are obtained by using special drying methods.

Employing a drum drying process (see Fig. 2.44), a pure gelatine solution of medium concentration is thinly applied to a drum that is heated by steam on the inside. This results in the spontaneous vaporization of the water and hence drying without having to progress through the gelling stage. The fine flakes thus produced are then ground to an extremely fine powder.

In the second method, which a spray-drying process (see Fig. 2.45), a gelatine solution and an additive – often more than four times the amount of the gelatine in the solution – are dried together.

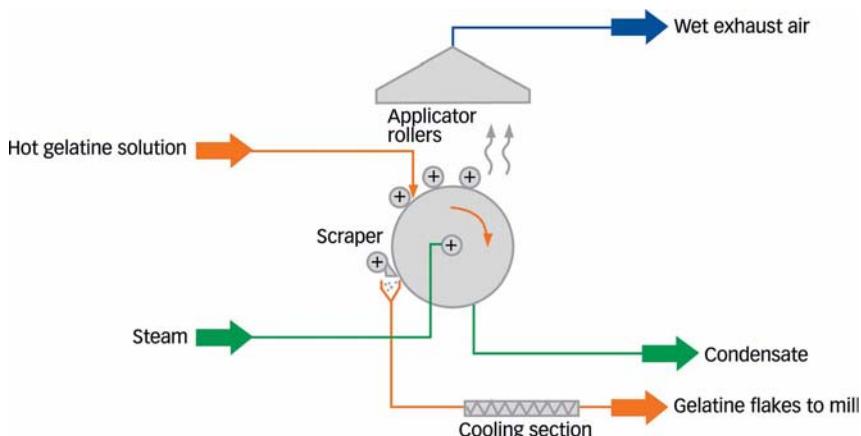


Fig. 2.44 Drum drying process for the manufacturing of pure instant gelatine.

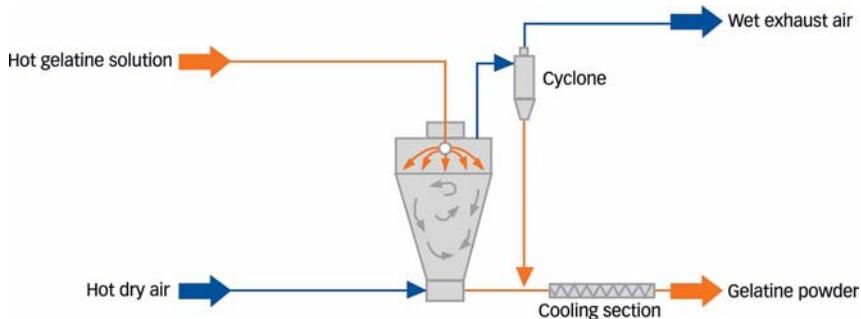


Fig. 2.45 Spray-drying process for the manufacturing of instant gelatine with additives like sugar, maltodextrin or starch.

Without such additives, high-quality gelatine can only be spray dried from very low concentrations of about 5%. This is because fibers tend to form in the drier. These cause blockages, as the water, because of its high surface tension, cannot evaporate quickly enough to prevent gelling taking place.

Spontaneous drying without having to go through the gelling stage gives the instant gelatine an amorphous form rather than the partially crystallized form of classical powder gelatine.

In the structure of the amorphous form, the three-dimensional network formed by the molecules is only weakly cross-linked. The molecular arrangement is random and disorderly and the physical inter- and intramolecular forces are very weak.

This unstable condition enables water to penetrate the instant gelatine structure with ease without the necessity of applying energy by using warm water to cleave the bonds. A gel-like texture is formed – a so-called pseudo-gel – but one that is not as strong as the physical-chemical data of the gelatine used would indicate.

As the fine particles of instant gelatine are difficult to wet, they are first thoroughly mixed with the other ingredients before being stirred into the cold liquid (see Section 3.1.4).

2.2.11

Gelatine Hydrolysate

Another modern gelatine product is gelatine hydrolysate (see Fig. 2.46), of which there are several types that are truly cold-water soluble. However, they possess no gelling power and are hence known as “zero-Bloom” types or, in terms of the European Food Regulations, “non-gelling edible gelatine”.

However, they still possess surface activity. The mean molecular weights of such hydrolysate types are within the range of approximately 500–25 000 g mol⁻¹.



Fig. 2.46 Gelatine hydrolysate (“zero-Bloom” gelatine) is a fine powder.

Gelatine hydrolysate is produced using the same raw material as that used for standard gelatine. However, in the case of hydrolysate, the collagen is broken down by means of multi-stage biochemical enzymatic digestion rather than the physical-chemical cleavage applied during the production of edible gelatine. The enzymatic process is carried out until a specified molecular weight is obtained (see Fig. 2.47). This gives the product its special quality of being soluble in cold water.

Frequently, a combination of enzymatic and chemical/physical hydrolysis is used. In a first step the manufacturer produces gelatine, and this is then hydrolyzed with enzymes until the desired molecular weight is achieved.

While only special collagenases can be employed for the direct enzymatic cleavage of collagen, gelatine can be hydrolyzed with many different enzymes such as pepsin, neurase, alkalase, bromelain, or papain. The selection of enzyme(s) and

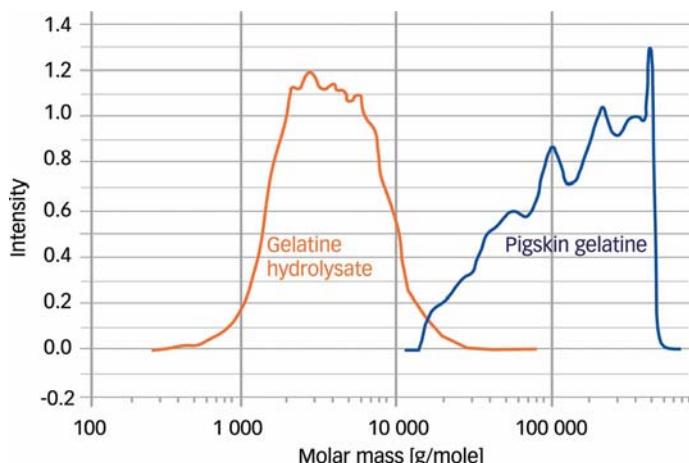


Fig. 2.47 Molecular weight distribution of gelatine hydrolysate compared with that of the gelatine prior to hydrolysis.



Fig. 2.48 Spray-drier with added agglomeration unit for the production of gelatine hydrolysate.

hydrolysis conditions essentially determine the sensory properties of the final product.

Gelatine hydrolysate, once it has gone through all the typical purification steps associated with the production of gelatine, is spray-dried to a powder (see Fig. 2.48). In contrast to standard gelatine, it can be easily dried from highly concentrated solutions. However, as experience has shown that spray-dried products are difficult to wet and tend to form lumps, they are usually agglomerated initially by spraying with steam.

Because of their numerous functional properties, gelatine hydrolysates find wide application in a number of industrial processes (see Section 3.1.4). They are particularly suited for use in the food industry, where, for example, they are frequently used as relatively taste-neutral protein ingredients and, in contrast to other proteins used for the production of hydrolysates, no bitter peptides are generated.

2.2.12

Environmental Aspects of Gelatine Manufacture

The manufacture of gelatine takes place via a number of different production steps, depending on the raw material used. As a result, different amounts of energy and water are required. The lowest consumption is in the production of pig-skin gelatine using the acid procedure. In this case, to produce 1 kg of gelatine, the manufacturer requires 20–25 kg of steam and 3–5 KWh of electrical energy. The water requirement is approximately 150 L kg^{-1} gelatine.

The energy balance is similar in the case of the alkaline procedure using hide split. However, the water requirement increases to about 400 L kg^{-1} gelatine. The reason for this is the fact that the water has to be changed about 20 times during the conditioning and washing processes.

If ossein material is conditioned using the alkaline process, a further 3–4 KWh, 15–18 kg steam and 100 L water per kg gelatine are required. These figures include the degreasing of the fresh bone material and the demineralization of the bone chips during pre-processing.

Because of the high water requirement and the high content of protein in the waste water, the gelatine industry views the improvement of the processes along with savings in energy and water as being of high priority (see Fig. 2.49).

A further priority is air exhaust purification. Up until a few years ago, exhaust air was subjected mostly to chemical washing. However, today, this process is being replaced to a much greater extent by biofiltration, a process developed by one particular gelatine manufacturer. In this method, the exhaust air is passed through, from below, an approximately 1.5-m thick bed of ground tree bark, wood chips, and some special types of shrubs. The bacterial flora that develops within this mass is capable of almost completely degrading the odor-producing substances. Such biofilters have been so successful in reducing odor emissions that they are now being increasingly used in other industries (see Fig. 2.50).

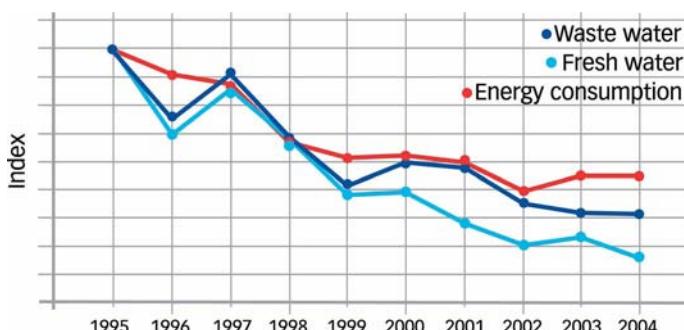


Fig. 2.49 The gelatine industry has continuously reduced its environmental impact. (Index 1995 = 100.)



Fig. 2.50 Biofilters have been extremely successful in reducing odor emissions in a natural way.

The treatment of waste water is carried out in many different ways, and the regulations pertaining to this differ among the various countries, and especially among the continents. Some manufacturers carry out mechanical pre-cleaning only and leave the rest to be processed by the local community. Frequently, however, gelatine factories have their own complete waste water treatment plants. The industry market leaders carry out comprehensive multi-stage clarification involving “mechanical cleaning”, “chemical clarification”, “comprehensive biological treatment” and subsequently “nitrification” and “denitrification”, so that no hazardous ammonium ions can enter the public water systems. If required, a final stage for the elimination of phosphate may be included.



Fig. 2.51 All components of the waste water from gelatine production are removable, completely biologically degradable and contain no hazardous materials.



Fig. 2.52 The sludge resulting from waste water treatment is a valuable and approved substance for use as a fertilizer in agriculture and forestry.

All the components of waste water are completely biologically degradable and contain no dangerous materials; the sludge resulting from a dedicated gelatine production is thus ideal for use as fertilizer for agricultural and forestry purposes. These materials – like all the by-products of gelatine production – are valuable and approved substances that can be used as starting materials for new regenerable products.

2.3

Quality Control and Certified Product Safety

On a worldwide basis, gelatine is one of the most thoroughly investigated and stringently controlled foodstuffs on the market. Edible gelatine has to comply with all relevant national foodstuff laws, and these invariably include specific regulations for gelatine. Pharmaceutical gelatine – provided that it has not been chemically modified for special applications – also has to fulfill these requirements as well as complying with the specifications of all relevant pharmacopoeias. The user or processor of gelatine thus obtains a product of specified technological quality with the highest possible degree of consistency. These qualities are specified in detail in the Certificate of Analysis provided with the product.

In order to ensure that supplies of gelatine comply with all required physical, chemical, microbiological, and technical production and quality standards, all reputable gelatine manufacturers have established certified Quality Management Systems according to the worldwide standard ISO 9000. In this way, all the process steps necessary to comply with international laws (see Table 2.10) and customer-specific quality parameters are guaranteed and documented. In the case of pharmaceutical gelatine, strict adherence is also guaranteed to the Food and Drug Administration's (FDA) "Guidance for Industry" (September 1997), the European CPMP's regulation the "Note for Guidance" (EMEA/410/01 Rev.2, October, 2003, Official Gazette No. 2004/C24/03 dated 28.1.2004) and the "Certification of Suitability to the Monographs of the European Pharmacopoeia" (Eur. Pharm. Ed. 5.0 (2005), section 5.2.8 – see Table 2.9).

2.3.1

The Quality Assurance Process

Quality Assurance monitors all the process steps involved in the manufacture of gelatine, from the selection of the raw materials to the delivery of the final product. It checks the origin of the raw materials, the methods of transport used, and subsequent storage. It defines and controls the production process, including packaging, storage, and subsequent transportation of the gelatine produced. Also, importantly, it trains personnel in all matters connected with product quality.

The basis of the quality assurance process is the continuous control of each production step during the manufacture of gelatine. These checks include comprehensive physical-chemical and microbiological in-process controls and other monitoring programs as well as checks on the cleanliness of the plant and machines used, the ambient air, the raw materials, intermediate products, and finished goods (see Info Box).

Table 2.9 Overview of regulatory requirements.

Europe:

- EU-Decision 1999/724/EC (28 October 1999)
- EU-Regulation (EC) No. 852/2004 and No. 853/2004 (29 April 2004)
- EU-Directive 1998/83/EC (3 November 1998)
- EMEA Note for Guidance (EMEA/419/01 Rev. 2, October 2003)
- EU-Directive 1999/83/EC (8 September 1999)
- European Pharmacopoeia (Edition 5.0, 2005)

United States:

- USA:FDA CGMP Regulation (Title 21, Code of Federal Regulations, Section 110, April 2005)
- FDA Guidance for Industry (1997)
- USDA Interim Final Rule (January 12, 2004)
- FDA Interim Final Rule (July 14, 2004)
- United States Pharmacopoeia (USP 29, 2006)
- Food Chemicals Codex, 5th Edition (2004)

Japan:

- MHLW Pharmaceutical and Food Safety Bureau: Notifications No. 1069 (October 2, 2001) and No. 0414004 (April 14, 2003)
- Pharmaceutical Affairs Law: Ministry of Health, Labour and Welfare (MHLW), Standard for Biological Ingredients (Notification No. 210, May 20, 2003, amended by Notification No. 262 July 5, 2004)
- MHLW Pharmaceutical and Food Safety Bureau: Notifications No. 0218001, 0218003 and No. 218004, February 18, 2004
- Food Sanitation Law: Standards for Foods, Food Additives etc., February 16, 2004
- Food Sanitation Law: Official Notice No. 0331006, March 31, 2004

Australia/New Zealand:

- Import Food Notice 44/01 (November 12, 2001)
- Import Food Notice 02/03 (January 21, 2003)
- FSANZ Food Standards Code (No. FSC 7, February 27, 2003)
- TGA Supplementary Requirements for Therapeutic Goods for Minimising the Risk of Transmitting TSEs (October 20, 2004)

South Africa:

- South African Standard (SABS 49 Edition 3, October 2001)

Brazil:

- Resolution DIPOA No. 5 (January 23, 2003)
- Animal Products Sanitary and Industrial Inspection Regulation (RIISPOA No. 30.691, March 29, 1952)

China:

- National Standard Food Additive Gelatine – GB6783-94
- National Standard Codex – Pharmaceutical Gelatine – QB2354-98

Table 2.10 Quality criteria for gelatine.**1. Microbiological criteria**

Microbiological parameter	Decision (EC) No. 2073/2005	Eur. Pharm. 5.0 (2005)	US FCC 5th Ed. 2004. (USA)	USP 29/NF 24 (2006)
Total aerobic bacteria		10^3 /g		10^3 /g
Coliforms (30°C)				
Coliforms (44.5°C)/ <i>E. coli</i>		0/g	0/25 g	0/10 g
<i>Clostridium perfringens</i>				
Salmonella	0/25 g	0/10 g	0/25 g	0/10 g

2. Residues

Element	Decision (EC) No. 853/2004	Eur. Pharm. 5.0 (2005)	US FCC 5th Ed. 2004 (USA)	USP 29/NF 24 (2006)
	mg/kg	mg/kg	mg/kg	mg/kg
As	1			0.8
Pb	5		1.5	
Cd	0.5			
Hg	0.15			
Cr	10	10.0	10.0	
Cu	30			
Zn	50	30.0		
Humidity (105°C)		15%	15%	
Ash (550°C)			3%	2.0%
SO ₂ (Reith Willems)	50	50.0	50.0	40.0
H ₂ O ₂ (European Pharmacopoeia 1986) (V ₂ O ₅)	10	10.0		

Info Box**Safety is achieved by**

- Processing material originating exclusively from healthy animals that have been approved for human consumption
- Accepting no Specified Risk Material (SRM) for the production process
- The influence of acid and alkali
- Sterilization of gelatine solutions; in the case of bovine gelatine at a minimum of 138 °C for at least 4 s
- Carrying out purification steps with, e.g., membrane filtration, silica gel, cellulose filters, and ion exchangers
- The implementation of DIN ISO 9000, HACCP and validated manufacturing processes according to “Good Manufacturing Practice” guidelines
- In-process controls including:
 - Physical, chemical, and bacteriological control of raw materials and checking for possible contamination
 - Physical, chemical, and bacteriological control of water used
 - Chemical control of the auxiliary products used
 - Physical and chemical control of the acid and alkaline processes
 - Continuous physical and chemical control of the neutralization and washing procedures
 - Automatic thermal and physical/chemical monitoring of the extraction process.
 - Optical control of the filtration process
 - Automatic physical/chemical control of salt concentration and degree of ion exchange
 - Continuous thermal monitoring of the first sterilization step
 - Automatic physical control of the concentration process
 - Thermal and bacteriological monitoring of the second sterilization step
 - Automatic control of air preparation and monitoring of the degree of decontamination and drying
 - Automatic physical control of the moisture content of the final gelatine
 - Monitoring of the particle size distribution subsequent to grinding
 - Physical, chemical, and bacteriological control of individual production components
 - Physical, chemical, and bacteriological control of packaging materials
 - Physical, chemical, and bacteriological control of the gelatine blends
 - Regular sanitary, hygienic, and bacteriological control of rooms, equipment, instruments, and personnel.

2.3.1.1 Raw Materials

Gelatine is manufactured from natural raw materials. These originate exclusively from animals that have been examined by the veterinary authorities and have been released for human consumption. This is a procedure prescribed by the appropriate regulatory authorities throughout the world. All supplying companies have to be registered with their national authorities and the veterinary approval status and origin of the material must be documented.

Adherence to hygiene regulations with respect to fresh raw materials is ensured, e.g. in Europe, by specifying a maximum of 24 h for transportation. Alternatively, constant refrigeration or freezing must be documented or the goods must be preserved with lime or salt. In some cases, the raw materials are dried prior to shipment (hide splits or bones). Gelatine manufacturers ensure compliance with these stringent hygiene regulations by auditing their suppliers on a regular basis.

Each batch of raw materials delivered to the manufacturer is immediately checked and the results are documented. This evaluation of incoming goods also serves to confirm the complete traceability of the raw materials and the consistency of quality as delivered by the suppliers.

2.3.1.2 Production

In addition to the raw material quality, the production process itself, with its acidic or alkaline pretreatment of raw material, its filtration, ion exchange, and sterilization stages is also an effective quality assurance measure. In the actual production process, a comprehensive HACCP monitoring system ensures that potential risks are reduced to an absolute minimum.

The production process in fact has been scientifically proven to be an effective barrier against possible BSE prions. In the USA, the Food and Drug Administration (FDA), with the support of the TSE Advisory Committee, has been monitoring the potential risk of animal-derived products, human donor blood, surgical instruments, medical devices, sterilization methods, and many other similar risk areas since 1997.

Subsequent to the evaluation of validation studies on the manufacturing processes used for bovine bone gelatine, the FDA, in 2003, commented on the safety aspects as follows: “*The data obtained from these new studies show that the reduction in BSE infectivity is sufficient to protect human health.*”

The studies in question were carried out by highly reputable European and American research institutes. The researchers based their work on a “worst case scenario”, i.e. as if the raw materials used had originated exclusively from BSE-infected cattle – a situation that would never occur in practice. The results of their investigations demonstrated that, even in such an extreme case, no residual BSE prions could be detected in the gelatine produced using various manufacturing methods. Even after injecting such a manufactured gelatine into the brains of experimental animals, no subsequent TSE disease was established.

The Scientific Advisory Committee of the FDA was thus the second important expert committee to confirm the safety of bovine bone gelatine. Already in March

2003, the Scientific Steering Committee (SSC) of the European Union had confirmed that “*The risk associated with bovine bone gelatine is close to zero.*”

In its opinion, dated January 18, 2006, the European Food Safety Authority (EFSA) stated the following:

- *The previous SSC opinion is confirmed.*
- *The residual BSE risk in bone-derived gelatine is regarded as being very small compared to the historical consumption of meat or meat products in the UK.*
- *There is no support for the request to exclude the skull and vertebrae of bovine origin older than 12 months from the material used in the production of gelatine.*

The safety of the actual production process is not the only argument that can be used. The time involved in processing is an additional safety factor: should, in an extreme case, a BSE infection in one of the animals from which raw material was derived be confirmed at a later stage, the comprehensive documentation available would still provide for enough time to identify the raw material batch involved and to remove it from the production process.

Furthermore, other scientific work has shown that the gelatine manufacturing process has the capability to destroy all relevant pathogenic organisms. This can be verified at any time by the appropriate regulatory authorities. And, as these production processes have been in use for a very long time and designated as being safe, gelatine is, and always has been, a safe foodstuff.

2.3.2

Standard Quality Tests on the Final Product

Apart from the quality tests prescribed by the authorities, gelatine manufacturers carry out numerous additional tests on the final product. These tests serve to check and document all the purity and technological parameters required by those who have to process the product further. There is a difference between standard analyses and supplementary customer-specific analyses. Several of these analytical procedures are described below. The complete versions of many of these testing procedures are available in: “Standardized Methods for the Testing of Edible Gelatine” as compiled by the Gelatine Manufacturers of Europe Association (www.gelatine.org).

Standard tests are carried out by gelatine manufacturers on each batch produced prior to delivery. These tests are described below.

2.3.2.1 Gel Strength (Bloom Value)

The primary property of gelatine utilized by the industrial processor is its gelling effect. Traditionally, this parameter mainly determines the price of a particular type of gelatine. Gel strength is thus – with the exception of non-gelling types – the most important single characteristic of gelatine.



Fig. 2.53 Two different modern testing instruments for Bloom measurement.

Gel strength is determined using the so-called Bloom test (see Fig. 2.53). In this procedure, the force required for a standard half-inch plunger to depress the surface of a gelatine gel to a depth of 4 mm is measured. The gel in question contains 6.67% gelatine and is aged for 17 h at precisely 10 °C prior to measurement. The force or mass registered in achieving the necessary depression of the surface is given in Bloom grams and is simply known as the Bloom. The Bloom values of standard gelatines range from 50 to 300 g. The range 200 to 300 g is designated as high-Bloom, that of 100 to 200 g as medium-Bloom and that of 50 to 100 g as low-Bloom.

Reproducible values for this method of measurement, which looks relatively simple at first glance, can only be achieved if the sample is prepared strictly according to the instructions of the prescribed analytical procedure. Gel strength is strongly dependent on concentration; thus, the slightest inaccuracy in weighing the gelatine or measuring the volume of water required can have a considerable effect on the results obtained.

However, precise weighing is only one of the preconditions for obtaining accurate results. For example, the sample vessels must be of defined form and geometry. During the dissolution step, care has to be taken to ensure the sample is kept at a temperature below 60 °C (optimally 50–55 °C) for 20 min, as the loss of water would otherwise increase the concentration and deliver a false Bloom value. The vessels must therefore remain closed during the dissolution process and any condensed water must be returned to the system. Furthermore, foam bubbles must be avoided during preparation of the solution.

Complete gelation under standard conditions is also important. Gelation is a slow reaction. Extremely rapid cooling can lower the measured Bloom value by up to 10% and very slow gelation can increase the value by the same amount.

The gel strength increases only slightly after 16–18 h (see Fig. 2.54). As standing time and temperature both exert considerable influence on the measurement,

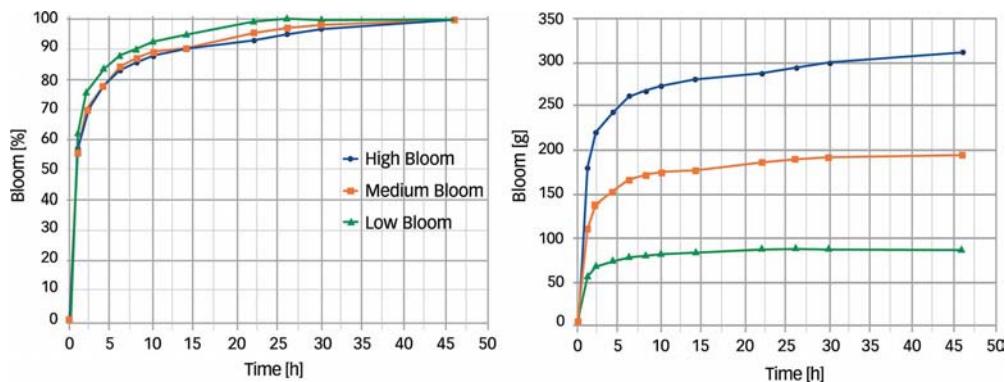


Fig. 2.54 Gel firmness (Bloom value) as a function of time spent in the cooling bath, in relative (left) and absolute (right) values.

gelation must be carried out in a water bath at 10 °C, and this the temperature may not deviate by more than +/–0.1 °C.

Only if all of these preconditions are adhered to and a precision texture analyzer is employed can the results be deemed to be accurate and reproducible, with small variations. In order to ensure that this is the case, Bloom analyses are almost always carried out in duplicate and the measurement conditions checked daily using well-documented control samples.

2.3.2.2 Viscosity

Viscosity is the second key property of gelatine, depending on the application involved. High viscosities are required, e.g. to stabilize food, pharmaceutical, and photographic emulsions. In the production of molded goods, however, the confectionery industry prefers gelatine of low viscosity in order to avoid the undesirable “tailing” effect (see Section 3.2.1).

Standard viscosity is measured primarily using a calibrated pipette, where the run-out time for 100 mL of a 6.67% gelatine solution at 60 °C is determined (results expressed as mPas). For special technical applications it can also be determined by the run-out time of 200 mL of a 15% solution at 40 °C, and the result is expressed as “degrees E”. In the case of gelatine hydrolysates, the viscosity is determined using a 10 or 20% solution at 25 or 30 °C. For some applications, a rotary viscometer, rheometer, or other specialized apparatus may be employed at various temperatures and concentrations (see Fig. 2.55).

2.3.2.3 pH

In some regulatory specifications, the pH is specified within a very wide range. However, it is also a criterion that can influence the further processing of gelatine. For example, it has considerable influence on foam formation and the inter-

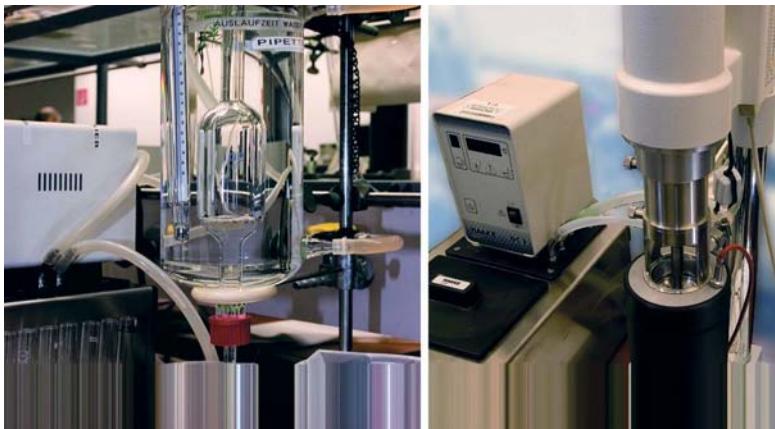


Fig. 2.55 Pipette (left) and rotation viscometer (right) for the determination of the specific viscosity of gelatine.

action of gelatine with the other components of a particular formulation. It is thus usually included in the Certificate of Analysis.

Measurement of pH is typically carried out on a 6.67% gelatine solution at 55–60 °C using a glass electrode. Frequently, however, other concentrations and temperatures are employed in order to simulate customer-specific process parameters.

2.3.2.4 Water Content

As a rule, air-dried gelatine contains 8–12% water on delivery; this is its equilibrium state under normal climatic conditions. Depending on the humidity of the surrounding air, gelatine can absorb or release moisture. For this reason, water vapor-tight packaging is recommended. If the water content exceeds 16%, there is a risk of lump formation and microbiological growth. Residual moisture is determined subsequent to drying for 16–18 h at 105 +/– 2 °C.

2.3.2.5 Color and Clarity

The visual method of determining color and clarity using a 6.67% solution of gelatine against a reference standard is widely used.

Clarity (see Fig. 2.56) can be determined with a nephelometer or spectrophotometer using a 6.67% solution at a wavelength of 620 nm. Other concentrations and temperatures are not uncommon.

Color can be determined in a spectrophotometer at 450 nm using a 6.67% solution. The result, however, may be influenced considerably if the solution is very turbid. For this reason, both values should be determined at the same time.

Deionized water is the standard of choice when determining color and clarity using an instrument.



Fig. 2.56 The clarity and color of a gelatine solution are measured either visually or using appropriate equipment.

2.3.2.6 Sulfur Dioxide and Peroxides

Sulfur dioxide and hydrogen peroxide can occur as residues of oxidation or reduction reactions carried out to lighten the color of a gelatine solution. They may also occur if such substances are used to stabilize the microbiological status of the gelatine solution during the production process.

Testing for peroxides is carried out with commercial test strips according to the procedure specified in the European pharmacopoeia. The strips, incorporating peroxidases and a redox indicator, are immersed directly in the gelatine solution, and a blue color develops if peroxides are present. Quantitative results can be obtained using iodometric titration, although other oxidizing substances such as nitrite would also be included in the determination.

Sulfite content is determined using the Reith-Willems or equivalent distillation method. During this reaction, sulfur dioxide is released by boiling with hydrochloric acid under an atmosphere of carbon dioxide and then oxidized to sulfuric acid by hydrogen peroxide. The amounts present are then determined by alkalimetry or gravimetrically after precipitation with barium sulfate. Alternatively, it can be determined using the Monnier-Williams method, which uses nitrogen instead of carbon dioxide.

2.3.2.7 Odor and Taste

A sensory evaluation should be carried out routinely on each batch of gelatine produced, especially if the gelatine is to be used for food applications. These tests are carried out by dissolving gelatine in water to obtain a solution of defined concentration. The sensory evaluation tests are normally carried out by specially trained staff. On an international basis, fruit juice is typically used as a medium; this is because gelatine is often used in formulations with a fruity taste.

2.3.2.8 Inorganic Components

The determination of ash and numerous heavy metal ions is prescribed by law. Such determinations are also of technological relevance: in the pharmaceutical



Fig. 2.57 HPLC, ICP and AAS (from the left) for the selective identification of inorganic gelatine components such as heavy metals, cations and anions.

and photographic sectors, for example, customers often require gelatine with a very low ash content.

The determination of total mineral content takes place by ashing the gelatine sample at 550 °C. Individual heavy metals are normally determined using state-of-the-art spectroscopic techniques such as AAS and ICP (see Fig. 2.57). In addition, certain cations such as calcium and a number of anions can be precisely quantified using HPLC.

2.3.2.9 Conductivity

Electrical conductivity is determined using a measuring cell and a 1% solution of gelatine. The value, expressed as $\mu\text{S cm}^{-1}$, enables the content of soluble salts in the gelatine to be estimated. The analysis is strongly dependent on temperature and is therefore carried out at 30 °C. The test is an excellent supplement to ash determination as conductivity and ash content together indicate the real salt content in a particular gelatine type.

2.3.3

Microbiological Tests

Gelatine is a foodstuff and pharmaceutical excipient and is thus subject to stringent requirements with respect to microbiological contamination. Prior to delivery, gelatine is subjected to several microbiological tests. The reason for this is that numerous microbes are capable of growing rapidly in a gelatine solution. Thus, before it is further processed, the user has to be certain that the microbial count is extremely low. The tests comprise determination of total aerobic microbial count as well as specific organisms. In this way, it can be assured that gelatine is free from particular microbes, e.g., *Escherichia. coli* and salmonella, which are capable of affecting humans, forming toxins or altering the appearance, consistency, or aroma of foodstuffs in a negative way.

To evaluate the required microbiological quality, gelatine samples are cultured in various nutrient media. Should any microbes be present, they are enriched



Fig. 2.58 TECRA equipment for automated salmonella detection.

and then differentiated. Subsequent to the precisely prescribed incubation times and temperatures, an evaluation is performed by visually counting the colonies formed. This can be done via characteristic color reactions with selective media or by using additional biochemical or immunological tests (see Fig. 2.58).

2.3.4

Special Chemical/Technological Tests

Special chemical/technological tests are often required for specific user applications and are carried out in conjunction with the customer. Examples are the determination of calcium or the Gold Number, both of which play a major role in photographic applications. Other possible additional analyses are described below.

2.3.4.1 Gelation Point, Melting Point, Gelation Time

The gelation point indicates the temperature at which a solution of gelatine gels. This is an important criterion, e.g. in the manufacture of capsules, but also in many other applications; this is because the gelation point is important in optimizing the production process being used. In the past, the gelation point was mostly determined indirectly by first establishing the melting point, a parameter that can be more precisely determined. Both gelation and melting points increase with increasing Bloom values and concentrations of the gelatines being used.

To measure the melting point, glass tubes approximately 4 mm in diameter and open at both ends are placed in a 10% gelatine solution. The solution is maintained at 10 °C for 2 h, after which the gelatine has solidified. The glass tubes are then removed from the gel in such a way that they contain about 1 cm of gel. The tubes are placed in a water bath and slowly warmed at $0.5\text{ }^{\circ}\text{C min}^{-1}$. Because of the hydrostatic pressure generated, the plugs of gelatine slide upwards once the melting temperature is attained. This temperature is designated as the melting point. In the case of a 10% solution of gelatine, the melting point is



Fig. 2.59 Tecam Gelation Timer (left and center) and the glass tube method (right) for the measurement of setting time.

within the range 21–34 °C. The gelation point was considered to be 5 °C below the melting point.

In certain applications, the gelation time is also an important parameter. For example, the gelatine layer on the dipping pins of a hard capsule machine or the layers on photographic film must gel within a very short period of time (see Fig. 2.59). Many different methods are used to measure this.

One of the simplest methods involves placing a 6.67% gelatine solution at 36 °C in an 8-mm diameter glass tube in a water bath at 24 °C and starting the timer. In order to ensure continuous mixing of the gelatine solution, steel balls of diameter 6 mm are dropped into the tubes at intervals of 30 s. When the gelatine sets, the steel balls stop moving through the solution. The time measured from the start to this point represents the gelation time.

When using the Tecam Gelation Timer (TGT, see Fig. 2.59, left and middle), a 25% solution of gelatine at 50 °C is placed in a water bath at 28 °C and the timer is started. The solution is then cooled until it sets. The point of gelation is indicated when the resistance of the gel formed becomes greater than the punch pressure of the TGT. At this point, the punch drive and time are stopped and the gelation time is indicated in minutes and seconds.

Gelation point, melting point, and gelation time can also be established by rheological measurements (see Fig. 2.60).

2.3.4.2 Rheology

The determination of standard viscosity is not suitable for the more concentrated gelatine solutions, for low test temperatures, or for describing the kinetics of gel formation. A rheometer should be used in such cases as it measures the viscoelastic behavior of gelatine. In this type of analysis, the complex viscosity η^* is determined (see Section 2.1).

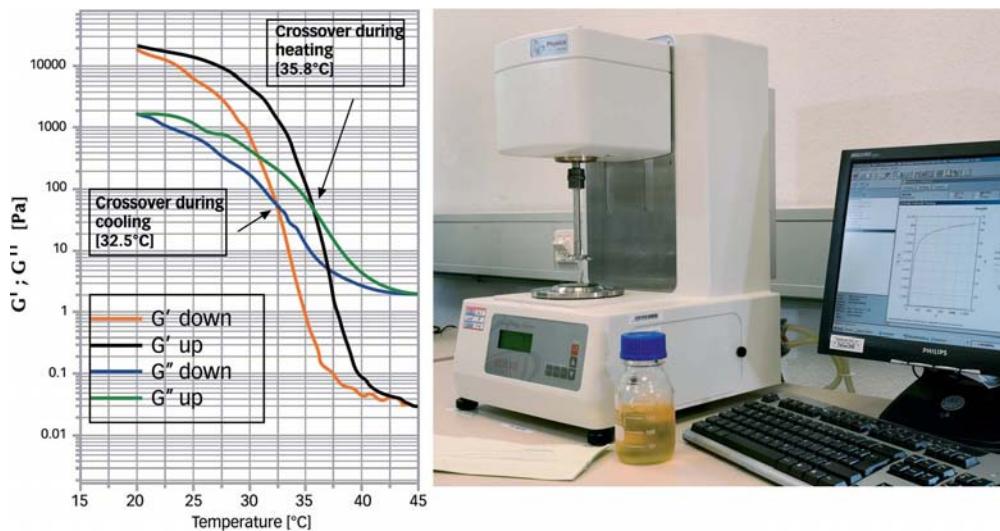


Fig. 2.60 Rheological determination of a gel (crossover cooling) and determination of the melting point (crossover heating) of gelatine, measured by a rheometer (right).

One interesting rheological variant is the measurement of the decrease in viscosity as a function of time and temperature. This information can be used to characterize the thermal stability of the peptide chains during thermal cleavage in specific customer applications. Viscosity is a much more sensitive parameter than the Bloom value for determining thermal degradation. It is all the more important if the gelatine solution used is to be maintained at a higher temperature over a period of hours, as in the case of the production of hard and soft gelatine capsules.

2.3.4.3 The Foam Test (foam capacity and stability)

In many application areas, the foaming behavior of a gelatine solution is a critical parameter. There are products that utilize both the foaming capacity and the stability of the foam (e.g., candy floss, marshmallows), while in other products foaming is less important or even undesirable (e.g., capsule manufacture or clear gels). There is no standard procedure for the determination of foaming behavior; most tests are specific to the application involved.

One test worthy of mention is that based on an EN standard (EN 12728, January 2000) – “Determination of foaming power – perforated disk beating method”. In this method, the foam is generated by beating 200 mL of a 5% gelatine solution at 35 °C in a glass cylinder with a perforated disk attached to a rod. The foam volume is read off after 40 strokes within 40 s and the stability is read off after 10 and 20 min (see Fig. 2.61).



Fig. 2.61 Determination of foaming power with the perforated disk whipping method. (Left: immediately center: after 10 minutes, right: after 20 minutes.)

2.3.4.4 Isoelectric Point

The isoelectric point (IEP) of a particular gelatine solution influences its ability to act as a stabilizer in complex systems. It also affects its foaming capacity and its interaction with other hydrocolloids. To determine the IEP of, e.g. a 5% gelatine solution, it is first completely deionized by treating with ion exchange resins. The pH of the solution obtained at 30 °C now corresponds to the IIP (isoionic point) of the gelatine; this is practically identical to the IEP. The IEP can also be determined using gel electrophoresis (isoelectric focusing, see Fig. 2.62).

The IEP of a particular gelatine is determined by the manufacturing process used. In the case of acid-conditioned type A gelatine it is between pH 6 and 9.5; in alkaline-conditioned gelatine it is between pH 4.7 and 5.6. In very special cases the IEP of alkaline-conditioned gelatine can even be as high as pH 6.5. Blends of types A and B gelatine and modified gelatines can exhibit an IEP of any value.

2.3.4.5 Molecular Weight Distribution

The molecular weight distribution is also an important and meaningful parameter for assessing the technological properties of gelatine. For example, the viscosity of a gelatine solution correlates relatively well with the amount of high molecular weight components it contains. For gelling power, however, the proportion in the molecular weight region of about $100\,000\text{ g mol}^{-1}$ is most relevant. The molecular weight distribution is used in the selection of special types of gelatine for particular applications or for obtaining certain functional properties by blending different types of gelatine or molecular weight fractions.

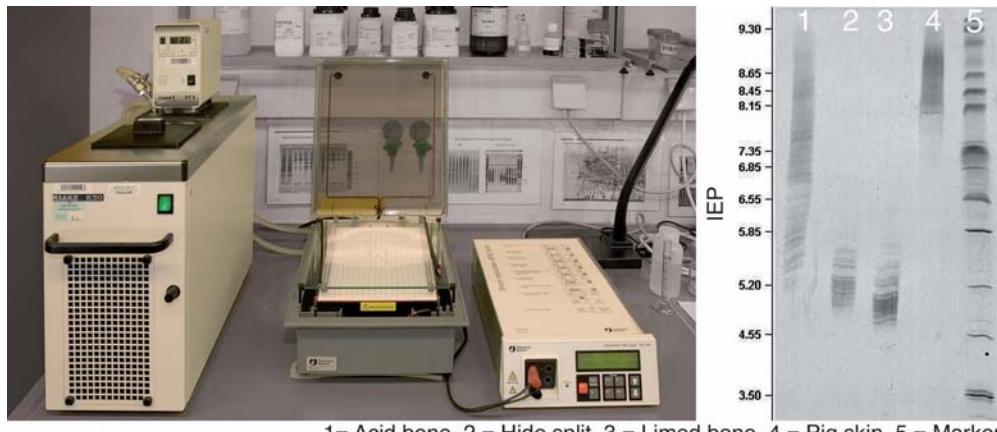


Fig. 2.62 IEP determination using gel-electrophoresis. The position of the individual bands on the gel (right) characterizes the IEP of the gelatine sample.

Molecular weight distribution is determined by gel permeation chromatography (e.g., GPC). The protein mixture (the gelatine solution) is dissolved in a buffer solution and injected into a chromatographic column containing a specific material of defined pore size. The proteins of the mixture penetrate the pores to different depths dependent on their size; they thus migrate through the column at different speeds. Small proteins penetrate the pores to a greater extent than larger ones and hence require a longer time to pass through the column. The molecular weight thus decreases with increasing retention time.

Each protein fraction leaving the column is represented by a peak on the chromatogram; the peak area corresponds to the quantity of protein. The detectors used to identify the protein peaks are based on UV, viscometric measurement, or light scattering.

2.3.4.6 Nitrogen Determination using the Kjeldahl Method

Organic nitrogen compounds – in particular proteins – can be quantified using the Kjeldahl method. The sample is hydrolyzed by boiling with concentrated sulfuric acid in the presence of a digesting catalyst. The nitrogen present is converted to ammonium sulfate. A sodium hydroxide solution is added and the ammonia is released. Ammonia is distilled off into a vessel containing boric acid and titrated with sulfuric acid. The protein content of the gelatine and gelatine hydrolysate is then calculated as a percentage by multiplying the nitrogen value determined by the factor 5.55, which is different from the factor 6.25 used for most other proteins.

2.3.4.7 Determination of Gelatine Protein

The determination of gelatine protein for identity testing, as required by the European and United States pharmacopoeias, can be carried out with the aid of a number of reactions. For example, mixing a dilute gelatine solution with trinitrophenol or a slightly acidified potassium dichromate solution produces a yellow precipitate, or the addition of tannin results in turbidity. Upon adding copper sulfate and sodium hydroxide solutions to a dilute solution of gelatine, a positive biuret reaction takes place, producing a violet color. This color reaction is suitable for the semi-quantitative determination of gelatine protein.

2.3.4.8 Hydroxyproline

Hydroxyproline is a very prevalent amino acid in collagenous protein and is specific for gelatine. It can thus be used for the qualitative and quantitative determination of gelatine and gelatine hydrolysate. The sample is first hydrolyzed with sulfuric or hydrochloric acid, and the released hydroxyproline is oxidized with sodium *N*-chloro-4-toluene sulfonamide, converted to a red dye with 4-dimethylamino-benzaldehyde, and quantitatively analyzed photometrically. On the basis of the proportion of hydroxyproline determined (in the case of air-dried gelatine normally 11–12%) the content of collagenous protein can be calculated.

In the case of final products, the hydroxyproline content should be used to determine the gelatine content if non-collagenous proteins are also present. If gelatine is the only protein present, the Kjeldahl method can be used to calculate the gelatine content.

2.3.5

Special Tests for Photographic Applications

2.3.5.1 Characterization of Photographic Properties

Complete characterization of the photographic properties of gelatine is not possible using physical and chemical tests alone. Other tests must be carried out that are appropriate for the applications envisaged. For the characterization of the behavior of photographic gelatines, special emulsions are used. These emulsions are also used for testing individual gelatine batches and are therefore a suitable tool for controlling the production of photographic gelatine. When testing the delivery of gelatine destined for such applications, special test emulsions are used; these are also used for production control. Depending on the type of emulsion, any substances present that may stimulate or inhibit the ripening process can be identified, and the photographic behavior of the gelatine can be tested and quantified. Ripening substances are those components generally present in gelatine that accelerate the photographic ripening process (see Section 3.2.7); inhibitory substances (restrainers) delay the process.

Once the photographic emulsions have been prepared and developed with the gelatine to be tested, they are poured onto photographic paper, dried, and exposed in stages under defined conditions. After development and fixation, the so-called

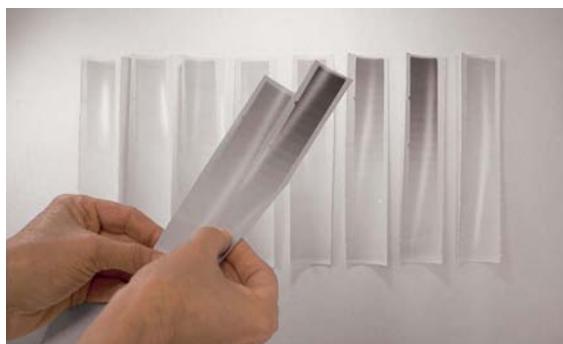


Fig. 2.63 The photographic behavior of gelatine is tested with sensitometer strips after exposure and development.

sensitometer strips (see Fig. 2.63) can be evaluated for sensitivity and fog and compared with a reference gelatine.

2.3.5.2 Hardening Behavior

The behavior of gelatine in the presence of organic or inorganic hardening agents or cross-linkers, a process that is always evaluated for photographic applications, is determined by changes in rheological behavior, e.g., viscosity, or by the disappearance of the “stirring vortex” (see Fig. 2.64). The hardening agent, as well as the parameters of the test itself, are normally selected according to the process to be used by the customer.

2.3.5.3 Gold Number

During the manufacturing process for gelatine, oxidizing agents such as hydrogen peroxide are sometimes used if certain special effects are intended or if the product is to be protected from microbiological contamination. A measure of the oxidative status of gelatine and an important parameter for photographic applica-



Fig. 2.64 Testing the hardening behavior of gelatine with the vortex test.

tions is the Gold Number. The more gelatine is subjected to oxidation the lower is its Gold Number. Depending on the applications envisaged, different Gold Numbers may be desirable. The Gold Number can be determined by titrating gelatine with tetrachloroauric acid.

References

- Babel W, Gelatine – ein vielseitiges Biopolymer, reprint by Gelita AG from the journal “Chemie in unserer Zeit”.
- Bailey A J and Paul R G, *J. Soc. Leather Technol. Chem.* 82(3), 104–110 (1998).
- Baily A J and Light N D, *Genes, Biosynthesis and Degradation of Collagen in Connective Tissue in Meat and Meat Products*. Elsevier Applied Science, London and New York (1989).
- Brinkmann J in: Brinkmann J, Notbohm H and Mueller P K (ed.) *Collagen, Primer in Structure, Processing and Assembly*, Springer, Berlin, Heidelberg, New York 1–6 (2005).
- Cole B in: F J Francis (ed) *Encyclopedia of Food Science and Technology* 2, Wiley, New York, 1183–1188 (2000).
- Cole C G B and Roberts J J, *Proceedings of the International Union of Leather Technologists and Chemists Societies Congress*, London, 57–64 (1997).
- Dick E, *Gelatine – neue praktische Erkenntnisse und Produktideen*, reprint by Gelita AG from the journal “Süßwarenproduktion”.
- Heidemann E, Peng B, Neiss H G, and Moldehn R, *Proceedings of the 5th IAG Conference: Photographic Gelatine*. Amman-Brass H and Pouradier J (eds.), Internationale Arbeitsgemeinschaft Photogelatin, Fribourg, Switzerland.
- Mueller H, Heidemann E, *das Leder* 44, 69–79 (1993).
- Prockop D J, *Matrix Biol.* 16(9), 519–528 (1998).
- Veis A, *The Macromolecular Chemistry of Gelatine*, Academic Press, New York and London, 392–396 (1964).

3**Practical Aspects****3.1****Basic Processing****3.1.1****The Functional Properties of Gelatine Compared with Other Hydrocolloids**

Gelatine is a highly versatile hydrocolloid in technological applications. Hydrocolloids can fulfill two primary functions: they either increase the viscosity of products or provide them with a special texture because of their gelation power. They also have other properties such as their ability to form and stabilize emulsions, prevent recrystallization, bind by adhesion, stabilize suspensions, clarify beverages, and form foams and films. Furthermore, they can be used to lower the calorific value of foodstuffs by increasing the water content or replacing part of the sugar or fat normally used.

None of the hydrocolloids currently on the market (see Fig. 3.1) is capable of covering all of the above-mentioned properties in all applications (see Tables 3.1 and 3.2). Gelatine, however, is the hydrocolloid that provides the greatest number of possibilities to the product developer. An interesting aspect with regard to other hydrocolloids, some of the more important of which are described in this

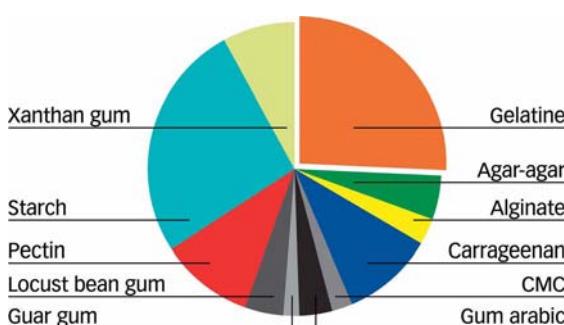


Fig. 3.1 Market share of the most important hydrocolloids for food applications.

Table 3.1 Comparison of frequently used hydrocolloids – rheological properties.

Hydrocolloid	Gel formation	Thickening effect	Transparency of the gel	Cold water solubility	pH-stability
Gelatine	+++ Thermoreversible, difference in melting/ gelling temperature low	+++	+++	0 With the exception of cold water-soluble instant gelatines and gelatine hydrolysates	++
Agar-agar	+++ Thermoreversible, difference in melting/ gelling temperature high	+++	+	0	++
Alginates	+++ (with calcium)	+++	+++	+++	+
Carrageenan	Kappa/ iota: +++ (with cations)	++	++	++	++
Lambda: 0		++	-	+++	++ (pH 3–11)
Carboxymethyl cellulose (CMC)	0	+++	-	+++	++ (pH 4–9)
Gum arabic	0	+	-	+++	++ (pH 1–10)
Hydroxypropylmethyl cellulose (HPMC)	+++ (Gel formation on heating)	+++	+	+++	

Locust bean gum	0	++	-	+	++ (pH 3–11)
Modified starches	+++	++	+	0	With the exception of physically modified starches
Native starches	+++	++	+	0	
Pectin	+++	++	+++	++	HM: pH 2.5–4.5 LM: pH 2.5–5.5
		- LM plus Ca^{2+} thermally irreversible			
		- HM plus sugar + H^+ thermoreversible			

Qualitative assessment: 0 = none; +++ = high

Table 3.2 Comparison of frequently used hydrocolloids – functional properties.

Hydrocolloid	Syneresis potential	Film formation	Emulsifier effect	Protective colloid effect	Effects with other hydrocolloids
Gelatine	0	+++	+++	+++	Flocculation possible with agar-agar, carraganeen, LM-pectin, alginates, gum arabic, CMC
Agar-agar	+++	+++	0	0	+ locust bean gum or guar: low level of syneresis, more gel elasticity
Alginates	++	+++	+++	+++	+ locust bean gum or guar: low level of syneresis, more gel elasticity
Carraganeen	K-Ca.: +++ I-Ca.: +	++	+++	+++	+ locust bean gum or guar: low level of syneresis, more gel elasticity
Carboxymethyl cellulose (CMC)	0	+++	+++	+++	Technological potential as with locust bean gum, guar, and HM-pectin
Gum arabic	0	+++	+++	+++	+ gelatine: coacervate formation
Hydroxypropylmethyl cellulose (HPMC)	+	+++	+++	0	Technological potential as with xanthan
Locust bean gum	0	+	+++	0	+ xanthan: increase in viscosity (= gel) + gelling agent: low level of syneresis
Modified starches	+	++	+++	0	+ gelatine: improved setting + guar: increase in viscosity
Native starches	+++	0	+++	0	+ gelatine: improved setting + guar: increase in viscosity
Pectin	+	+++	0	0	Flocculation possible with gelatine
Xanthan	0	++	+++	+++	+ locust bean gum: increase in viscosity (= gel) + guar: increase in viscosity

Qualitative assessment: 0 = none; +++ = high

chapter, is their combination with gelatine in order to expand their range of properties and possible applications. For more details see the various chapters on applications.

3.1.1.1 Agar-agar

Agar-agar, a hydrocolloid extracted from red seaweed, is one of the oldest known gelling agents. Its gelling properties are based on its high molecular weight polysaccharide chain structure. Agar-agar swells in cold water but does not dissolve; it must be heated to at least 85 °C to achieve complete dissolution. Only specially modified so-called “fast-dissolving” agar types dissolve at temperatures between 60 and 80 °C.

Agar-agar gels are thermoreversible. However, the difference between the melting and gelling temperatures is very large. A 2% gel solution, for example, sets at around 30 °C but must be heated to over 85 °C to return it to the liquid state. In contrast to gelatine – a substance that melts in the mouth – flavor release with agar-agar is quite different. In addition, its texture is very firm and it possesses little elasticity. It is stable at neutral pH but rapidly loses its firmness in an acid medium when heated. Agar-agar is thus normally used at pH values between 4.5 and 5.5. Agar-agar gels take longer to set to a firm gel than, e.g., pectin gels, but require less time than gelatine gels.

Because of its heat resistance, agar-agar is ideal for use in products destined for hot climates or where further heat processing is required. One such example is the highly popular Japanese dessert “mitsumame”, a cube of agar-agar gel containing fruits and colorants. The manufacturer can pasteurize the gel in its packaging without melting the cube.

If, however, a faulty acid product of this nature has to be remelted and returned to the production process, it should be borne in mind that hydrolysis may occur at the required melting temperature.

In comparison with other hydrocolloids, agar-agar is considerably more expensive, a factor that can only be partially compensated by its high gelling power. As

Table 3.3 Advantages and disadvantages of agar-agar in comparison to gelatine.

Advantages	Disadvantages
High melting point	Low gel elasticity
Small quantities required	Poor release of flavor due to higher melting point
High gelling power	Low transparency
Fat barrier film	No emulsifying properties
	Soluble in hot (85 °C) water only

a result, agar-agar tends to be more and more used in those areas where its unique property of heat resistance is indispensable.

3.1.1.2 Carrageenans

The carrageenans are a family of substances which exhibit a high degree of chemical heterogeneity. They are extracted from various species of red algae. Because of their chemical structure and functional groups, the carrageenans have enormous swelling power. Thermoreversible gels can also be formed in conjunction with certain ions. The gels formed are not stable in acid medium and hence can only be used above pH 4. They are frequently used for the stabilization of suspensions; for example, they react favorably with milk proteins, thus preventing the formation of cocoa deposits in chocolate drinks.

Extracted carrageenan is a complex mixture of polysaccharides with a sulfate content of 15–40%. The precise composition is dependent on the type of algae extracted; the mixture obtained, however, can be fractionated by multi-step precipitation, each fraction having its own property profile. The three most important fractions are the kappa, iota, and lambda carrageenans, kappa and iota being able to form thermoreversible gels in the presence of potassium ions. Iota carrageenan also forms a gel in the presence of calcium ions. Kappa and iota carrageenans are soluble in cold water, but only as sodium salts; in their calcium and potassium forms they require temperatures in excess of 70 °C to dissolve.

Pure kappa gels are not quite as suitable for food applications because of their very firm and brittle texture. They are also prone to syneresis. Kappa carrageenan cannot be used in foodstuffs that exhibit a dry-substance content in excess of 50%, as this causes the gelling temperature to increase considerably. High temperatures in combination with acid media, conditions frequently found in food applications, also result in the rapid degradation of carrageenan.

Iota carrageenan forms transparent, elastic gels. Its gels are similar to those of gelatine and are completely syneresis-free. One of the major differences is the high melting point of iota gels, which results in another form of flavor release and a different mouth feeling.

As it is only weakly cross-linked, iota carrageenan can be readily dissolved by applying mechanical energy. However, it rapidly returns to the gel form once the mechanical energy ceases. This is known as thixotropic behavior. This property can be utilized, for example, in preparing cold milk desserts; these are liquefied by stirring and then filled into packages where they solidify. Modern paints are often thixotropic in nature too.

Because of their chemical structure, lambda carrageenans do not form gels. They are primarily used as thickeners. They are soluble in both cold and warm media.

Because of the heterogeneity of the extracted carrageenans, blends of various fractions are primarily used in order to obtain a constant technological property profile. Blends of kappa and iota carrageenans with locust bean gum are also available. In this way, the texture is improved and syneresis is reduced by the locust bean gum.

Table 3.4 Advantages and disadvantages of carrageenan in comparison to gelatine.

Advantages	Disadvantages
High melting point	Turbid gels if not refined
Gels vary in firmness and elasticity depending on the type used.	Poor release of flavor (iota)
The iota texture is similar to that of gelatine in confectionery applications.	In some types, the presence of ions is necessary for gel formation. This can have a negative effect on the entire system.
Iota carrageenan with locust bean gum provides very elastic gels.	Kappa: syneresis may occur during storage.
Lowers cholesterol	Allergenic potential
Gels rapidly	Possibly carcinogenic ^[a]
Fat barrier film	

^a Study by Joanne Tobacman, University of Iowa College of Medicine, 2001.

Refined carrageenan, i.e. carrageenan that has been subjected to an exhaustive purification process, is traditionally used in the food industry. Various semi-refined types are also available, but only certain ones may be used without restriction in food applications. One such type is for example, is PNG (Philippine Natural Grade). This particular type has a high proportion of kappa fractions and hence possess very high gelling power. It is also somewhat more economical than refined products because of the less complex manufacturing process involved; however, it does contain cellulose that is otherwise removed by filtration during the comprehensive refining process. Refined carrageenan thus provides a clear solution whereas PNG exhibit some turbidity.

3.1.1.3 Alginates

Alginic acid is extracted from the cell walls of brown algae. It is a chain-like cross-linked polysaccharide that is insoluble in water. Its sodium, potassium, and ammonium salts – the alginates – are, in contrast, soluble in cold water. Alginate solutions are highly viscous, even at low concentrations. They are stable within the pH range 5–10 and can be hydrolyzed in acid medium. Alginates are used as thermoirreversible gelling, thickening and stabilizing agents and for the formation of films.

The technological properties of alginates are dependent on the presence or absence of calcium ions. They are suitable as thickening agents, e.g., when no calcium ions are present. In the presence of calcium, the divalent ion induces a so-called “egg-box” cross-linking; if these cross-links are numerous, the alginate gel formed is no longer reversible.

Table 3.5 Advantages and disadvantages of alginates in comparison to gelatine.

Advantages	Disadvantages
High melting point	Short, brittle texture
Propylene glycol alginates (PGA) expand applications in the low-pH range	Poor release of flavor due to poor melting behavior
Soluble in cold water	Restricted application at low pH
Fat barrier film	Syneresis may occur during storage
	React with metallic ions (Fe, Zn, Co, Mn) and proteins
	Enriched with chemicals
	Prone to delivery problems

The “egg-box” reaction can be inhibited by esterifying some of the acid groups; alginates can thus be used in products such as milk that contain calcium. Such propylene glycol alginates are also more acid-resistant and can thus be used in an acid medium, e.g., as thickening agents in salad dressings.

Alginates have differing chemical structures depending on the species of algae; this gives them different technological properties. Similarly to agar-agar, alginates are normally supplied as blends developed for specific applications.

3.1.1.4 Pectin

Pectin is a component of the cell walls of many fruits and vegetables. It is produced industrially mainly from the skins of citrus fruits and the residues of apples used for the production of juice. In confectionery applications, it is the third most frequently used gelling agent after starch and gelatine. Furthermore, pectin has a protective colloid function, increases viscosity, and has excellent flavor-releasing properties. It is unstable in alkaline media and at increased temperatures at neutral pH.

Commercially available pectin comprises mainly the methylated esters of polygalacturonic acid and their sodium, potassium, calcium, and ammonium salts. The degree of esterification is dependent on the production process and is normally between 55 and 75%. The basic types are hence designated low-methoxy (LM) or high-methoxy (HM) pectin, respectively.

Dissolution temperatures should be above 50 °C in order to avoid “pre-gelatinization” – where the solution tends to gel prior to the actual production process. Temperatures in excess of 80 °C are regarded as ideal. Gel formation is dependent on the process temperature, the degree of esterification, the solids content of the solution, and the presence of ions, especially calcium and hydrogen.

Highly esterified pectins form thermoreversible gels that exhibit a short and sticky texture. Relatively inelastic, they can be easily deformed. Preconditions for the gelation reaction are a pH lower than 3.6 and a solids content between 60 and 80% (by weight). Both gelation temperature and speed increase with increasing solids content and decreasing pH. To prevent “pre-gelatinization” with a high dry substance content, a high pH is required; this, however, is not desirable in foodstuffs for sensory reasons. Thus, buffer salts – so-called retarders – are added to adjust the gelation speed to that required. In this way, taking into account the degree of esterification, pectins can be produced that gel at slow, medium, and rapid rates. These can be used for the production of acidic gel products. The buffer salts also vary the texture from smooth to brittle.

The lowest concentration level required for gelation of highly esterified pectins is about 55%. Products with a solids content much less than 60% or that do not contain additional acid require LM pectins with a low level of esterification. LM pectins gel according to the same mechanism as HM pectins. However, relatively independently of dry substance content and pH, they form thermoreversible gels because of the reaction with the di- and tri-valent ions in the medium, usually calcium. The gels thus formed have somewhat different gelling and melting temperatures. Temperature, pH, and sugar content are nevertheless important with regard to gelation temperature and rate. Texture, however, is principally dependent on the ratio of calcium to pectin used.

Pectins with low esterification values set immediately under the proper conditions. Furthermore, of the LM products on the market, amidated pectins enjoy the largest market share. The NH₂ groups of the amidated pectins shorten the lengths of the sections capable of reacting with calcium; thus, they have a defined degree of affinity for calcium so that gelation is easier to control. This results in the formation of softer gels.

Gel formation is also influenced by the source of the pectin. Highly esterified pectins extracted from citrus fruits react readily with divalent calcium whereas apple pectins are less reactive. As a result, gels from citrus fruit pectin that have reacted with divalent calcium are more brittle and elastic, tend to suffer from syneresis, and are not as spreadable as those obtained from apple pectins – an important attribute in jams. This ability to influence texture can be utilized up to a dry substance content of about 70% in practice. At higher concentrations, the gels of both types become very similar in their properties. In this case, the texture is influenced more by the buffer salts added to slow down the gelation rate. The high degree of sensitivity of citrus pectins to ions, however, always presents a danger of “pre-gelatinization”.

3.1.1.5 Locust Bean Gum

Locust bean gum is a hydrocolloid extracted from ground locust bean seeds. It can be dissolved in water at temperatures above 85 °C. The solutions that are formed have high viscosities, even at low concentrations and higher temperatures. The strong synergistic reactions between locust bean gum and other hydrocolloids make them suitable for other applications involving gel formation,

Table 3.6 Advantages and disadvantages of pectins in comparison to gelatine.

Advantages	Disadvantages
Higher melting point	Gelation difficult to control
Excellent flavor carriers	No elasticity
Rapid gelation	Poor melting behavior
Fat barrier film	Poor emulsifiers
	Possible pesticide contamination

stabilization, and emulsification. Locust bean gum, for example, improves the firmness and elasticity of agar-agar, alginate, and carrageenan gels.

A non-ionic molecule, locust bean gum is not influenced by the pH or ion content of the medium. However, it is degraded at extreme temperature and pH. The primary application areas for locust bean gum are in the production of baby foods, pet foods, and ice cream. In ice cream, it slows down melting and hence delays the growth of ice crystals. Locust bean gum is also used as a thickener in soups, where it dissolves only upon heating.

3.1.1.6 Gum Arabic

Gum arabic is a dried and ground natural resin. It is exuded from the trunks and branches of the *Acacia Senegal* tree when the surface of the bark is broken. *Acacia* trees of this type grow mainly in the Sahel zone in North Africa. This polysac-

Table 3.7 Advantages and disadvantages of locust bean gum in comparison to gelatine.

Advantages	Disadvantages
Not genetically modified	No film formation
High pH stability	Non-transparent
	No gel formation
	Allergenic potential
	Problems with digestion
	Prone to delivery problems

Table 3.8 Advantages and disadvantages of gum arabic in comparison to gelatine.

Advantages	Disadvantages
Not genetically modified	Non-transparent
Can be processed in high concentrations and thus used as fiber: it is prebiotic, cholesterol-lowering, and is said to prevent cancer	Does not form gels Allergenic potential
Soluble in cold water	Prone to delivery problems

charide is used mainly as a thickening agent. It exhibits a gelling effect only at very high concentrations and in conjunction with high solids content, e.g., as found in pastilles. Gum arabic is readily soluble in water; 50% solutions can be easily prepared at 25 °C.

The viscosity of a solution of gum arabic is directly dependent on the molecular weight of the polymer chains, which, however, do not occur uniformly in the final product. The quality of the harvests of gum arabic tends to vary considerably according to the climatic conditions of the particular harvesting year. Thus, the viscosities achieved can vary by up to 50%. In addition, the viscosity is influenced by other matrix factors such as pH, salt content, and temperature. Gum arabic is sensitive to both pH and temperature; this has to be taken into account if the product is subjected to additional heat treatment.

The main application areas for gum arabic are in the manufacture of pastilles, film-coated tablets, and spray powder flavors. Given its large molecular size, it is also able to prevent the recrystallization of sugar. Finding alternatives to gum arabic has always been a priority, mainly because of the uncertain climatic conditions and frequent droughts in regions where the acacia trees grow. Climatic variation also influences the price, which can vary enormously. Gum arabic, for example, has been replaced by carboxymethylcellulose in microencapsulation applications. Gelatine hydrolysates, which can also be used in the manufacture of cold-water soluble products, are also viable alternatives for vitamin coating processes and the sealing step in panned confectionery products.

3.1.1.7 Modified Cellulose

Cellulose is the most abundant biopolymer in the world. It is produced industrially from trees, cultivated plants, grasses, and seed fibers. To make cellulose water-soluble, it has to be chemically modified; this is done by substituting active groups onto the free hydroxyl groups of the polysaccharide molecule. By varying the type and number of the groups introduced in this way, the relevant technological properties of cellulose can be altered over a wide range. The types of modi-

fied cellulose produced for industrial use are methyl-, hydroxypropylmethyl-, hydroxypropyl-, carboxymethyl-cellulose, and other related cellulose ethers.

One of the most popular of the cellulose ethers is sodium carboxymethylcellulose (CMC), a modification which readily dissolves in cold water. CMC is stable within a pH range between 3 and 11, the optimal range being from 7 to 9. Like all cellulose ethers, it is stable at higher temperatures. Color intensification occurs only at temperatures over 140 °C, and thermal degradation only at temperatures over 200 °C.

CMC does not gel at typical application concentrations; instead, it forms pseudoplastic aqueous solutions. Thermoreversible gels form only at very high concentrations. CMC is mostly used for increasing the viscosity of solutions rather than for forming gels, the viscosity decreasing with increasing temperature. It is also used as a thickening agent, an emulsion stabilizer in combination with, e.g., milk casein, and as a suspension-forming agent. CMC is capable of binding large amounts of water even at low viscosity, especially in the form of its calcium salt. This particular property is utilized by the food industry to delay the stalting of bread.

CMC has also essentially replaced gum arabic in microencapsulation applications. When gelatine and CMC are mixed in certain ratios, they are not compatible at specific concentrations and pH values (see Fig. 3.2). This effect is utilized in microencapsulation applications.

This phenomenon is called complex coacervation and is influenced by the type (isoelectric point) of gelatine used as well as by the proportion of CMC in the solution, its degree of substitution, its molecular weight, and the temperature and pH of the solution. Depending on these parameters, the reactivity of both hydrocolloids ranges from true compatibility to turbidity to phase separation – this

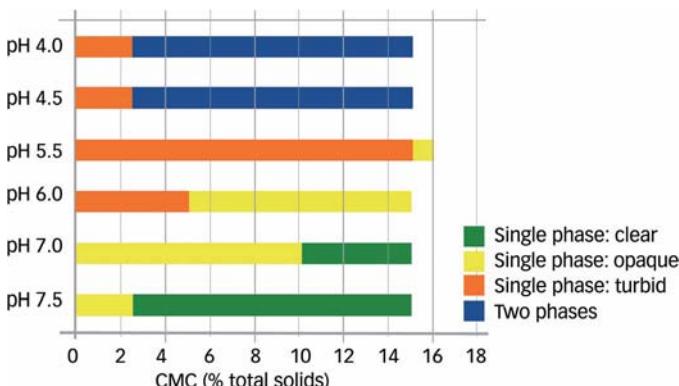


Fig. 3.2 Whereas limed bone gelatine is compatible with CMC over a wide range of conditions, mixtures of pigskin gelatine and CMC may be incompatible depending on concentration and pH-values.

Table 3.9 Advantages and disadvantages of modified cellulose in comparison to gelatine.

Advantages	Disadvantages
Soluble in cold water	Non-transparent
Stable at high temperatures	Chemically modified
High degree of water binding	Does not form a gel (CMC)
Gel/film formation on warming (HPMC)	Allergenic potential

latter property even being desired in microencapsulation applications (see Section 3.2.9).

A second representative of the group of cellulose ethers is hydroxypropylmethyl cellulose (HPMC). This variant forms a gel or film upon heating. HPMC was first used as a plant-based substitute for gelatine in the manufacture of pharmaceutical hard capsules. However, these capsules fall well short of the visual quality and size consistency of gelatine capsules. Furthermore, the costs of production are higher than those for gelatine capsules (see Section 3.2.3.6).

3.1.1.8 Starch and its Derivatives

Starch has a long tradition as a thickening and gelling agent in the food industry. In comparison with other hydrocolloids, it is inexpensive, but the native form has limited uses only in the food industry. Native starch is normally either not at all or very slightly resistant to high temperatures, acids, and shear forces. It also lacks the consistent properties that are required by modern production processes. These were the main reasons for the development of physical, chemical, enzymatic, and genetic modifications of starch exhibiting new or improved properties for use in a wide range of applications. The chemical and genetically modified varieties, however, must be declared as such for use in foodstuffs. In the pharmaceutical sector, modified potato starch is used in the production of soft capsules. The capsules produced in this way, however, do not have the same quality as gelatine capsules (see Section 3.2.6.2).

Native starch comprises two fractions. The first is amylose, a linear molecule that gelatinizes when heated and then, on cooling, forms a gel via the so-called “pudding effect”. The texture of such gels is short and sticky and they are always turbid. The second starch fraction is amylopectin, a branched molecule that dissolves in hot water to form clear, highly viscous solutions. High concentrations are required for gel formation. The ratio of amylose to amylopectin is dependent on the plant source from which the starch is extracted. This ratio has an important influence on the technological behavior of the starch. Starches with higher amylose contents form firmer gels; a disadvantage, however, is that such gels tend to retrograde, a process whereby the stored water is released. This undesirable process can be prevented by chemical modification: bulky groups such as

Table 3.10 Advantages and disadvantages of starch/modified starches in comparison to gelatine.

Advantages	Disadvantages
Wide application range through specific modification	Possibly genetically modified
An inexpensive hydrocolloid	Not suitable for low-carb products
No E-No. for native starch (foodstuffs) – just EU	Short, sticky texture Low transparency Do not form films Allergenic potential (modified starches)

phosphates are substituted onto the amylose molecule, and the resulting looser structural alignment prevents the water from being squeezed out.

Another example of chemical modification is “cross-linked starch”. This type is more stable to temperature, shear forces, and acids, in addition to exhibiting a greater water-binding capacity than native starch.

The “thin-boiling” starches frequently used in confectionery applications are also chemically modified. They are prepared from wheat, corn, and sometimes potato starch by treating with acid. They have a higher gelatinization temperature and form gels more easily than does native starch; however, their viscosities tend to drop below those of the starting materials. If these chemically modified starches are used solely as gelling agents, the required concentration is between 9 and 12%, the final product has a sticky texture and is often opaque. These starches are mainly processed at low concentrations together with another gelling agent, primarily gelatine.

Oxidized starches produced by slightly conditioning starch with an oxidizing agent are also frequently used in confectionery applications. They have lower gelatinization temperatures than acid-modified starches and form clear gels; however, the gels formed are not very firm and therefore are normally used in conjunction with other gelling agents.

Pre-gelatinized starches for low temperature use on the other hand are prepared mechanically. They swell in cold water, and any technological properties they may have are not improved by modification. The gelatinized starches prepared in this way are not quite as soft in texture as those prepared traditionally by heating; they are also less viscous and turbid.

One example of a starch, genetically modified by cross-breeding, is waxy corn starch, a product consisting of almost 100% amylopectin. This type of starch does not form a gel. Oxidized waxy corn starches are used in the confectionery industry as alternatives to gum arabic.

Table 3.11 Advantages and disadvantages of xanthan gum in comparison to gelatine.

Advantages	Disadvantages
Excellent stability with respect to pH, temperature, salts and enzymes	Non-transparent
Soluble in cold water	Does not form gels
	Allergenic potential
	Possibly genetically modified
	<i>Xanthomonas campestris</i> (fermentation microorganism) is a plant pathogen

Starches of high amylose content, in excess of 50%, can also be obtained by genetic cross-breeding. These gel faster and are firmer than those produced from native starch. Because of their high gelling temperatures, these starches are often chemically modified or blended with conventional thin-boiling starches.

3.1.1.9 Xanthan Gum

Xanthan gum is a high molecular weight biopolysaccharide produced by the fermentation of solutions containing carbohydrates by the microorganism *Xanthomonas campestris*. This bacterium forms this substance in its fermentation medium for the purpose of binding water. *Xanthomonas campestris* is a plant pathogen; thus, very high standards must be adhered to in the manufacture of xanthan gum.

Xanthan gum is soluble in cold water and forms a highly viscous solution. These solutions are relatively insensitive to changes in pH and maintain their viscosities over a wide temperature range.

Aqueous solutions of xanthan gum are thixotropic, i.e. the viscosity decreases during pumping or stirring. Once such mechanical effects cease, the original viscosity is regained.

Xanthan gum itself is not capable of forming a gel. It is, however, used as a binding agent for soups, sauces, and dressings and is able to inhibit crystallization in ice cream. It is also used as a fat substitute in low-calorie products. Xanthan gum is sometimes processed along with guar gum, as the blend has a higher viscosity than either constituent on its own. It can form a thermoreversible gel with locust bean gum because of the synergistic effects generated. It stabilizes small particles, drops of oil, or air bubbles by entrapping them in the gel matrix.

3.1.1.10 Gellan Gum

Gellan gum is also a biopolysaccharide produced by fermentation. It is soluble only at temperatures over 75 °C. It possesses enormous gelling power, a concentration of 0.05% being enough to produce a strong gel. Depending on whether

Table 3.12 Advantages and disadvantages of gellan gum in comparison to gelatine.

Advantages	Disadvantages
Only low concentrations required for most applications.	Sometimes reacts sensitively to ions. Gelation is difficult to control (cf. pectin).
Increases the gelation rate, gelation temperature, and melting point of gelatine.	Very expensive, small market volume Manufacturer's monopoly

gums acylated at a low or high level are used, the texture has various degrees of hardness and elasticity. Acylated at a low level, gellans form strong, clear, but brittle gels. Gellan gum is very reactive, i.e. gel formation is initiated by all types of ions. In contrast, highly acylated gellan gums are more elastic and are more comparable with gels prepared from a combination of xanthan gum and locust bean gum. Combinations of the two basic types of gellan gum produce quite different textures.

Gelatine can be associated with gellan gum in the manufacturing of ready-to-eat jelly desserts. The control of sequestering agent, calcium levels, and concentrations of gelatine and gellan gum makes possible the production of stable products which provide quicker setting and higher melting resistance in hot weather.

3.1.1.11 Conclusion and Outlook

This overview demonstrates that individual hydrocolloids have their own particular technological properties. This is reflected in their traditional application areas, some of which are even dependent on availability of supplies. One example is the thickening of milk by adding carrageenan algae during cooking, as practiced in Ireland and Normandy. Today, manufacturers of ready-to-use products must constantly develop innovative products, open up new marketing channels, or simply produce more economically. And new challenges often demand hydrocolloids with special properties. However, hydrocolloid A cannot always simply be replaced by hydrocolloid B. Alginate gels, for example, are clear and elastic, but they do not melt in the mouth. Pectin gels are not elastic but can be easily deformed. And native starches are not capable of forming films.

When blending hydrocolloids, the possibility of vigorous reactions has to be taken into account; these can be both positive and negative. Gellan gum, for example, accelerates the gelling speed of gelatine and substantially increases gel firmness, but reduces color and clarity. On the other hand, citrus pectin, almost as good as gelatine in terms of the color and clarity of the gel produced, reduces the firmness of the gelatine gel. Carrageenan has an even stronger negative effect on the firmness, color, and clarity of gelatine gels (see Fig. 3.3).

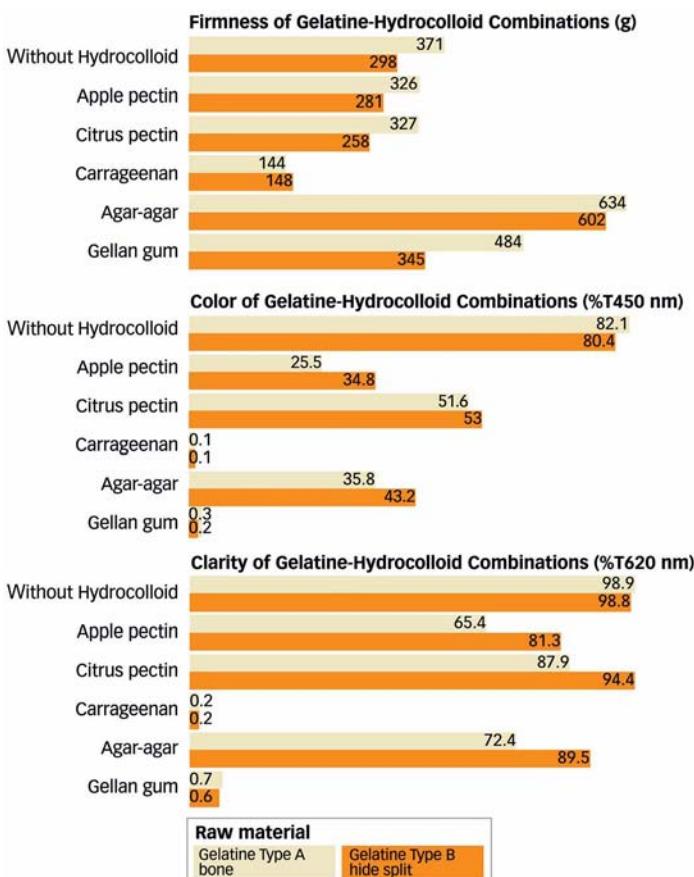


Fig. 3.3 Firmness, color and clarity of gelatine/hydrocolloid blends.

Combinations of gelatine and agar-agar, however, have created new opportunities. Such a combination enables considerably higher degrees of firmness to be achieved than with gelatine alone, and the melting point of the gel can increase up to 80 °C. In the case of fruit gummies, the melting temperature can be increased to about 50 °C, hence making the product suitable for marketing in tropical climates. However, if these hydrocolloid interactions are to be fully utilized in practice, numerous other factors have to be taken into consideration.

If, for example, increasing amounts of agar-agar are added to a solution of pig-skin gelatine, the melting point does not significantly increase, at least initially. From a concentration of about 3%, however, the melting point increases rapidly, reaching its maximum at about 5%. Any further increase in concentration makes no further difference (see Fig. 3.4).

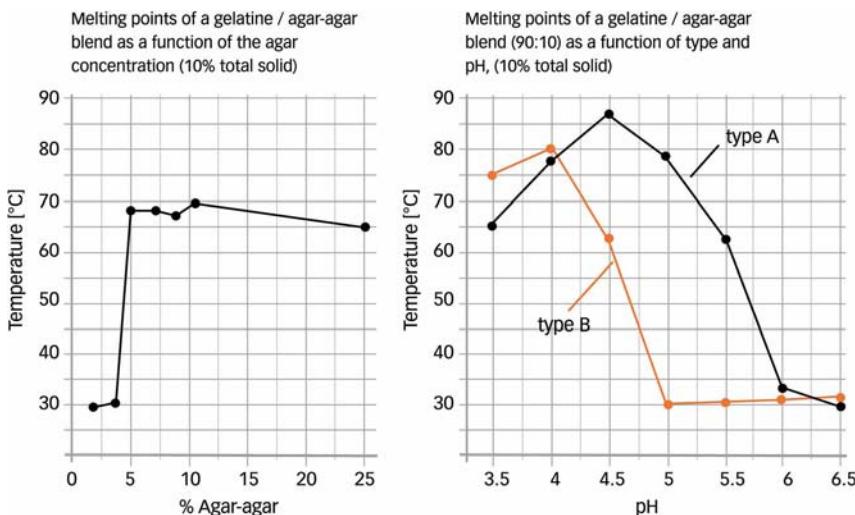


Fig. 3.4 Left: melting points of blends as a function of agar-agar concentration (type A gelatine, pH 5.3). Right: melting points of gelatine/agar-agar blends as a function of gelatine type and pH.

The type of gelatine used also has an influence on the heat stability of the mixture. In the case of a 90:10 gelatine/agar mixture, the maximum melting temperature with pigskin gelatine occurs at pH 4 and in the case of limed ossein gelatine at pH 4.5. This emphasizes the important role isoelectric point plays.

Because of the incompatibility of hydrocolloids with one another, an entirely new and specialized branch of the industry was developed – the compounding industry. Here, specific blends of hydrocolloids are prepared for many applications. Of course, the application specialists of the hydrocolloid industry itself can be of assistance, too, in solving such application problems.

A further method of obtaining new hydrocolloids is the specific blending of hydrolyzed hydrocolloid fractions. For example, locust bean gum combined with agar-agar fragments rather than normal agar-agar improves the elasticity but decreases the firmness of gels. In the case of agar-agar itself, partial hydrolysis decreases the dissolution temperature, thus facilitating processing.

Bearing this in mind, complex blends of different substances or hydrolyzed fractions are necessary in order to obtain a defined property profile. Such solutions, however, tend to be expensive both in manufacture and in further processing, especially in comparison with gelatine (see Table 3.13). For, in the case of gelatine, the user gets not only a gel former of unique texture but also an emulsifier and a stabilizer. And gelatine is an inexpensive hydrocolloid which from the nutritional point of view is completely digestible and has minimal allergenic potential. Also, it is not chemically modified and contains no pesticides. Thus, using alternatives to gelatine frequently involves accepting sensory or technological dis-

Table 3.13 Assessment of gelatine.

Advantages	Disadvantages
Multifunctional (texture, surface activity, emulsifier, stabilizer, film former)	Low stability to heat
Melts at body temperature with rapid and intense release of flavor	Low gelation temperature
Unique texture, elasticity and brilliance	Slow gelation
Transparent	Soluble only at higher temperatures (exceptions: Instant gelatine and gelatine hydrolysates)
Easy to process	BSE discussion
No E-No. (food)	Animal source (vegetarians/vegans)
Preventive function in osteoarthritis and osteoporosis	Religious reservations
Protein enrichment	

advantages and a higher price, unless high temperatures or extreme pH values have to be used or there are religious or personal reasons for not using animal-based substances.

3.1.2

Dissolution Kinetics and the Rheological Behavior of a Gelatine Solution are Central to Process Optimization

When selecting a powder gelatine, the focus is frequently on parameters such as Bloom, color, clarity, or viscosity. Properties such as the degree of grinding, foam formation, setting temperature, or setting time, however, although not normally considered as important, can exert considerable influence on the production process.

Depending on the final product, the gelatine has to be processed either as a low- or high-percentage solution. Preparing such solutions with powder gelatine is technologically relatively simple compared to using other hydrocolloids. However, in practice, other problems tend to occur, e.g., the formation of lumps or foaming, if the process involved has not been adapted completely to the specific type of gelatine involved. The lumps formed comprise dry particles of gelatine that adhere to each other and that are very difficult to dissolve afterwards without using mechanical means. If these swollen fines agglomerate, they tend to incorporate other dry particles, consequently preventing them from being wetted.

3.1.2.1 Process Steps for Dissolution

The dissolution process consists of a number of process steps: dispersion of the powder gelatine, swelling of the dry gelatine particles, and their dissolution by warming. Traditionally, this takes place in a two-step process. The gelatine is stirred into cold water, allowed to swell, and then heated to form a solution. The swelling and dissolution steps can, however, take place simultaneously – and therefore more quickly – in a one-step process, whereby the gelatine is directly stirred into hot water. Providing the process parameters are selected correctly and an appropriate apparatus is used, thermal degradation of the protein chains, excess foaming, and the formation of lumps can be avoided.

3.1.2.2 Factors Influencing Dissolution – Particle Size

In the ideal dispersion process, the powder gelatine is brought into the liquid with a minimum of stirring so that each individual particle is rapidly surrounded by it. During subsequent swelling, the gelatine particles take on five to ten times their weight as water. The water diffuses from the surface into the body of the particles. The time required for this process depends on the surface area of the particles. As the surface area of a particle increases in proportion to the square of its linear dimension and the volume in proportion to its third power, small particles have a greater specific surface area than large ones, so that the cross-section of the particles to be penetrated by the water is smaller. Therefore, they swell more quickly and dissolve more rapidly upon warming.

The time required for complete dissolution is especially dependent on the degree of granulation of the gelatine. The dissolution curves of high- and low-Bloom gelatines of identical particle size are thus very similar in nature (see Fig. 3.5).

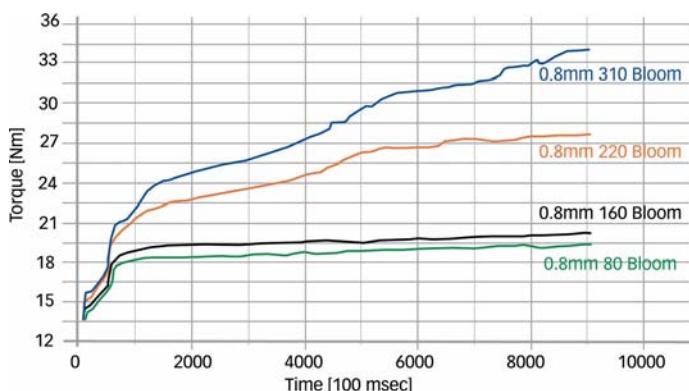


Fig. 3.5 Dissolution curves of granulated gelatine of different quality but with the same particle size.

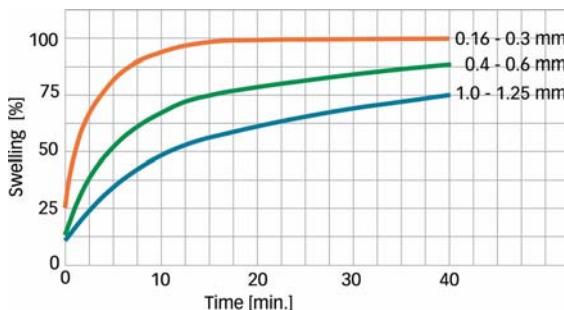


Fig. 3.6 Swelling behavior of the same powder gelatine at 18 °C as a function of particle size.

As a guideline, finely ground particles (0.1–0.3 mm) swell within a few minutes in cold water (see Fig. 3.6); medium-sized particles (0.3–0.8 mm) take about 10 min, and large particles (over 2.0 mm) require an hour to swell completely.

In the case of smaller particles, the absolute surface area increases disproportionately, so that lumps are more likely to form. To compensate for this, cold water should be used; the particles then take up water more slowly and the surfaces do not become “tacky”. Although this reduces the formation of lumps, it prolongs the process by a few minutes. Another possibility is to stir intensively. Here, however, there is a risk of excess foaming at a later point as too much air is introduced into the system. The air bubbles that are formed are difficult to remove, especially from highly concentrated solutions.

3.1.2.3 Factors Influencing Dissolution – the Matrix

Apart from the degree of granulation and the temperature, the composition of the surrounding liquid and the concentration of the gelatine also influence dissolution behavior.

In aqueous solutions of citric, tartaric, or acetic acid, for example, gelatine dissolves somewhat more quickly than in pure water. This effect is not utilized in practice in order to avoid loss of quality brought about by acid-induced hydrolysis of the gelatine. In contrast, concentrated sugar or salt solutions delay the dissolution process, as these substances, which have a great affinity for water, compete with the gelatine particles for the available water. This also can give rise to the formation of lumps and to undissolved gelatine particles. Furthermore, processors should initially dissolve the gelatine in water or at least subject it to pre-swelling before adding it to a system containing high concentrations of salt or sugar.

In addition, the gelatine particles also compete with each other for the water. Thus, the higher the concentration, the longer they take to swell. Therefore, there is a limiting concentration value up to which gelatine can be easily dissolved. This is about one part gelatine to two parts of water. Higher concentrations of gel-

atine are possible but are much more difficult to produce without foam because of the very high viscosities involved.

3.1.2.4 Traditional Two-step Processing versus the Modern Hot-Melt Process

In the two-step process, the cold-swollen gelatine is placed in a water bath at 60–70 °C or a in a vessel heated by an external mantle or heating coil to a similar temperature. The solution that is prepared can then be further processed. At temperatures over 50 °C, the internal structures formed within individual particles during previous drying of the gelatine are completely broken down; a disperse molecular “random coil structure” is formed. The ordered structures typical of gels no longer exist. At the same time, because of the lower temperature, thermal degradation is minimal, and there is no need for intensive stirring. This reduces the amount of air taken up by the solution.

The absolute dissolution time can be reduced by using processes that, in contrast to the two-step process, do not necessitate a pre-swelling step. In such a one-step hot-dissolution process, the powder gelatine is added to water at 80 °C under vigorous stirring. The gelatine immediately swells and dissolves. These one-step dissolution processes were previously recommended only for concentrations up to a maximum of 15%. Today, however, in the interest of shortening production processes, even highly concentrated solutions are prepared using the hot-melt process.

These modern methods, however, require special apparatus and processes. In the confectionery industry for example, the gelatine is dispersed in a special gelatine dissolution apparatus at 80–90 °C under vigorous stirring (see Fig. 3.7); the colloidal suspension is then pumped, together with sugar and glucose syrup, into

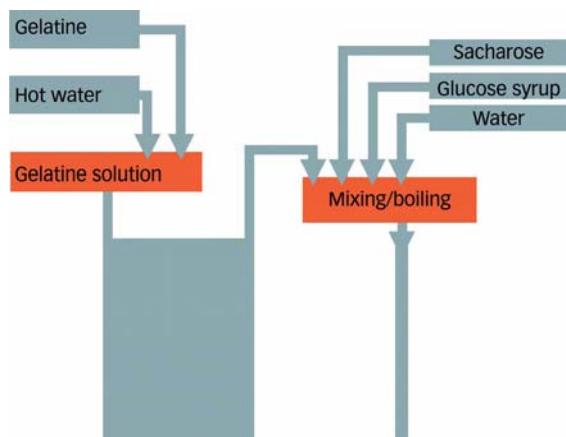


Fig. 3.7 Flow chart of a modern dissolution process for highly concentrated gelatine solutions in the confectionery industry.

a continuous sugar boiler where, if any undissolved particles of gelatine are still present, these are then dissolved completely. In the subsequent vacuum part of the equipment, any air bubbles created by the vigorous stirring are removed, and, at the same time, part of the water is evaporated off; the temperature of the solution drops as a result. The final outcome is a bubble-free solution.

Hot-melt processes, in contrast to traditional two-step processing, have the major advantage that the gelatine can be further processed within minutes – the entire swelling process becomes unnecessary. The required apparatus is expensive and the resulting solutions can be very hot. As such, they should be processed immediately, therefore avoiding the loss in quality brought about by the thermal degradation of the peptide chains.

In addition, in the one-step process, the significantly increased rapid lump formation brought about by the higher temperature must be avoided. Such lumps can be formed during dispersion if the gelatine added is too fine or if the stirring speed is too low. Thus, in the accelerated, one-step process, the use of a frequency-regulated stirrer is optimal; in this way, the stirring intensity and the particle size of the powder gelatine can be balanced optimally. Also, with such a variable stirring system, the rotation speed can be reduced in proportion to the degree of dispersion desired. This in turn reduces the amount of air taken in, and hence foaming, during the dissolution process.

If such equipment flexibility is unavailable, the degree of grinding of the powder gelatine must be optimally adapted to the conditions of the equipment being used. The rule of thumb is that, for all hot-melt processes, a powder gelatine containing a low proportion of dust is the safest material to use. Such a gelatine allows for a moderate stirring speed and the development of a lump-free solution at an acceptable processing speed. However, if high concentrations are being used, the dimensions of the stirrer also have to be taken into account. The viscosity of a dispersion of coarsely ground gelatine also increases more rapidly than that of finely ground gelatine shortly after the addition of the gelatine (see Fig. 3.8).

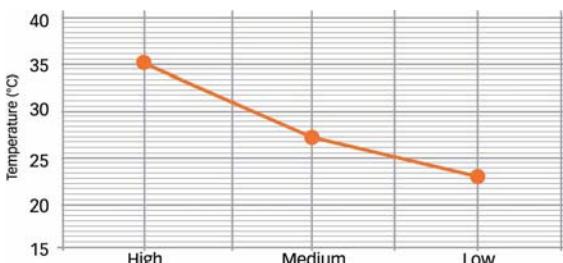


Fig. 3.8 The stirrer is subjected to maximum mechanical force shortly after addition of gelatine due to the rapid increase in viscosity of the solution.

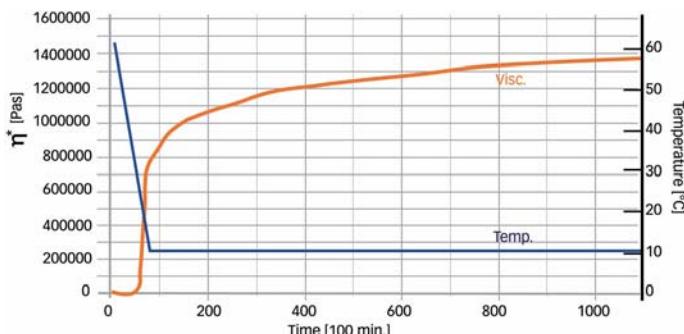


Fig. 3.9 Viscosity of a gelatine solution on cooling.

3.1.2.5 The Viscous Behavior of a Gelatine Solution During Further Processing

When a finished gelatine solution is being further processed, the viscosity is an important criterion (see Fig. 3.9). In the case of molded articles such as fruit gummies, where flowability is important for production purposes, a low-viscosity gelatine is normally used. High-viscosity gelatine on the other hand is required for creams. Low-viscosity gelatines have the disadvantages that they require setting times that are a little longer and the final product softens more at higher ambient temperature.

The viscosity of a gelatine solution is a function of the raw material, the conditioning process, the concentration, and the temperature (see Figs. 3.10 and 3.11). In solutions of identical gelling power, the viscosity of alkaline-conditioned gelatine and neutral or slightly alkaline-extracted types is 30–50% higher than that of acid-extracted gelatine from raw material that has undergone the same pretreatment. However, the viscosity of a particular gelatine solution at different concentrations cannot be precisely derived directly from the standard viscosity as provided by the manufacturer. Since there is no linear correlation, it is not possible to predict an exact value from a single-point measurement.

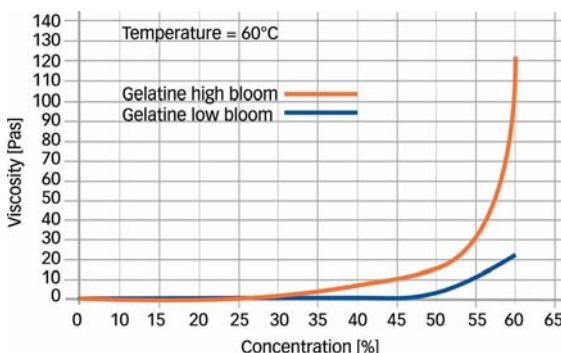


Fig. 3.10 Viscosity of a gelatine solution as a function of the Bloom value and concentration.

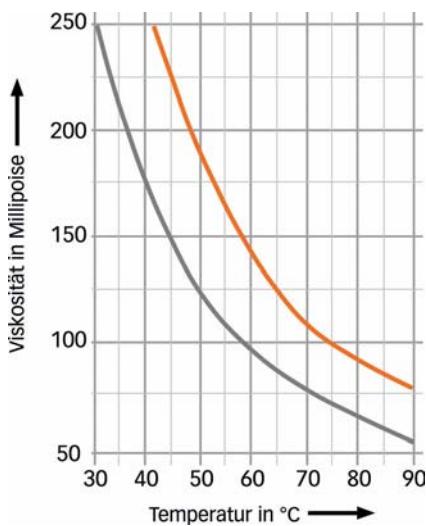


Fig. 3.11 Viscosity of different 10% solutions of gelatine as a function of temperature.

Rheological measurements have shown that at least at the concentrations normally employed in the processing of gelatine solutions in numerous applications there is almost Newtonian behavior. Structural viscosity is present only in the case of higher concentrations of high-Bloom gelatine. However, in the normal case, there will be no problems associated with the dimensions of piping, pumps or other equipment. Gelatine solutions have a high degree of shear stability and are thus easily pumped without quality loss.

3.1.2.6 Setting Temperature and Setting Time

During the course of processing products containing gelatine, they are cooled, and this results in the conversion of gelatine from the sol to the gel state. The setting time and temperature are influenced by the temperature profile during cooling, the type of gelatine employed and the composition of the aqueous system. However, in addition to the gelatine type and concentration, the interaction of gelatine with other components of the formulation and the overall water content of the system are major factors.

With increasing amounts of water, setting begins at lower temperatures. The actual sol/gel transition, however, requires less time. This can be explained by the fact that a firm gel can only be formed if the gelatine molecules are arranged in a three-dimensional network that is subsequently stabilized by hydrogen bonds and ionic and hydrophobic interactions. The more mobile the gelatine molecules are at the beginning of the cooling process in a system the more rapidly do they achieve the ideal spatial arrangement for gel formation.

In brief, if there is a lot of water in a particular system, the viscosity of the solution drops (see Fig. 3.12) and the longer gelatine molecules move more

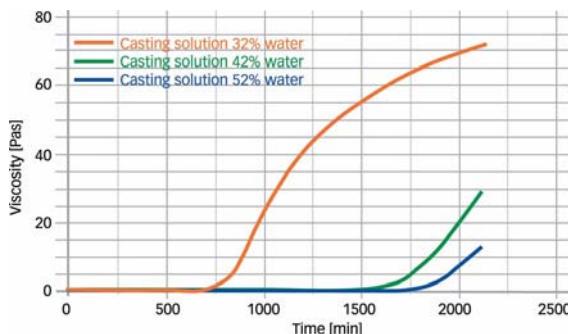


Fig. 3.12 Viscosity of a fruit gummie molding solution on cooling as a function of its water content.

easily and rapidly. This gives rise to faster solidification times, but at lower temperatures.

3.1.2.7 Process Optimization in Practice

In summary, the particle size distribution of the powder gelatine and its viscosity are the most important technical factors for the optimal processing of gelatine. Under certain circumstances, however, the setting behavior of the gelatine system can also be of importance, especially when processing time is an important factor.

During the manufacturing of soft shell capsules, for example, the gelatine mass on the cooling drum must set in less than one minute and on the dipping pins of the hard shell capsule machine in less than 15 s. In the preparation of photographic layers, the required setting time is even less. And even in the production of cereal bars, where gelatine hydrolysate is used as a natural “adhesive,” the time required for binding through loss of water is a critical factor in the production process. For fruit gummies, in contrast, this is not the case; here, drying takes place on a bed of starch simultaneously with the gelling process. The time-limiting factor in this process is the drying process, which, with a few exceptions, is much longer than the gelling process.

For the dissolution process, the high temperatures sometimes used as well as the length of time these temperatures are held have to be taken into account to prevent the degradation of technological properties of the gelatine solution. More specifically, this is manifested by an irreversible decrease in viscosity, a loss of gelling power, an increase in the color, and inferior organoleptic properties. The extent to which these occur is a function of temperature, time, and pH.

Within the temperature range 60–70 °C, gelatine solutions can be kept for several hours without much loss of gelling power. For example, after two hours at 60 °C, a solution will retain 98% of its original gelling power (see Fig. 3.13).

A gelatine solution may even be heated to between 90 and 100 °C without much loss in gelling power provided that the temperature is maintained for only

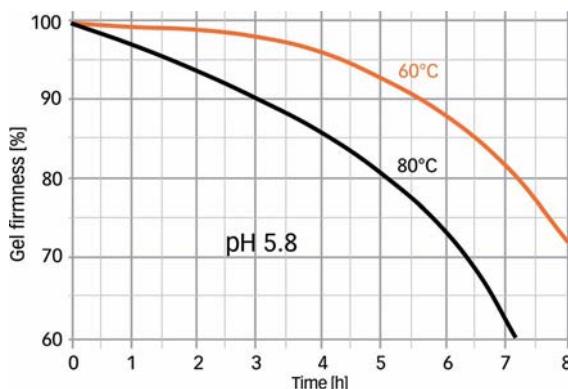


Fig. 3.13 Relative decrease in gel firmness of a gelatine solution as a function of storage temperature and storage time.

a few minutes. However, temperatures over 100 °C, e.g. as found in autoclaves or during the boiling of highly concentrated sugar solutions, should be avoided whenever possible, as in this case, the loss in gelling power can be extreme, even if the holding time is very short (see Fig. 3.14). Thus, for sterilized products, higher concentrations of gelatine must be used to compensate for anticipated losses in gelling power.

A higher degree of degradation takes place when the pH of hot gelatine solutions is within the strongly acidic or alkaline range (see Fig. 3.15). Thus, if acid or alkali has to be added, this should take place as late as possible during the process.

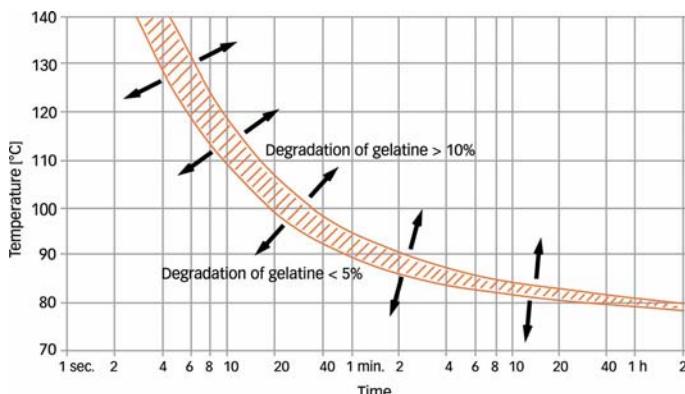


Fig. 3.14 Critical and non-critical heating/temperature conditions for the quality of gelatine solutions at pH 5.0.

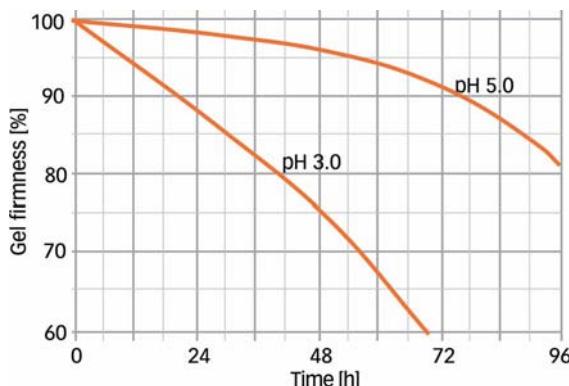


Fig. 3.15 Relative decrease in gel firmness of a 6.67% gelatine solution at 60 °C as a function of the pH and storage time.

To protect the gelatine from the effects of acid, buffer salts may be added. This enables the acidity to be increased to strengthen the flavor profile.

An additional parameter is the type of gelatine used. Pigskin gelatine, for example, is more thermally stable at slightly acidic pH than neutral or slightly alkaline-extracted ossein and hide split gelatines. Alkaline media exert the opposite effect (see Figs. 3.16 and 3.17).

Therefore, only a very detailed understanding of the dissolution and rheological behavior of the specific type of gelatine used, its interaction with other compo-

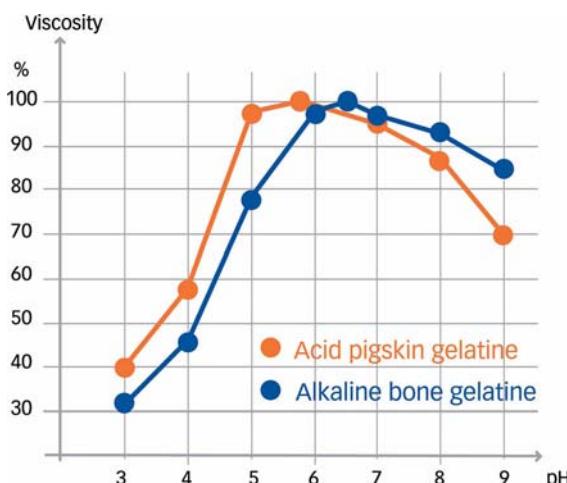


Fig. 3.16 Decrease in viscosity after 3 hours at 70 °C and different pH levels.

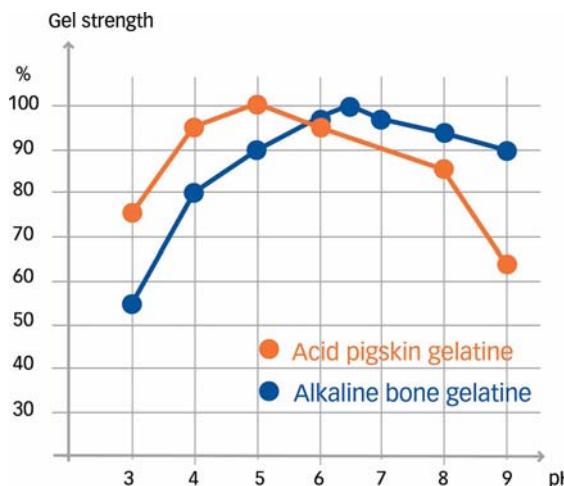


Fig. 3.17 Decrease in gel firmness after 3 hours at 70 °C and different pH levels.

nents of the formulation, and consideration of the time and temperature profiles will ensure optimal production processing. Problems such as lump formation during dissolution, excessive foaming, loss of gelling power, and quality losses during storage or additional production processes should be reduced to a minimum from the very beginning (see Table 3.14). Such optimization, within reason, is possible in cooperation with the gelatine manufacturer. This approach guarantees an efficient production process and allows for the manufacture of products of consistently high quality.

Table 3.14 Indication of a less than optimal dissolution process.

– *In the gelatine solution:*

- Lump formation
- Severe foaming
- Very long dissolution times
- Gelatine particles in the solution

– *In the product:*

- Decreased degree of clarity
- Varying product quality and texture
- Changing viscosity
- Collapsing foam
- Syneresis
- Increased degree of crystallization



Fig. 3.18 One leaf of gelatine always produces the same gel strength.

3.1.2.8 Special: Processing Leaf Gelatine

Leaf gelatine (see Fig. 3.18) is primarily used in domestic households, the fine bakery and pastry industries and in catering. The central factor here is that one leaf of gelatine – regardless of the brand – dissolved in a given quantity of water always exhibits the same gel strength. This has been standardized by the few worldwide manufacturers of leaf gelatine. The gelling power of powder gelatine as sold in small units for domestic use is, however, not standardized, so that the amount to be used must first be determined and then weighed precisely because each brand might well have a different gelatine quality and quantity in the sachet.

For processing (see Fig. 3.19), the leaves are first placed in cold water and allowed to swell for several minutes. The swollen leaves are then removed from the water and gently squeezed.

For warm dishes, the swollen, squeezed gelatine can be added directly to the heated mixture, where it dissolves readily. Heating should then be stopped, however, as the gelatine would otherwise lose a portion of its gelling power. The same effect occurs when processing raw kiwi, pineapple, and papaya fruits. This is because these fruits contain proteolytic enzymes that decompose protein. The enzymes must be deactivated by blanching briefly prior to being processed.

For cold dishes such as creams and curds, the swollen and squeezed gelatine should first be dissolved in a little liquid. Several tablespoons of the

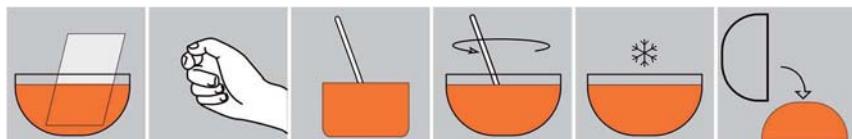


Fig. 3.19 Processing of leaf gelatine: 1) Swelling in cold water. 2) Squeezing out. 3 and 4) Dissolving in a warm fluid 5) Chilling. 6) Turning out.

cold mixture can then be stirred into the gelatine solution, followed by the rest of the mixture.

Alternatively, the gelatine, subsequent to swelling and squeezing, can be dissolved in a microwave oven and then mixed with the cold mixture in the same way.

Info Box 3.1

Practically unlimited shelf life when dry

If gelatine is stored under dry and odor-free conditions, it can be stored for a practically unlimited period without noticeable loss of quality. Its low water content protects it from microbiological decomposition.

In contrast, gelatine solutions present an excellent medium for microorganisms. For this reason, all gelatine provided to the customer is guaranteed to correspond to the highest possible microbiological quality requirements (see Section 2.3). However, should microorganisms enter the solution from the water, from the atmosphere, or from poorly cleaned equipment, they can grow exponentially within a very short period of time, with far-reaching consequences. Some microorganisms form CO₂, and the solution may suddenly begin to foam after a few hours. Others release proteolytic enzymes that can rapidly diminish the gelatine quality (see Fig. 3.20). Also, the organoleptic properties of the gelatine worsen whenever there is microbial contamination. Therefore, gelatine solutions should always be prepared under hygienic conditions and are best stored between 55 and 60 °C – the best compromise between thermal degradation and microbiological risk. It is, however, always best to conduct any additional processing without delay.

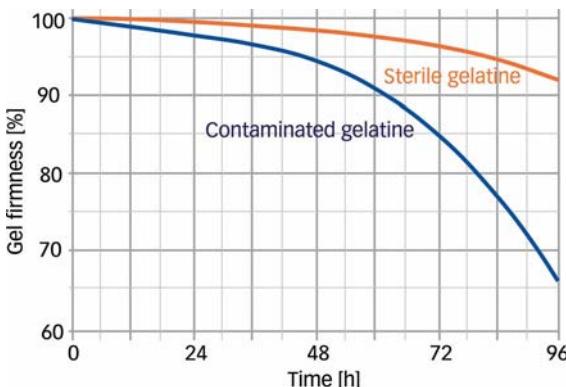


Fig. 3.20 Relative decrease in gel firmness by proteolytic enzymes brought about by microbiological activity.

3.1.3

The Typical Properties of Instant Gelatine Must be Taken into Account when Processing

Ready-made mixes for desserts and cake fillings cannot always be dissolved in warm water subsequent to processing. In this case, the developer or user requires a special type of cold-water-soluble gelatine to utilize the advantages of the full range of properties of gelatine. In the ideal case, the cold-water-soluble gelatine in question should possess precisely the same properties as warm-water-soluble gelatine. This, however, cannot be completely attained with the typical cold-water-soluble or “instant” gelatine.

Instant gelatine, unlike traditional powder gelatine, can be processed cold, because of a special drying process (see Section 2.2.10) during production. This drying process gives it the amorphous structure that causes it to be cold water-soluble while still allowing it to form a gel-like structure after dissolution. As a result, dessert powders, ready-to-use cake mixes, and whipped cream powder containing instant gelatine can be added directly to other cold liquid components or whipped cream; separate swelling and dissolution by heat are no longer necessary. In comparison with conventional powder gelatine, instant gelatine also exhibits other typical properties, which also have to be taken into account when processing.

As in the case of standard powder gelatine, mass firmness, general thickening behavior, and foam formation are highly important for the user and product developer. There are also a number of common properties for the two types: high-Bloom instant and powder gelatinates both achieve a high degree of firmness more quickly than low-Bloom types; both also have similar foaming properties and enhanced mouth feeling and texture. However, at comparable concentrations and Bloom values, the firmness of gelatine dissolved in a warm medium and then chilled is significantly higher than that obtained by an instant gelatine in cold water (see Fig. 3.21). This is because normal instant gelatine is not a true gel but rather a partially solidified mass or pseudo-gel. This in turn means that a higher concentration of instant gelatine would be required to achieve the same results. In practice, however, this is rarely relevant. As instant gelatine is normally used for specific purposes, typical gel firmness is unimportant.

The kinetics of solidification are also different. In the case of instant gelatine, the kinetics are faster than with powder gelatine, although type A instant gelatine sets more quickly than type B (see Fig. 3.22).

Other important factors are particle size distribution and mean particle size. In the case of fine blends, the gelling process occurs much more quickly than with medium and large particles. The final degree of firmness after one hour is also significantly higher. Because of this, instant gelatine is ground as finely as possible after drum drying (see Fig. 3.23).

Agglomerated instant gelatine, in spite of its larger particles, dissolves faster and without the formation of lumps because of its special structure. Gels are

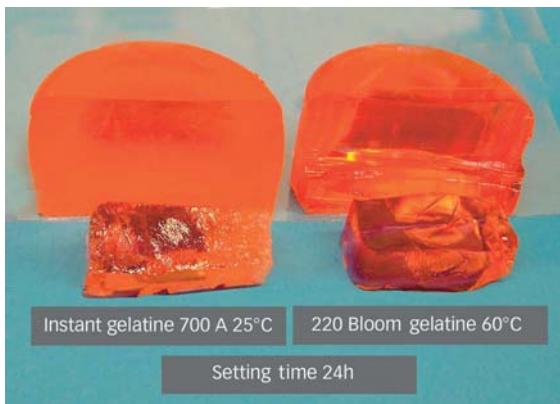


Fig. 3.21 At comparable concentrations and Bloom values, the firmness of a standard gelatine gel (right) is significantly higher than the pseudo-gel obtained by an instant gelatine (left).

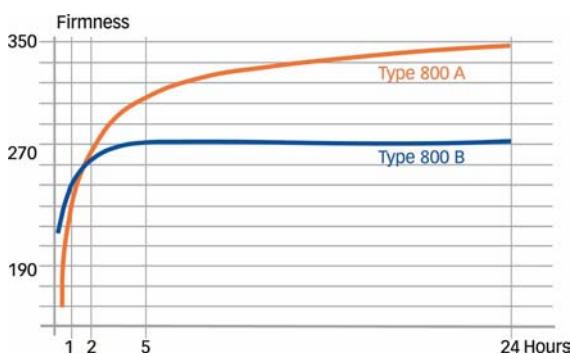


Fig. 3.22 Firmness of two instant gelatines (types A and B) as a function of time.

thus formed quickly and have properties comparable to gels prepared in warm media.

Apart from these gelatine parameters, the overall product composition also has an effect on both the kinetics and the final degree of solidification. This is especially the case when the other components are also polyelectrolytes and their charges change with pH. In addition, the temperature of the mass is also important.

The most frequently used property of instant gelatine, apart from its gelling property, is its ability to form foams. Here, as with powder gelatine, type A instant gelatines show better foaming properties than type B instant gelatines.

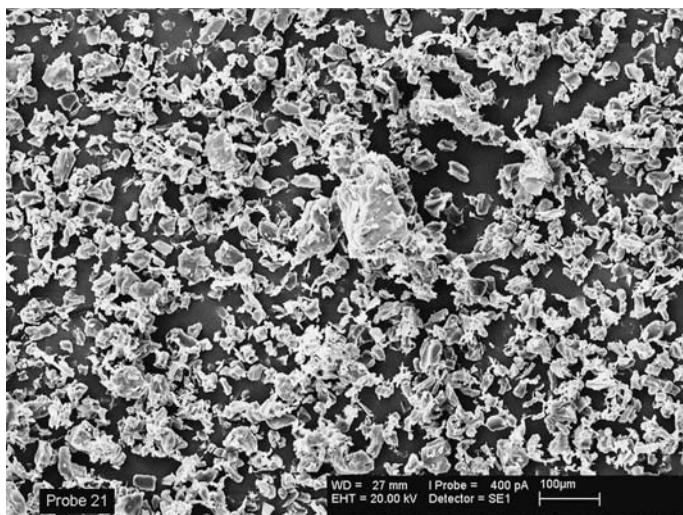


Fig. 3.23 Microscopic image of instant gelatine. Most particles are within the range of about 20 μm .

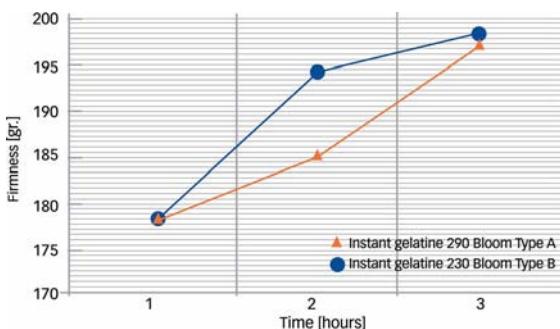


Fig. 3.24 Comparison of the setting behavior of different instant gelatinates in a mousse-au-chocolat recipe.

The mean foam density of a foam prepared under standard conditions can be varied using different types of instant gelatine (see Fig. 3.24). Acid-conditioned types generate a higher but less firm volume of foam than alkaline-conditioned types. High-Bloom instant gelatine also produces a lighter foam than the lower-Bloom types.

As with gel firmness, foam formation is strongly dependent on pH. Foam formation and stabilization are usually greatly improved if the processing pH is significantly different from the isoelectric point (IEP) of the gelatine.

While processing instant gelatine, there is a risk of lump formation when stirring into a liquid; this is because of the rapid and intensive swelling that takes place. To avoid this phenomenon and ensure homogeneous distribution of the

Info Box 3.2**Soluble in cold water but really gel-forming – agglomerated instant gelatine**

Instant gelatines, which have been on the market since the early 1970s, are mainly used as thickeners for creamy mixtures. For many years, users have been searching for a gelatine type that is soluble in cold water but which forms a clear and firm gel. Numerous patents have been submitted, but it is only relatively recently that a product has been developed fulfilling these criteria.

After stirring into cold water, this newly developed innovative agglomerated product, containing natural additives, dissolves rapidly and lump-free to form a true gel which can be cut, and is almost identical to that produced using warm water (see Fig. 3.25). In this way, for the first time, clear gels such as table jellies and cake glaze

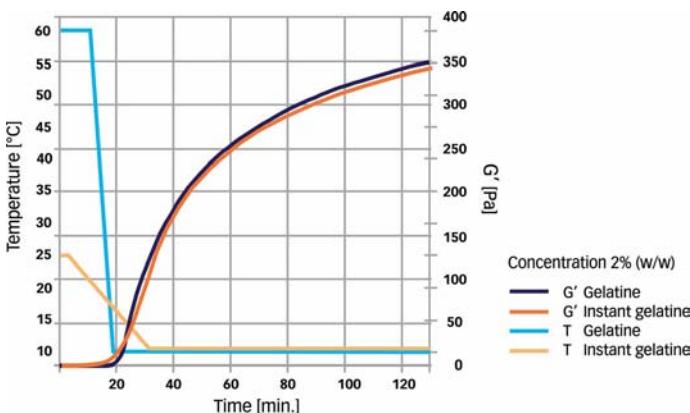


Fig. 3.25 Comparison of the network formation of a gelatine solution dissolved at 60 °C and a specially agglomerated instant gelatine dissolved at 25 °C during chilling.

components, instant gelatine must always be pre-mixed with other fine-particle components of the formulation. A blend of one part gelatine to five to seven parts sugar, cocoa, milk powder, or confectioners' sugar has proven to be suitable. Such a mix can then be added to cold water without the formation of any lumps.

Typical instant gelatines do not form clear gels in cold water. Therefore, they are primarily used for the preparation of creamy desserts and cake fillings along with milk, cream, or yogurt. Selection of the most suitable type of instant gelatine is – as with gelatine in general – highly dependent on the type of processing used and on the desired characteristics of the product envisaged. Desserts, for example, should be ready for serving as quickly as possible after preparation, i.e. the gelatine must set rapidly. The situation is different, however, in the case of cream fillings as used in households, pastry shops, bakeries, and in industry. Here, the

Info Box 3.2 (continued)

can be prepared by using only cold water. The gels are not quite as firm as those made using warm water. However, firmness can be achieved by using higher concentrations (see Fig. 3.26).

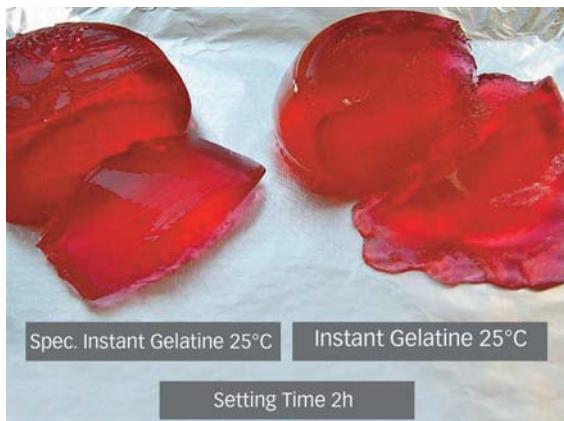


Fig. 3.26 With specially agglomerated instant gelatine, a clear gel can be obtained in comparison with standard instant types.

Table 3.15 Physical/chemical properties of three typical instant gelatines and a newly developed agglomerated instant gelatine.

Type	Instant (acid)	Instant (acid)	Instant (alkaline)	Agglomerated instant gelatine (acid)
Bloom [g]	270–310	220–260	215–245	190–230
Viscosity (mPas)	4.8–6.0	3.2–4.2	6.0–7.2	3.5–4.7
pH	4.7–5.7	4.7–5.7	5.4–6.0	4.7–5.7
Bulk density (g L ⁻¹)	300–450	300–450	300–500	300–400
Fraction > 0.16 mm (%)	0–5	0–5	0–5	90–95
Fraction > 0.1 mm (%)	0–12	0–12	0–12	95–100
Moisture [%]	0–4.0	0–4.0	0–4.0	<9

gelatine should remain in liquid form slightly longer in order to allow the larger quantities to be processed over a period of time and set later for stabilizing and to make ready for serving.

Depending on these product-specific processing factors, the quantities required are between 0.1 and 3% by weight based on the final product. The whipped cream also contributes towards firmness in most products and should be considered in this calculation. Instant gelatine is also frequently used by the “Compounding Industry” and is blended with highly variable ingredients to form intermediate products. Overall, in comparison with warm water-soluble powder gelatine, instant gelatine is a highly specialized area, its world market share being approximately 0.5% of the total edible gelatine market.

3.1.4

Gelatine Hydrolysate – a Non-gelling but Versatile Product

Gelatine hydrolysate is a special type of non-gelling gelatine. It is produced from the same raw materials as those used in the manufacture of powder, leaf, and instant gelatine. However, the protein chains of the collagenous raw materials are further cleaved using chemical, thermal, or biochemical processes – or a combination of these. The low molecular weight fractions thus obtained have, in contrast to standard gelatine, a number of special technological properties. For example, they are soluble in cold water and they do not form gels even in highly concentrated solutions at the temperatures normally used in processing. They do, however, possess other properties typical of gelatine. During the manufacture of gelatine hydrolysate, very little bitter peptide is produced compared to the amount formed with other hydrolyzed proteins, so that it is more neutral in taste.

The principal technological property of gelatine hydrolysate is its attractive molecular profile. This contributes to its wide range of applications. The molecular profile is dependent on the raw materials and, especially, the manufacturing process used. Generally, the mean molecular weight of gelatine hydrolysate is about $2000\text{--}20\,000\text{ g mol}^{-1}$, the profile ranging from free amino acids to peptides and collagenous proteins. However, by employing precisely controlled enzymatic hydrolysis, a product can be obtained with a mean molecular weight within a specified range (see Fig. 3.27).

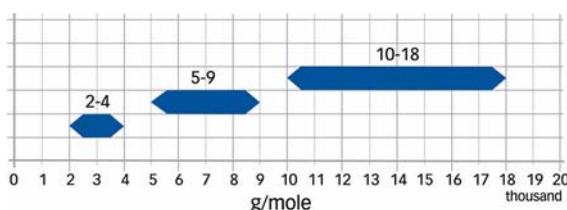


Fig. 3.27 Specific ranges of mean molecular weights of gelatine hydrolysates can be manufactured on demand.

Table 3.16 Typical application areas for gelatine hydrolysate.

Function	Typical applications
Increasing solubility and dispersion	Instant teas, protein blends, beverages, shakes
Emulsification and stabilization	Low-fat sandwich spreads, vitamin-embedding, stabilization of low-fat cheeses
Improvement of texture	Hot dogs, cheese spreads, ready-made meals, beverages, candy chews, fruit gummies
Formation and stabilization of foams	Protein bars, marshmallows, cheese spreads, desserts (e.g., mousses), low-fat sandwich spreads, powdered cocoa and coffee drinks
Binding of water	Ready-made meals, fresh meat
Cohesion and adhesion, fixing	Cereal bars, protein bars, tablets, licorice pastilles, panned products
As a carrier	Instant teas, pharmaceutically active substances, spices, plant extracts
Coacervation	Clarification of beverages (beer, wine, and juices)
“Functional ingredient” in nutritional applications	Protein enrichment, osteoarthritis prophylaxis, substitution of carbohydrates and fats (low carb/low-fat products, diabetic foods), low-salt foods, sports nutrition, beauty products

If gelatine hydrolysate is used for its technological rather than its nutritional properties, its excellent solubility is only one of the valuable characteristics that can be utilized by the product developer in the food industry (see Table 3.16).

For example, gelatine hydrolysate reduces surface tension and enables a foam to be formed. At the same time it stabilizes the foam by preventing small air bubbles from combining to form larger ones, hence causing the foam to collapse. In addition, by using concentrations of hydrolysate in the range 1–3%, the processor can produce desserts that are much creamier and softer in texture as well as having a higher volume after whipping. However, gelatine hydrolysate not only promotes foam formation, it also stabilizes the resulting foam (see Fig. 3.28).

During foam formation, pH has practically no influence. Coagulation reactions are also rare under the usual temperature and pH conditions employed. Since gelatine hydrolysate is normally compatible with sugar, sugar substitutes, hydrocolloids, and proteins, it is easy to process, even at higher concentrations and in more complex formulations. This is also the case with reduced fat and calorie foodstuffs; in fact, it even enhances mouth feeling and, therefore, the enjoyment of the product. The excellent miscibility of gelatine hydrolysate makes it an ideal

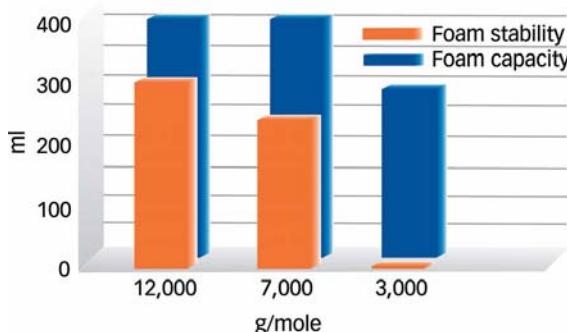


Fig. 3.28 Foam formation and stabilization as a function of the mean molecular weight of gelatine hydrolysates.

substance for enhancing the efficacy of other foaming agents such as hydrolyzed milk protein. Casein, for example, because of its very low buffering effect even in the form of an alkaline salt, can only be effectively used in the presence of a strong acid if the solution also contains gelatine hydrolysate. The hydrolysate in this case acts as an acid-resistant, acid-buffering stabilizer.

Another technological and frequently used property of gelatine hydrolysate is its high emulsifying capacity. This particular parameter, which is also dependent on the molecular weight of the hydrolysate, determines the quantity of oil that can be emulsified by a protein under standard conditions. The emulsifying effects of gelatine hydrolysates are shown in Fig. 3.29.

The concentration of gelatine hydrolysate required for this application is 3–5%. Hydrolysates of higher molecular weight increase the viscosity of the solution. They also provide a protective function for colloids, which prevents the particles from discharging electrically and hence destroying the emulsion. In addition, the water binding capacity of the solution is improved.

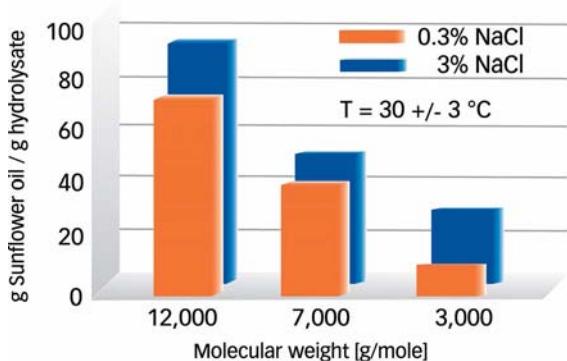


Fig. 3.29 Emulsifying capacity of gelatine hydrolysates as a function of the mean molecular weight.



Fig. 3.30 Gelatine hydrolysate has excellent adhesive qualities; these enable it to be used for the production of various types of bars.

This particular property is utilized by manufacturers to produce cold-water-soluble vitamin E and A tablets as well as coloring agents like carotenoids. In this application, gelatine hydrolysate is used as an emulsifier and stabilizer for the oily vitamins. The resulting emulsions are subsequently spray-dried (US Patent No. 3 608 083). If cold-water solubility is not required, classical gelatine types can be used.

Gelatine hydrolysate also possesses excellent adhesive qualities, which enable it to be used for the production of various types of bars, in which a concentration of approximately 7% causes binding of the dry substance ingredients. The use of sugar for this purpose requires very high concentrations. The food industry is thus able to utilize this property for the production of low-sugar and hence low-calorie bars – products that are enjoying increasing popularity throughout the world (see Fig. 3.30). And, as no sweet components are required for binding the dry ingredients, bars containing gelatine hydrolysate can also be developed with spicy, salty, or herbal flavors.

This functional property of gelatine hydrolysate in spicy foodstuff production is supplemented by its flavor-enhancing property. A high concentration of peptide-bound glutamic acid intensifies salty and spicy flavors. This means that the concentrations of salt, spices, and other additives can often be substantially reduced – a very important factor in the processing of meat, ready-made meals, and, especially, dietary foods. Recent studies have also shown that gelatine hydrolysate in fruit juices enhances their sweet and fruity taste.

A further application of gelatine hydrolysate is in the clarification of beer, wine, and fruit juice (see Fig. 3.31). This is based on the fact that gelatine hydrolysate reacts with negatively charged pectins and tanning agents to form cross-linked compounds.

During these reactions, insoluble agglomerates are formed that precipitate and cause other turbid particles to precipitate. In this way, the taste is improved



Fig. 3.31 Gelatine hydrolysates are used for the clarification of beer, wine and fruit juice in many countries around the world.

by the removal of specific components. The process also enables the beverage to be subsequently filtered more easily (see Section 3.2.4). There are some specially developed products on the market that prevent clarification from occurring: here, gelatine hydrolysates are added to beverages containing fruit pulp to enhance nutritional appeal and where sedimentation is considered to be a defect.

In practice, the processing of gelatine hydrolysate is much simpler than that of other proteins (see Table 3.17).

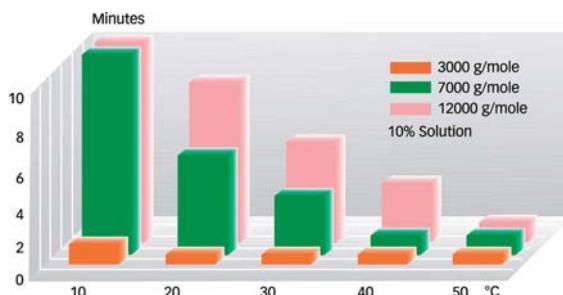
Gelatine hydrolysate dissolves completely in cold water, and is the only gelatine product with this property. Only when highly concentrated solutions are required is it recommended to use heat. Solutions containing up to 60% gelatine hydrolysate can be prepared using cold water.

The use of warm water may be necessary if the dissolution speed is to be increased (see Fig. 3.32). However, care should be taken to avoid the formation of foam and lumps. This can be achieved by using a stirrer with variable speeds.

Subsequent to dissolution, a clear yellow solution is obtained, the color intensity being dependent on the concentration of hydrolysate used. The viscosity of the solution is dependent on temperature, concentration, and molecular weight of the hydrolysate (see Fig. 3.33). Hydrolysates of low molecular weight produce solutions of low viscosity that, even in relatively high concentrations, are easy to process.

Table 3.17 Overview of proteins used in foodstuffs.

Product	Dissolution behavior	Influence of temperature	Other
Gelatine hydrolysate	Cold water-soluble Solutions up to 60% solid content	Non-sensitive No coagulation	Foam formation pH-independent
Egg albumin	A) Powder: At least 30 min of pre-hydration 4× excess water recommended B) Crystalline products: At least 120–180 min pre-hydration. 7× excess water recommended.	Coagulation occurs at concentrations of: –8% at 105–107 °C. –40% at 65 °C.	Not suitable for products containing fat. “Excess whipping” leads to foams collapsing. Allergenic potential.
Hydrolyzed milk protein	No pre-hydration required 15× excess water recommended.	Non-sensitive No coagulation	Less sensitive for products containing fat. Requires sugar to form a stable foam.
Hydrolyzed soy protein	No pre-hydration required. 15× excess water recommended.	Non-sensitive. No coagulation.	Allergenic potential. Less sensitive for products containing fat. Requires sugar to form a stable foam. Allergenic potential. Genetically modified material often used as starting material.

**Fig. 3.32** Dissolution speed of gelatine hydrolysates as a function of temperature and mean molecular weight.

In many countries, food processors inject such solutions into boiled ham in order to maintain the juice content.

In some applications, the dry gelatine hydrolysate powder can be stirred directly into the product. Examples of such “water-free” processing are the fining of wine mash and the addition of hydrolysate powder during the mechanical tumbling of meat.

Gelatine hydrolysate is supplied to the food industry as a spray-dried powder. It is frequently also subjected to agglomeration to increase the speed of water absorption. Agglomerated products tend to clump less and can also be processed without generating dust (see Fig. 3.34).

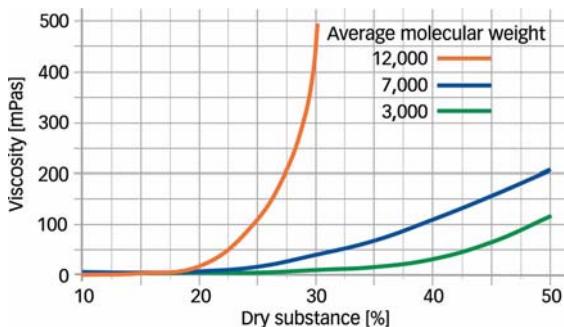


Fig. 3.33 Viscosity of gelatine hydrolysate solutions as a function of mean molecular weight and concentration at 25 °C.



Fig. 3.34 Agglomerated gelatine hydrolysates (right) tend to clump less. They can therefore be dissolved more easily than standard types.

Info Box 3.3**Gelatine hydrolysate is becoming increasingly popular as a “functional ingredient”**

To date, the food industry has mainly made use of the technological properties of gelatine hydrolysate. However, this substance is also a very useful “functional ingredient”. It is a high-quality, easily digestible protein that contains neither carbohydrates nor fats. In contrast to other proteins, it has practically no allergenic potential. It is gluten-free, contains no purines, and has a typical protein energy content of 345 kcal/100 g. Scientific studies and clinical observations carried out over recent decades have also shown that certain special types – marketed as collagen hydrolysates – have a protective effect on joint cartilage.

It has thus become an important food additive for patients suffering from osteoarthritis and for athletes whose joints are subject to extraordinary mechanical stress, the recommended daily dose being 10 g (see also Chapter 4).

All types of powdered gelatine hydrolysate can be stored practically indefinitely provided that the environment is dry and odor-free. Dryness is particularly important as, because of its low water content of 5–8%, the hydrolysate tends to absorb water from the air more rapidly than conventional gelatine, which has a water content of 10–12%.

3.2

Gelatine Applications

3.2.1

Confectionery and Gelatine Desserts

Fruit gummies are ideal examples of what makes gelatine unique as a gelling agent. In the mouth they absorb water rapidly, the melting point decreases to body temperature, the gel melts, and the aromas and flavors are released. This behavior is not demonstrated to this extent by any other hydrocolloid. In the confectionery industry, gelatine is not only used for its thermoreversible gelling, but also for its foaming, foam-stabilizing, binding, and emulsifying qualities as well as for its ability to control crystallization. Specially developed gelatines are available for all applications in the confectionery industry.

3.2.1.1 Fruit Gummies

Fruit gummies are extremely popular throughout the world. The reasons for this are many and various, but it is mostly because of their most important texturizing agent – gelatine (see Table 3.18).

3.2.1.1.1 Processing the Slurry

Fruit gummies are composed of essentially four ingredients: glucose syrup, sucrose, gelatine, and water (see Fig. 3.36). These are initially processed as a slurry. This requires a vessel to dissolve the gelatine, a weighing/mixing system, and a boiler.

In modern one-stage hot-melt processes, the powder gelatine is added to water at 80–90 °C under vigorous stirring. The powder swells and dissolves simultane-



Fig. 3.35 Gelatine is used in the confectionery industry in numerous applications.

Table 3.18 BASIC RECIPE – Fruit Gummies.**Ingredients:**

A: Sucrose	31.5%
Glucose syrup 40 DE	40.9%
	6.6%
Water	4.7%
B: Gelatine, 260 Bloom, type A	7.0%
Water	14.0%
C: Citric acid, 50%	1.9%
Flavors and colorants	as required
D: Anti-adhesive agent	

Process:

A is boiled to 87% solids and cooled to 90 °C.

B is dissolved at 60 °C.

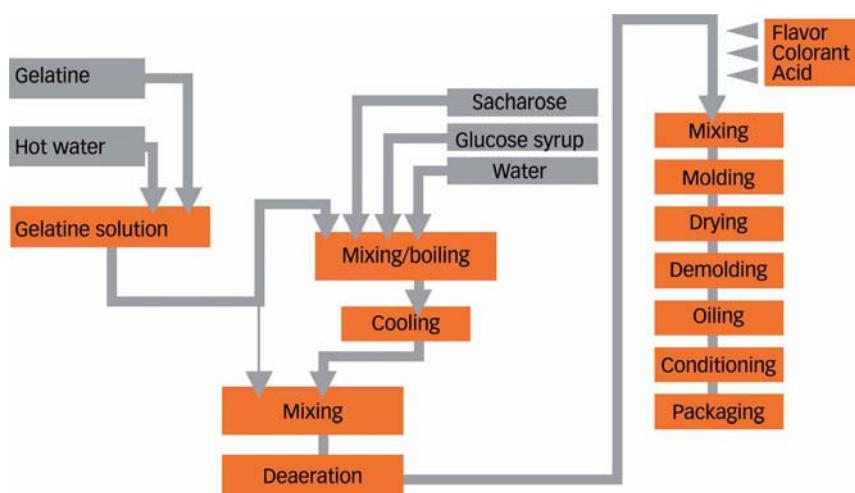
B and C are slowly added to A and stirred until a homogeneous mass is formed.

The mass is placed in starch molds.

After 48 h at room temperature, the gummies are removed from the starch and oiled with D.

Conditions:

Water content at deposition process	25%
Temperature at deposition process	75 °C
Relative humidity of air	30–40%
Moisture of the starch powder	<6.0%

**Fig. 3.36** Production flow chart for fruit gummies.

ously (see Section 3.1.2). The recommended ratio is 2 parts water to 1–1.5 parts gelatine.

In the weighing system, the gelatine solution, glucose syrup, and sucrose are mixed according to the formulation being used. The slurry is then heated until the sugar crystals are completely dissolved. A number of very different processes can be used to achieve this. In the traditional process, favored by many manufacturers, heating takes place in open pans, and in this case the gelatine is added toward the end of the process. The sugar mass is then cooled to <100 °C to avoid foaming and splashing. Today, closed systems are mainly used, either as batch or continuous systems (see Fig. 3.37). The formulations must be adapted to the type of equipment being used. Usually, a given formulation cannot be used in another system without modifications.

In modern systems, the hot solution is fed into a vacuum chamber to adjust the solids content. Air bubbles, if generated by stirring, are removed, and a portion of the water is removed by evaporation, which causes the slurry to cool to approximately 80 °C. The residual water content is about 25%.

If thermal processing is too excessive, the gelatine is hydrolyzed too much. This is typically the case in lengthy processing carried out at atmospheric pressure; consequently it is not recommended. It is certainly advantageous if the gelatine can be added after the boiling process and after the sugar solution has cooled.



Fig. 3.37 Continuous weighing/mixing dissolution system for the production of the molding mass for fruit gummies.



Fig. 3.38 The slurry is molded into forms (right) using a Mogul machine (left).

However, the glucose syrup must be more highly concentrated, as the water introduced by the gelatine solution cannot be evaporated afterwards. Furthermore, air also enters the system when the gelatine solution is added and must be accounted for in the case of fruit gummies, as the absence of air bubbles is an important quality criterion.

3.2.1.1.2 Molding using the Mogul Machine

The slurry is then molded into forms using a Mogul machine – the specialized equipment designed for making fruit gummies (see Fig. 3.38). The addition of colorant, acid, and flavor takes place immediately prior to molding to minimize the effects of time and temperature at low pH and to avoid the inversion of the sucrose and the hydrolysis of the gelatine or other hydrocolloids used and the loss of any volatile flavor components. The mixture is then fed into the molding chambers of the machine and filled into the negative forms pressed into the starch trays.

To achieve optimal molding, the following criteria must be fulfilled: the solution must be fluid enough to flow easily through the valves and completely fill the molds, and it must separate cleanly from the nozzle at the end of each molding step. If the molding mass is too viscous, i.e. too cold or too highly concentrated, “tailing” may occur as a result of the solution not separating cleanly when the valve is closed. This brings about the formation of gel fibers, causing the products to adhere to each other and form long chains. As a result, the starch is contaminated as the latter cannot be completely removed when the gummies are subsequently separated from the starch.

Consequently, when the starch is dried, these residues melt and are distributed homogeneously by the movement of the starch. At the same time, the starch becomes discolored, which is brought about by the gelatine contained in the product residues reacting, in a Maillard reaction, with the carbohydrates of the starch to produce brown-colored reaction products. If the process is repetitive, the starch will take on an intense brown coloration and will be denatured, i.e. the content of cold water-soluble by-products will increase, which in turn affects the Mogul pro-

cess in a negative manner. In the longer term, this type of contamination renders the starch unsuitable for the Mogul process.

The Mogul process can be regarded as a circulatory system. It starts in the drying chamber where the dried and set fruit gummies in the starch trays are stacked. The stacks are fed into the destacker of the Mogul machine. This removes individual trays from the stack, turns them over, and empties the product and starch into a sieve station, where they are separated. In a separate process, the water absorbed by the starch from the fruit gummies is evaporated off and the starch is recycled in new trays in the Mogul machine. In the imprinting station of the machine, the negative molds are formed and subsequently filled with liquid gum masses via numerous nozzles.

3.2.1.1.3 Drying

The filled trays are stacked and taken to the drying room where the molding solution solidifies as the gelatine sets. At the same time, the products lose water; this water is either absorbed by the starch or vented to the atmosphere. Depending on the storage temperature and storage time, the water content of the finished product is reduced to 14–19%.

The drying parameters are dependent on the type of hydrocolloid being used. Products containing gelatine, pectin, and agar-agar are normally dried for up to 48 h at room temperature. Gums that are molded with a higher water content must be stored longer, up to 72 h, at the same temperature. For special products (pastilles, jelly babies, etc.) temperatures of 35–70 °C are used. The more water that the gel releases during this production step, the firmer the structure becomes. In this way, the texture can be varied by the drying process in starch molds. However, the final water content must be low enough to guarantee microbiological stability.

The water content of the starch used for molding must also be adapted to the type of hydrocolloid, otherwise it may adhere to the finished product and affect its transparency (see Table 3.19).

If the water content is too low, problems can occur when the negative molds are being imprinted; this is because the molds become somewhat unstable and even small vibrations can cause them to collapse. Starch also produces a lot of

Table 3.19 Optimal properties of molding powder for different hydrocolloids.

Hydrocolloid	Water content (%)	Temperature (°C)
Gelatine	5–8	26–37
Starch	5–8	37–49
Pectin	5–10	37–49
Agar-agar	5–8	26–43
Gum arabic	5–8	26–37

dust in this case; therefore, there is an incalculable risk of dust explosion. On the other hand, if the water content is too high, the starch can adhere to the product and is difficult to remove during the later stages of the process. It can also have a negative effect on the appearance and taste of the product.

3.2.1.1.4 Starch-free Molding

Starch-free molds, e.g., silicone molds, do not absorb water. Such molds are not suitable for use with all hydrocolloids, as the gums being produced have to be molded with their final water content. Furthermore, the hydrocolloid used must have a short setting time, a criterion that is fulfilled, for example, by pectin. If the molding mass is too viscous because of the dry substance necessary for microbiological stability, molding may well be impossible unless the viscosity can be decreased by employing a higher molding temperature.

Fundamentally, gelatine is suitable for both processes. Because of the setting time requirements for starch-free molding, a large number of silicone molds are necessary if continuous production giving throughput comparable with the traditional Mogul process is to be carried out. This could well raise questions about the economics of the process.

One of the main advantages of starch-free molding is that a separate drying step is no longer necessary; hence the production time and storage costs can be reduced. Products manufactured using starch-free molds have sharp contours and are extremely uniform. One disadvantage is that the manufacturer is restricted to using one shape of mold. If other product contours are to be produced, all the molds have to be replaced. This is a considerable investment and also requires refitting of the machines. When starch is used, it is only necessary to replace a few gypsum positive molds to produce and imprint new product shapes.

Another alternative is to mold in blisters prepared directly by the machine. These negative molds are made of plastic foil and are filled with the gummy molding solution and closed off once the solution has set. The setting process can be accelerated by intensive and rapid cooling. Moreover, the blisters serve as packaging for the final product and eliminate the need for investment in expensive silicone molds. This change in format, although still leading to a more expensive process than classical methods, is feasible at reasonable cost. Overall, packaging is more expensive than in the case of classical fruit gummies, as each item is individually packaged.

For this reason, starch-free molding has remained relatively unimportant.

3.2.1.1.5 Finishing

As soon as the product has attained its final texture, it is sieved to remove the starch powder or separated from its starch-free mold by special pins or compressed air. To prevent the product from sticking to the starch-free mold, the molds are coated with a release agent such as vegetable oil. Care should be taken to ensure that the oil used does not become rancid during storage, as this can affect the taste of the product. The same is true of the starch process, as some oil is

also added to improve the sharpness of the contours of the negative molds during imprinting and to reduce the generation of dust.

The product is now subjected to a number of additional processes. It is moistened with steam, either sugar or a mixture of sugar and citric acid is sprinkled over it, or it is oiled with wax to give it a shiny surface. This oiling process takes place in an oiling drum and should last at least five to six minutes, as the oil must have time to be worked into the product and become stable. If this does not occur, the wax tends to run off the product and collect in the packaging, and the product becomes somewhat turbid after a short period of time. Subsequently, the product is packaged and delivered to the customer.

3.2.1.1.6 Remelting

Products with molding faults can be returned to the production process, thereby increasing the overall yield. Products formulated with gelatine are placed in cold water and slowly heated until an approximately 50% solution is obtained.

This solution can then be added to the slurry prior to boiling. As these solutions already contain the fruit acids of the final product, there is a substantial risk that the hydrocolloids will be hydrolyzed and the sucrose will be inverted. It is almost impossible to separate the colored recycled products. For this reason, the remelt solutions are normally used for the manufacture of dark products, as they have a higher concentration of gelatine to compensate for the more extensive hydrolysis caused by the addition of acid during the boiling process. Typical aromatic products of this nature are blackcurrant and wild fruit gummies. Licorice, with its black color and strong inherent aroma, provides the best protection against possible quality changes.

3.2.1.1.7 Selection of the Most Suitable Type of Gelatine

The temperature to which the slurry is subjected and the duration of the process are two of the parameters that are critical and most relevant to the quality of the overall process. If the thermal stress applied to the gelatine is too high, it is hydrolyzed, resulting in a product that is very soft and sticky. In the extreme case, the product may be prevented from setting completely or the thermal stability will be affected; both factors can lead to major problems, especially during the summer months. The foaming capacity and viscosity of the gelatine used are also of considerable importance. Both of these parameters should be relatively low to ensure optimal processing. On the other hand, it is most important to keep in mind that very low viscosity can prolong setting times considerably.

If these technological requirements are compared with the properties of available gelatines, it becomes clear that type A gelatine offers a number of advantages in this application area: at pH 3.5 (the typical pH for fruit gummies), type A gelatine exhibits the least amount of thermally-induced Bloom degradation. In comparison with traditional, almost neutral, type B gelatine, its specific viscosity is lower. However, there are also type B gelatines available that exhibit a low viscosity.

Table 3.20 Common defects found in gummy confectionery products, with suggested causes and remedies.

Problem	Cause	Remedy
Gum does not set	Damage to gelatine	Reduce exposure to heat and acid
	Gelatine not dissolved	Ensure that correct dissolution procedures are followed: 2 parts water per part gelatine, agitation and heat to at least 60 °C
	Possible ingredient interactions	Discuss your formulation with your gelatine supplier
Gum is turbid	Possible ingredient interactions	Discuss your formulation with your gelatine supplier
	Gelatine not completely dissolved	Ensure dissolution guidelines are adhered to
	Air bubbles entrapped	Review gelatine solution preparation technique and deaeration steps in process
Graining/sugar recrystallization	Too much sucrose	Increase use of glucose or DE of glucose
	Too little gelatine	Increasing gelatine level will help inhibit crystallization
	Too much moisture	Increase cook temperature to give higher soluble solids; review formulation
Gum is brown/yellow	Over exposure to heat	Reduce exposure to heat – shorten cook time or add gelatine after cooking
	Maillard browning	Remove reducing sugars from formulation if possible.
Gum is too soft	Gelatine level low	Increase level
	Incorrect Bloom	Increase Bloom
	Damage to gelatine	Reduce exposure to heat and acid
	Inappropriate use of sweeteners	Review glucose, sucrose, moisture level and other sweeteners
Gum is too hard	Gelatine level high	Decrease level
	Incorrect Bloom	Decrease Bloom
	Inappropriate use of sugars	Review glucose, sucrose and other sweeteners
Poor surface appearance	Incorrect starch condition	Review ideal conditions for depositing (temperature, starch moisture, and temperature) and drying conditions. Contact your starch supplier

Table 3.20 (continued)

Problem	Cause	Remedy
“Cupping” or indented backs	Solids at deposit too low	Cook to a higher temperature to increase solids
Off flavors/odors	Poor quality ingredients	Review raw material qualities
	Contaminated molding starch	Ensure starch is correctly handled and dried to 5–8% moisture
Stickiness	Moisture too high	Cook to a higher temperature to reduce moisture or review formulation
	Water content below equilibrium humidity	Adjust sweetener use to appropriate equilibrium humidity for environment
	Acid added too early	Add acid just prior to depositing to avoid damaging the gelatine and inverting sucrose; review formulation
Drying out	High water activity	Adjust sweetener use to appropriate water activity for environment
Variable product quality	Poor process control	Review control of conditions in batch make-up, cooking and drying

In most cases, the use of a high-Bloom type A gelatine is recommended. This specific type of gelatine provides desired texture, has excellent clarity, and is neutral in color and flavor. Additional advantages of high-Bloom type A gelatine are its high melting point and rapid setting properties.

The texture of fruit gummies can be varied by selecting different gelatine Bloom values and concentrations. The more gelatine that is contained in the product, the firmer the final texture will be. The manufacturer can obtain an equivalent firmness at lower concentration by using a gelatine with a higher Bloom value (see Section 2.1).

The type of gelatine is also important: in fruit gummies, type A gelatine demonstrates a more effective gel formation than a type B gelatine; a firmer gel is the result. In changing from type B to type A gelatine, selecting a lower Bloom type is usually appropriate. Correspondingly, when changing from type A to type B, a higher Bloom value of type B is necessary or a higher concentration, if a comparable texture is desired.

As the firmness of the final product is not the only quality criterion of importance, changing the type of gelatine and the firmness (Bloom value) also alter parameters such as thermal stability, setting time, setting behavior, etc. The manufacturer must always take these parameters into consideration when a formula-

Table 3.21 Specific density of confectionery.

Product	Density in g cm ⁻³
Chocolate marshmallows	0.17–0.25
Extruded marshmallows	0.25–0.35
Molded marshmallows	0.40–0.50
Meringues	0.35–0.40
Nougat	0.80–1.10
Chewable candies	0.90–1.20

tion that has always functioned on his equipment is to be modified by changing the type of gelatine.

3.2.1.2 Mallows

The foaming and foam stabilization properties of gelatine are utilized by the confectionery industry in the production of extruded, molded, and recrystallized marshmallows (the latter known as meringues), wafer and candy bar fillings, chews, and nougats. These products have a wide range of textures, ingredients, dry substances, and degree of aeration (see Table 3.21).

3.2.1.2.1 The Function of Gelatine in Marshmallows

If a concentrated solution of sugar is whipped, a foam is formed. Because of the poor stability of the foam, no substantial volume can be obtained and only a very high specific density. Once whipping ceases the foam collapses.

If gelatine is added to the sugar mass, a very large volume of foam is formed. Gelatine not only decreases the surface tension which facilitates foam formation, it also stabilizes the air/liquid phase interface by forming a film. At the same time, by setting, it prevents phase separation through drainage (see Section 2.1). In these ways, gelatine fulfills all the requirements of a typical foaming agent. The whipping behavior of an optimally selected gelatine is comparable with that of egg white or albumin powder (see also Info Box 3.4).

In the case of marshmallows or aerated chews, gelatine prevents the recrystallization of sucrose. If sucrose crystals are desired, the sucrose/glucose syrup ratio must be changed to favor sucrose. The addition of crystallization seeds such as icing sugar is also a proven method for initiating recrystallization. In chewable candies and candy bar fillings, another property of gelatine is utilized – that of an oil-in-water emulsifier – to facilitate the permanent incorporation of milk fat into the final product.

3.2.1.2.2 General Considerations for the Selection of Various Types of Gelatine

There is a basic rule that governs the selection of the most suitable type of gelatine for the production of mallows: Type A gelatines have a better foaming capac-

Box 3.4**Technological properties of selected whipping agents****Albumin**

Albumin powder must be pre-hydrated for at least 30 min. For complete dissolution, a ratio of one part albumin to 4 parts water is recommended. Crystalline products require 120–180 min for pre-hydration and an excess of water of approximately 1:7.

Albumin is also sensitive to heat. With 80% sugar it coagulates at 105–107 °C; with 40% sugar it coagulates at 65 °C.

Albumin cannot be used in formulations containing fat, and overwhipping causes foams to collapse.

Hydrolyzed milk protein

This requires sugar to form a stable foam. Less sensitive with respect to fat and heat than albumin. No prehydration necessary; the protein-water dissolution ratio is 1:15.

Hydrolyzed soy protein

Behaves technologically much like hydrolyzed milk protein. Dissolution ratio 1:15.

ity than type B, i.e. they generate a higher foam volume and guarantee better foam stability.

In the production ofmallows, the color of the gelatine solution is less important than it is in fruit gummies. Even relatively dark gelatines at low concentrations produce a white foam. The clarity of the gel in such applications is also of no consequence. Many processors prefer a high-Bloom gelatine for producing foams. As the setting times are shorter, the foamed products rapidly attain the required firmness.

Depending on the final product and the sales distribution channels involved, the most suitable gelatine must be selected from the point of view of foaming behavior, texture, and storage stability, and must be implemented in cooperation with the gelatine manufacturer. High-Bloom gelatines are often blended with gelatine hydrolysates in order to achieve the optimal solution for an individual application.

3.2.1.2.3 Marshmallows and Meringues

In the production of marshmallows and meringues, the four main ingredients – glucose syrup, sucrose, gelatine solution, and water – are weighed, mixed, and boiled to a slurry according to the corresponding formulation (see Section 3.2.1.1.1).

The addition of colorant and flavor takes place just prior to whipping. In the case of recrystallized meringues, approximately 5% icing sugar is added to

Table 3.22 BASIC RECIPE – Molded Marshmallows.**Ingredients:**

A: Sucrose	37.4%
Glucose syrup 60 DE	16.0%
Water	13.4%
B: Invert sugar	16.0%
C: Gelatine, 220 Bloom	3.2%
Gelatine Hydrolysate	0.6%
Water	13.4%
D: Flavors and colorants	as required
E: Icing sugar/starch 1:1	

Process:

A is boiled to 88% DS and cooled to 90 °C.

C is dissolved at 60 °C.

B, C and D are added sequentially to A and whipped by a foaming machine.

The mass is deposited in molding starch.

After 24 h at room temperature, the marshmallows are removed from the starch and rolled in the icing sugar/starch mixture E.

Conditions:

Water content at deposition	20–25%
Temperature at deposition	75 °C
Relative humidity of air	30–40%
Moisture content of the starch powder	<6.0%
Specific weight of the foam	0.45 g mL ⁻¹

the cooled mass; the sugar crystals act as crystallization seeds. Should non-crystallized marshmallows be produced, 7–10% invert sugar or 7% sorbitol should be added to prevent recrystallization.

Subsequently, the slurry is whipped in a pressure foamer using filtered compressed air. Alternatively, this can be carried out mechanically without pressure. During the whipping process, the temperature of the slurry must remain above that of the setting point of the gelatine being used; if this is not the case the films forming around the air bubbles are destroyed irreversibly.

Technological requirements must also be taken into account (see also Info Box 3.4). For example, if extruded marshmallows are to be produced using a continuous process, rapid setting must take place after whipping, and the foam must be stabilized. In this case, very high-Bloom gelatine should be used (240–280 Bloom) at a concentration of 3–5% of the final product. To prevent the extruded marsh-

Table 3.23 Common defects found in marshmallows, with suggested causes and remedies^a.

Problem	Cause	Remedy
Product does not set/collapses	Damage to gelatine Possible ingredient interactions	Reduce exposure to heat and acid Discuss your formulation with your gelatine supplier
Poor foam stability	Drying cast product at too high a temperature Starch for cast product too hot Ensure that the best gelatine grade for whipping is used Underbeating Overbeating	Reduce drying temperature Reduce temperature of starch at casting Discuss grade with gelatine supplier to ensure appropriate selection Increase speed and/or time of beating Reduce batch size Reduce time and/or speed of beating. This is not a problem generally associated with gelatine products
	Viscosity too high	Reduce solids content Change sweeteners to reduce viscosity Increase temperature
Yellowish color	Over exposure to heat pH too high	Reduce exposure to heat – shorten cook time or add gelatine after cooking High pH (>6) promotes Maillard Reaction. Adjust formulation to lower pH
Marshmallow is too soft	Gelatine level low Incorrect Bloom Damage to gelatine Inappropriate use of sweeteners	Increase level Increase Bloom Reduce exposure to heat and acid Review glucose, sucrose and other sweeteners
Marshmallow is too tough or rubbery	Gelatine level high Incorrect Bloom Inappropriate use of sugars Solids too high	Decrease level Decrease Bloom Review glucose, sucrose and other sweeteners Reduce cook temperature Check moisture losses during beating on open beater

Table 3.23 (continued)

Problem	Cause	Remedy
Stickiness	Moisture too high	Cook to a higher temperature to reduce moisture
	Packed too soon after forming	Allow product to stabilize and form a protective crust before packing
	Low water activity	Adjust sweeteners to produce appropriate water activity for environment
	Acid added too early	Add acid just prior to depositing to avoid damaging the gelatine and inverting sucrose
Drying out	High water activity	Adjust sweeteners to produce an appropriate water activity for environment
Shrinkage	Product extruded too hot	Reduce extrusion temperature
	Back pressure at beating too high	Recommended maximum back pressure 80 psi
Gritty texture	Sugar recrystallization	Ensure that process dissolves all crystals
		Increase use of glucose syrups to suppress sucrose recrystallization
		Dry starch to moisture 5–8%
Crusty outer surface	Starch for cast product too moist	
	Poor hygiene	Review plant hygiene, including ingredient storage
	Sub-standard quality ingredients	Review raw material quality
Off odors and flavors	Contamination of starch for cast product	Ensure that starch is free of microbes by handling appropriately and drying to moisture 5–8%
	Poor hygiene	Review plant hygiene, including ingredient storage
	Moisture too high	Review water content in formulation
Fermentation	Sub-standard quality ingredients	Review raw material quality, particularly with respect to microbiological parameters

^aAspects of this guide were drawn from the reference Lees & Jackson, Sugar Confectionery and Chocolate Manufacture, St Edmundsbury Press, 1999.

mallows from sticking to each other they are placed on a continuous belt covered with a thin layer of starch and sprinkled with a mixture of either starch and icing sugar or starch and dextrose.

In the case of molded marshmallows (see Table 3.22), the mass must be able to flow after whipping if it is to be processed in a Mogul machine. Rapid setting is not necessary in this case, as the product dries in the starch bed. Medium-to-high-Bloom gelatines at concentrations ranging between 4 and 6% are suitable for this process.

3.2.1.2.4 Soft Caramel Chews/Nougat/Caramel Candy Bar Fillings

Soft caramel chews, nougat, and caramel fillings for candy bars would appear at first glance to be quite different types of confectioneries. However, almost all of these have one thing in common: they contain fat emulsified in a supersaturated sugar solution. Air bubbles as well as solid components such as nuts or sugar crystals may also be processed into the emulsion. In this type of product, the confectionery industry uses gelatine principally to improve chewability, to control the recrystallization of sucrose, and to increase the emulsion and foaming capacities.

For aerated chewy candies (see Table 3.24), gelatine and the other ingredients such as colorants, flavors, and fruit acids are added to the boiled mass, which has previously been cooled to approximately 90 °C. As there is no subsequent evaporation step, the water content of the gelatine solution must be calculated when preparing the dry substance. It is necessary to operate with a highly concentrated gelatine solution containing very little water.

In the manufacture of recrystallized textures, crystallization seeds such as icing sugar are added during this production step. In order to prevent the sugar crystals from melting and promoting uncontrolled recrystallization, the temperature of the mass must be kept at approximately 90 °C.

Subsequently, the mass is cooled to its optimal temperature for molding and stretched manually or by machine until the necessary amount of air has been incorporated. Alternatively, whipping can take place using special boilers or continuous mixers. The aerated mass is then formed into a strand on a conical-shaped drum and cut into separate pieces. Extrusion systems or other types of roller drums can also be used (see Fig. 3.39).

In foamed products with no crystalline phase, gelatine acts primarily as a texturizer and foam stabilizer; it enhances emulsification, and, together with the glucose syrup, prevents recrystallization of the supersaturated sucrose solution.

In contrast, in foamed products containing sugar crystals, gelatine exercises an influence over both texture and recrystallization. In contrast to chewy candies and fruit gummies and because of the presence of sucrose crystals – that render the texture short – the texture is not primarily influenced by gelatine; the other ingredients such as sucrose, glucose syrup, and fat are the significant contributors in this application.

Most manufacturers use low-Bloom (70–140) gelatine. The concentrations used range between 0.5 and 2.5%. This prevents the aerated mass from becoming too viscous, thereby placing unnecessary mechanical stress on the strand-forming

Table 3.24 BASIC RECIPE – Chewy candy.**Ingredients:**

A: Sucrose	36.20%
Water	9.40%
B: Corn syrup 42DE	46.90%
Hardened vegetable fat	5.30%
Lecithin	0.40%
C: Gelatine, 125 Bloom, Type A	0.30%
Water	0.60%
D: Citric acid monohydrate	0.67%
Flavor and colorant	as required

Process:

A is boiled to 100 °C.

A is mixed with B and boiled to 122 °C.

The sugar mass is cooled to approximately 90 °C and then C (dissolved separately) and D are added while stirring.

The mass is then placed in the pulling machine and pulled for 10–15 min until the aeration and opacity are adequate.

The mass is passed through the cutting and wrapping machine.

Conditions:

The moisture content in the final product should be between 6 and 10%.

**Fig. 3.39** Cone roller for the forming of fruit chews.

Table 3.25 Common defects found in chewy candy, with suggested causes and remedies.

Problem	Cause	Remedy
Unwanted recrystallization	Uncontrolled seeding of mass	Inclusions such as nuts that are cold can seed crystallization. These should be warmed before addition to the mass
	Sugar syrup supersaturated	Use higher levels of glucose syrup. Gelatine will also help to inhibit crystallization
	Undissolved sugar crystals in mass	Ensure that cooking process dissolves all sugar
Sticky product	Solids content is too low	Cook to a higher solids
	Sucrose inversion from over cooking or introduction to acid at too high a temperature	Shorten cooking time Add acid at the lowest possible temperature and certainly not during cooking
Retraction/shrinking	Mass is too elastic	Allow the rope to relax before feeding to cut and wrap machine
		Lower levels of gelatine if they are high
		Add viscosity-enhancing ingredients (gelatine, gum Arabic, maltodextrin, starch)
		Decrease content of high molecular weight sugars (increase glucose content or glucose DE)
Cold flow	Mass viscosity is too low	Temper to a lower temperature
	Solids content is too low	Cook to a higher solids
		Reformulate to have lower levels of reducing sugars or polyols
		Add viscosity-enhancing ingredients (gelatine, gum Arabic, maltodextrin, starch)

machine. High concentrations of high-Bloom gelatines may cause undesired shrinking of the final product.

3.2.1.3 Bar Products

In muesli and cereal bars, gelatine binds the dry ingredients. As gel formation is of secondary importance in this application, the use of a gelatine hydrolysate is an attractive option (see Info Box 3.5 and Table 3.26).

The use of gelatine hydrolysate in these applications is based on its strong adhesive properties. A concentration of only 7.5% in the final product is adequate in

Info Box 3.5**Use of gelatine hydrolysates in bar products:**

Confectionery:	Chocolate bars Cereal bars
Dietetic products:	Protein bars Power bars Bars for special diets
Bars with:	Joint protection protein Low-carb diet bars
Snacks:	Spicy cereal bars Sweet cereal bars

Functionality of gelatine hydrolysates in bar products:

- Foam formation
- Cohesion/adhesion
- Texture improvement
- Processability
- Solubility

Health aspects of gelatine hydrolysates in bar products

- Joint health*
- Muscle build-up
- Fitness
- Weight reduction
- Carbohydrate reduction
- Fat reduction
- Protein enrichment

order to achieve the desired degree of adhesiveness. Much higher concentrations of sucrose are necessary to obtain the same effect, and, if sugar substitutes are used, these often constitute over 50% of the bar filling. This particular type of binding agent, however, causes so much water to be taken up that the A_w value is often over 0.6; the result is that the final product cannot be packaged without first undergoing an additional heating step.

In contrast, if 5% gelatine hydrolysate is used, only 10% sugar substitute is necessary to achieve the desired binding capacity. Because of its excellent solubility in water and low viscosity compared with other proteins, gelatine hydrolysate can be added as a 50% solution. This results in much less water being included in the product. The cereal and muesli bars that are produced not only have less carbohydrate, but the water content is also reduced to within the range 8–12%; this corresponds to an A_w value of 0.40–0.55. The bars can then be packaged immediately without additional heat treatment. Another advantage for the manufacturer is the fact that no sophisticated technology is required to dissolve the gelatine hy-

Table 3.26 Functions of gelatine hydrolysates in bar products.

Function	Type of bar	Foam formation	Cohesion/adhesion	Texture improvement	Taste improvement
Confectionery:					
	Chocolate bars	++	-	+	++
	Cereal bars	-	++	+	+
Dietetic products:					
	Protein bars	++	+	++	++
	Power bars	++	+	++	++
	Special nutrition bars:	+	+	++	++
	Joint protection bars	+	+	+	
	Low-carb diet bars	+	+	+	
	Beauty bars	+	+	+	
Snacks					
	Spicy bars	-	++	+	+
	Candy bars	-	++	+	+

++ Recommended + Suitable – Not recommended.

drolysate; a double-walled vessel with a stirrer is all that is necessary. The water that is used should have a low microbial count; this avoids the necessity of exposing the product to further heat treatment to remove any microorganisms that may be present.

Practice has shown that a combination of gelatine hydrolysate and sugar or sugar substitute provides a product with a pleasant and soft but chewable texture. Furthermore, recrystallization of the sucrose is prevented, and, since less binding agent is required, the concentration of other ingredients such as dried fruits can be increased. This enables the product to be differentiated from others on the market. Gelatine hydrolysate also gives a crunchy texture, which also differentiates it from the other sugar-based agglutinating agents.

New market segments have paved the way for salty and/or spicy bars with a firm, crispy texture. These can be produced using only gelatine hydrolysate as a binding agent, and the manufacture is technologically simple: the gelatine hydrolysate is dissolved along with the other ingredients such as fat and spices at 70 °C and then processed with the dry substances into a homogeneous mass, pressed into long forms, cooled to room temperature, and cut into bars. The bars have a low water content and can be packaged immediately.

In the case of protein bars (see Table 3.27), not only the technological properties of gelatine hydrolysate are important but also its nutritional and sensory qualities. Gelatine hydrolysate blended with other proteins give a malleable and soft mass.

Gelatine hydrolysates are highly purified sources of protein and, in contrast to other comparable plant-based products such as soy, have the least amount of bit-

Table 3.27 BASIC RECIPE – Protein-fortified cereal hazelnut bar.**Ingredients:**

A: Roasted hazelnut pieces	24.9%
Wheat germ crispies	17.6%
Gelatine hydrolysate	12.2%
Apricot pieces, dried	5.9%
Corn flakes	4.5%
Oat flakes	2.9%
 B: Sorbitol powder	 9.2%
Gelatine hydrolysate	8.3%
Fructose	7.0%
Water	4.8%
Vegetable fat	2.6%
Salt	0.1%

Process:

Dry ingredients A are mixed.

Ingredients B are dissolved at 70 °C.

B is added to A and mixed in a suitable machine at low speed until a homogeneous mass is achieved.

The mass is pressed into a bar mold and cooled to room temperature.

The mass is cut into bars and packed.

ter taste. They contain no purines and exhibit a minimal allergenic potential. Furthermore, gelatine hydrolysates are well suited for the optimization of the amino acid content of a bar when special nutritional aspects have to be taken into account. One example is a nutritional bar for athletes which includes the highly important amino acids lysine and arginine that are present in high concentrations in gelatine and are readily available for use by the body (see Section 3.2.5). Another possible and attractive opportunity is the positioning of a protein bar for use in bone and joint health-related applications (see Chapter 4).

Bars containing whipped fillings can also be produced using blends of gelatine: in this type of “marshmallow” cereal bar, the gelatine products act as binding agents and foam stabilizers. The optimal gelatines are dissolved together and then whipped. Boiled sugar solution and melted fat are then added in a stepwise manner to the gelatine foam. The dry ingredients are then mixed in and the homogeneous mass processed into finished products as in the case of classical cereal bars.

3.2.1.4 Gelatine Desserts

At the beginning of the 20th century, when immigrants arrived at Ellis Island in New York they were given a gelatine dessert as a “Welcome to America” gift. Gelatine jellies are still the national dessert of the United States. The “Jell-O” prod-

Info Box 3.6**How does the flower get into the jelly?**

In Mexico, three-dimensional leaves, flowers, or even miniature sculptures formed within table jelly are extremely popular as desserts. However, they can also serve as small, personal presents or as table decoration at feasts and celebrations. In Mexico, such items are commercially marketed by small family businesses, but are also prepared in private households. Training courses on offer throughout the country enable people to learn the necessary techniques (see Fig. 3.40).

The basic method involves first preparing a slightly sweet and naturally flavored gelatine solution in a specially shaped form and allowing it to cool. Once the jelly is firm enough, it is turned out of the form and the “artist” can get to work: using a needle or a small knife, he or she can insert the tool and, using fine movements, create the desired three-dimensional form within the jelly. In a subsequent stage, using a syringe filled with food colorant, designs can be created or specific objects depicted. Flavor, color, and form can be combined almost at will and there are practically no limits to creativity. This particular Mexican application could well be of interest for other markets.

ucts produced by the market leader alone are regularly used in about two-thirds of all households. But even outside the United States, gelatine desserts represent one of the largest application areas for edible gelatine. In Mexico (see also Info Box 3.6), the per capita consumption is even higher than that in the United



Fig. 3.40 In Mexico, three-dimensional leaves, flowers or even miniature sculptures formed within table jelly are extremely popular as desserts. Gelatine makes many such fantasies possible.

Table 3.28 BASIC RECIPE – Maria Mole.**Ingredients:**

Gelatine 180 Bloom	21.7%
Hydrolyzed casein	2.0%
Flavor and color	as required
Sugar	to complete 100%

Process:

The dry mix is dissolved in water and heated until boiling.

The mix is transferred to a beater bowl and beaten together with sugar for 10 to 15 min until a meringue consistency is achieved.

The mass is filled in a tray greased with margarine or butter and cooled until it is firm.

The firm mass is cut into pieces and covered with grated coconut.

States, and the same applies to Poland. In these countries, gelatine jellies in a wide variety of forms, colors, and flavors are served for breakfast, eaten as snacks or as a dessert, or used for making fruit cake. They are also used, artistically garnished, at birthday parties and weddings. In Great Britain, “Ice cream and Jelly” is one of the most popular desserts served, in Brazil, the same applies to “Maria Mole”, a cooled gelatine marshmallow sprinkled with coconut (see Table 3.28), in Australia, gelatine jellies are used as components of birthday cakes, and in Germany, table jelly is a standard dessert. One alternative to powder gelatine mixes that is especially popular in Great Britain is the concentrated gelatine cube, called a “jelly tablet”. These cubes of gel with their color and flavor can be individually dissolved in warm water and set again as a dessert. Furthermore, “ready-to-eat” jellies are available on a worldwide basis in individual portion packages. As a result of this success story, gelatine desserts represent the second largest single food application today. You will usually find that a fruit-flavored gelatine jelly shakes on the spoon and melts in the mouth.

This classical gelatine dessert is composed of powder gelatine and other dry ingredients including sugar, fruit flavors, colorants, and acidifiers (see Table 3.29).

To prepare the dessert, the powder is dissolved in about six times its amount of hot water, fruit juice, or milk. It is cooled in the refrigerator until firm enough to serve. If instant gelatine is used, cold water-soluble products can be produced.

Popular colors are intense reds, greens, and yellows coupled with flavors such as raspberry, lemon, cherry, strawberry, or orange. Products resembling puddings and flans with chocolate and caramel flavors are also available. These desserts can also be prepared with milk and are very popular in Mexico.

A very exceptional type of jelly is found in Japan. Here, gelatine is added to tea or coffee. Because of the components of these beverages, alkaline-conditioned

Table 3.29 Gelatine desserts (powder blend).

Ingredient	Proportion as % of dry mass
Gelatine of:	
- 280 Bloom	approx. 9.3
- 260 Bloom	approx. 9.8
- 240 Bloom	approx. 10.2
- 220 Bloom	approx. 10.8
- 200 Bloom	approx. 11.3
- 180 Bloom	approx. 11.9
Fruit acid	approx. 1.5
Sodium citrate buffer salt	approx. 1.4
Sodium chloride neutral salt	approx. 0.5
Flavor and colorant	As required for desired intensity of flavor and color
Sugar	Make up to 100%

hide or bone gelatine is the best choice because acid-conditioned pigskin gelatine tends to generate turbid gels. Such jellies are also often prepared in the home using leaf gelatine.

For standard desserts, gelatines of 230–250 Bloom are used. The gelatine content of the powder is normally between 10 and 12%, depending on the Bloom value, so that the concentration in the finished product is about 1.5–2.0%. With respect to texture, color, transparency, melting and sensory properties, there are no significant differences between comparable gelatines of type A and B. The gelatine used for these mostly transparent desserts should have a high degree of clarity. Syneresis, or loss of water after gelling, can differ in gelatine desserts depending on whether a Type A or Type B gelatine is used. Gelatine desserts made using Type A gelatines tend to lose less water after gelling compared to those made using Type B gelatines. This behavior may be a result of the differences in isoelectric points (IEP) for Type A and Type B gelatines.

In the case of ready-to-eat products, the temperature conditions existing between production and consumption can be very different; they vary enormously from a controlled cooling chain to unrefrigerated street sales in hot countries. Depending on the sales distribution channels, the powder formulations used may have to be modified. To ensure a gel capable of withstanding heat when the cooling chain is less than optimal, an extremely high-Bloom gelatine is used. The concentration is also increased so that the melting point is raised. Using gelatine with a Bloom of 250–270, the gelatine concentration in the finished product should exceed 2.5%. This ensures adequate stability of the gel structure at 25–30 °C.

Great attention must also be paid to pH when formulating. Although it increases the degree of fruitiness of a dessert, low pH also produces softer gels, especially if the gelatine solution has been maintained at an elevated temperature

for a long period of time. Higher pH values mitigate this undesirable effect even though the dessert may taste less fruity and have a shorter shelf life. A good compromise in this case is to use a pH of 3.7–3.9. This range can be achieved by buffering with sodium citrate, although higher degrees of acidity can be used without the pH being reduced too drastically. Other neutral salts are also added to increase the ionic strength of the solution and strengthen the gelatine network structure.

Gelatine desserts are also suitable for the preparation of cold “baked” cakes. These are composed of, for example, frozen fresh fruits with table jelly or a table jelly-cream-cottage cheese mixture on a sponge cake base. The top of the cake firms up in the refrigerator because of the gelatine and can then be cut into portions. When using fresh fruit or juices, it should be kept in mind that pineapple, papaya, kiwis, and figs all contain enzymes capable of cleaving proteins so that the gel firmness may be reduced. Therefore, these particular fruits should be blanched first for such an application, a process that denatures the enzymes.

3.2.1.5 Other Confectionery Applications

Sugar-coated candies consist of a core that is coated with over 100 very thin films of chocolate or sugar in a rotating coating pan. One of the most popular products of this kind is sugar-coated chocolate buttons which are similar to “Smarties®”. To obtain the proper result, the cores have to be specially pretreated. This “pre-coating” process improves the adhesion between the core and the external layer, prevents the migration of fat or liquid and renders the core mechanically more stable. A 70–80% sugar solution containing gelatine is usually used; solutions containing gum arabic and sugar can also be used. In the case of diet panned products, sugar can be replaced at the same concentration, for instance, by xylitol.

Mostly, highly viscous gelatines with strong film formation properties are employed. The major advantage of a gelatine film is that it possesses the elasticity that no other hydrocolloid exhibits. It is also possible to seal centers when using concentrated gelatine hydrolysate solutions at around 50% with the advantage of not requiring heat for solution maintenance. Gelatine gives a very white and homogeneous aspect to the centers in comparison with gum arabic. The quality of the gelatine is important mainly to enhance the color of white panned products and also for achieving a color closer to that expected in hard panned products. Gelatine makes it easier to perform the whitening step with titanium dioxide.

Gelatine also has advantages when panning big centers such as those in chocolate eggs. In this case, the gelatine, besides being used for sealing, can also be added in a concentration of 2% to the panning syrup. This step should be carried out carefully in order to prevent crystallization. It has also been observed that this particular gelatine application, in addition to producing a whiter and more regular surface, seems to lessen the impact of the movement of the panning equipment, thus avoiding deformation of the center, cracks, or spots on the covering.

Compressed tablet-like candies made of powder contain, for example, icing sugar or dextrose compressed along with flavors, a binding agent, and other in-

redients into a large tablet form. Effervescent tablets also contain baking soda and acids for the generation of carbon dioxide. Lozenges are prepared from rolled out dough made of sugar and a hydrocolloid in a way that is similar to making Christmas cookies, and subsequently cut and dried.

If hydrocolloids are used only as binding agents as described above, their gelling capacity is not a selection criterion. Gelatine hydrolysate is a technologically and economically attractive alternative to the cold-water-soluble gum arabic; furthermore, it enables a more rapid drying of the tablets when it is used alone. Gelatine and gelatine hydrolysate act in the same way as starch by prolonging the dissolution time in the mouth. Alginates on the other hand allow for rapid disintegration. If the dry substances can be compressed directly, a binding agent is unnecessary.

The intense color of licorice originates from its own natural concentrated juice; it otherwise consists of flour, starch, sugar, and aromas. Gelatine is used as a binding agent and texture enhancer in licorice products.

Another specialty application area for gelatine hydrolysate is as a carbohydrate-free carrier and filler for the production of spray- and fluidized bed-dried instant beverages and aromas. Here, gelatine hydrolysate is an important alternative to gum arabic and modified cellulose derivatives; for example, it can be used for the production of carbohydrate-free instant beverages for diabetics.

3.2.1.6 Interaction with Other Ingredients

In confectionery products, gelatine is only one of many ingredients. Any substance that is added to a pure gelatine/water solution can alter the behavior of the entire system. This should always be taken into account when developing new products or altering formulations, as both positive and negative effects have been scientifically demonstrated with hydrocolloids such as carrageenan, pectin, and gum arabic as well as with native and modified starches, maltodextrin, and various sugars.

3.2.1.6.1 Sugar

Sucrose and many monosaccharides have a stabilizing effect on a gelatine gel, most likely because they facilitate hydrogen bonding. This is reflected in an increase in setting speed and melting point. This type of synergistic effect is most significant in the case of the sugar alcohols such as glucitol (sorbitol) and sucrose. The monosaccharides glucose and fructose have less effect (Gekko et al. Biosci., Biotech., Biochem., 56 (8), 1992).

This enhancing effect can also be observed at low concentrations of glucose syrup. At higher concentrations, certain incompatibilities occur, especially when glucose syrups with higher amounts of oligosaccharides are used. It is assumed that these polysaccharides displace gelatine molecules from the aqueous solution. The result is a gelatine suspension that causes the gel to become turbid. Furthermore, the gel becomes weaker, as not all of the gelatine can participate in the gelling

process. There are also other factors that may contribute to this turbidity, e.g., the molecular weight, the ash content, and the electrical charge of the gelatine.

In addition, sugars can cause the gelatine solution to take on a brown color. This is the result of a thermally induced Maillard reaction between the reducing sugars such as fructose and the protein. Honey, for example, is also a source of reducing sugar. Glucose syrups themselves do not contain reducing sugars, but some types do contain high concentrations of fructose. Maillard reactions also occur when sucrose is split into glucose and fructose by the action of acid and heat.

With respect to gelatines, type B varieties take on a more intense brown color than those of type A. The reason for this is the higher amount of unprotonated amino groups in type B gelatines that can readily participate in the Maillard reaction.

3.2.1.6.2 Sugar Substitutes

Increasing numbers of consumers today select their foodstuffs according to the amount of sugar they contain; they do this to control their sugar intake in order to maintain control of their figures and to prevent dental caries. The confectionery industry has risen to this challenge by producing products with reduced amounts of sugar. The necessary formulation modifications to achieve this should not negatively influence the enjoyment of the product to any significant extent, nor should it necessitate any major changes in the production methods.

Studies carried out on standard gels have shown that sugar substitutes have no significant influence on the color or clarity of the product. In comparison to gels containing sugar, those containing sugar substitutes also exhibit no decrease in gel firmness.

Furthermore, no significant changes in either melting or setting points have been observed to date, and no detectable deviations from standards such as glucose syrup and/or sucrose are observed in foaming behavior. In contrast, the type of gelatine and the pH exert a much more significant influence. Many sugar substitutes are unsuitable for the complete replacement of glucose syrup or sucrose in most formulations. This is because they would crystallize out when used at the necessary concentrations because of the low water content of these products. Thus, in practice, at least individually, they are not suitable as substitutes for traditional sugar.

Rheological experiments and sensory evaluations have shown that even those sugar substitutes that do not tend to crystallize at the typically high dry substance contents of fruit gummies only lead to satisfactory results in individual cases. Combinations of various sugar substitutes may possibly produce acceptable molding masses. The combination of gelatine, sucrose, and artificial sweeteners has been successfully used to produce light gelatine desserts. This formulation reduces the calories in 63% of products and the sugar content in 72%. It also reduces the packaging size from 85 g to 30 g (see Table 3.30). However, experimental trials specifically designed for the application in mind are always necessary to establish the basis for an optimal combination.

Table 3.30 BASIC RECIPE – Gelatine dessert (reduced sugar).

Ingredient (g)	C/As	AcK/C	AcK/As	STD
Acesulfame-K	0	0.05	0.05	0
Cyclamate	0.09	0.21	0	0
Aspartame	0.2	0	0.15	0
Gelatine, 250 Bloom	7.65	7.65	7.65	7.65
Fruit acid	1.17	1.17	1.17	1.17
Sodium citrate buffer salt	1.08	1.08	1.08	1.08
Sodium chloride neutral salt	0.45	0.45	0.45	0.45
Flavor	0.5	0.5	0.5	0.5
Sucrose	18.86	18.89	18.95	74.15
Water	500	500	500	500
Total	530	530	530	585

C: Cyclamate.

As: Aspartame.

AcK: Acesulfame K.

STD: with sucrose.

3.2.1.6.3 Hydrocolloids

The combination of several hydrocolloids in confectionery applications is of interest under certain conditions. On the one hand, it is possible to produce variants to traditional textures; on the other, the choice of suitable hydrocolloids can help to optimize individual parameters such as the melting point of fruit gummies. Economic factors of course also play an important role when selecting a hydrocolloid (see Table 3.31).

Pectin gels are sticky and in part thermoreversible, and have a brittle structure with a short texture. Gelatine can be added to make the texture longer and the gel more elastic. On the other hand, pectin can raise the melting point of a gelatine gel. These particular combinations are comparable with products manufactured with gelatine to improve clarity and texture.

Agar-agar gels are also very clear. Compared to gelatine, they have a shorter and less elastic texture. Agar-agar sets more slowly than pectin but can be processed in starch-free molds. The characteristic property of agar-agar gels is their high resistance to temperature. The combination of gelatine and agar-agar in fruit gummies can also increase temperature stability without significantly affecting either clarity or texture.

Gum arabic produces opaque products with a somewhat harder but chewy texture. The texture is frequently modified, i.e. rendered softer, by using gelatine. Special types of gelatine may be used to partially or, in some cases, completely replace gum arabic in formulations for pastilles.

Table 3.31 Comparison of current hydrocolloids used in confectionery products.

Hydrocolloid	Concen- tration (%)	Strengths	Weaknesses
Gelatine	5–12	<ul style="list-style-type: none"> – Easy to dissolve and process – Excellent clarity and release of aroma – Unique texture (melts in the mouth) – Multifunctional (whipping agent, emulsifier, binding agent) 	<ul style="list-style-type: none"> – Hydrolyzes at high temperature and low pH – Products can melt at high storage temperatures
Thin-boiled starch	9–12	<ul style="list-style-type: none"> – Inexpensive – Well suited to continuous processing 	<ul style="list-style-type: none"> – Relatively long drying period – Turbid gels – Viscous, adhesive, pasty texture – Requires much water for dissolution
Pectin	1–1.5	<ul style="list-style-type: none"> – Rapid gelling – Excellent clarity – Stable in acid medium 	<ul style="list-style-type: none"> – Requires precise maintenance of pH, dry substance and temperature – Short, brittle texture – Difficult to dissolve (requires large excess of water and high temperature)
Agar-agar	1–1.5	<ul style="list-style-type: none"> – High melting point – Excellent clarity 	<ul style="list-style-type: none"> – Difficult to dissolve (requires large excess of water and high temperature) – Very expensive – Rapid acid hydrolysis at temperatures over 70 °C – Short texture
Gum arabic	35–45	<ul style="list-style-type: none"> – Soluble in cold water – Roughage 	<ul style="list-style-type: none"> – Long drying period – Expensive – Quality fluctuation

Starch gels are always turbid, their texture is pasty, and they tend to be sticky. Therefore, the confectionery industry normally processes starch together with gelatine; this provides firmer, rubber-like textures that are much less sticky. If, for example, a thin-boiling starch is combined with gelatine, a gel of shorter texture and higher resistance to heat can be produced. However, the clarity of the finished product should not play a major role if this effect is to be utilized to its full extent.

Because of the highly complex interactions that are possible (see Section 3.1.1), the experience and knowledge of the gelatine manufacturer should always be utilized when developing new products or making major changes to existing formulations.

3.2.2

Dairy Products and Pastries

Milk is one of the oldest foodstuffs in the world. It is a perishable product from the microbiological point of view and is subject to stringent storage restrictions. At an early stage, therefore, methods were sought to render its valuable components storable. Butter and cheese were the result. It has only been in the relatively recent past that intensive research has enabled pasteurized, pH-neutral milk and cream desserts as well as fermented milk products such as fruit yogurts and fruit curds to be produced. The popularity of these products was also made possible by the use of hydrocolloids, especially gelatine; without these, the quality of these storable products, as required by consumers, could not have been achieved.

3.2.2.1 Stirred and Thermally Treated Fermented Milk Products

Milk is primarily composed of fat, proteins, sugar, and water; therefore, it is a complex oil-in-water emulsion. Milk has its own emulsifier-stabilizer system in the form of the protein casein. Casein, at neutral pH, binds the mineral calcium; this allows milk to be boiled without curdling. If, however, the calcium is dissociated from the protein by the addition of acid, the enzyme rennin, or other fermentation agents, the milk will curdle by forming a casein gel. This property is utilized by the dairy industry to produce cheese, fermented milk, curds, and yogurt.

During this process, casein loses its stabilizing and emulsifying properties. This loss can be compensated for in part by gelatine, as this can take on the emulsifying function in the oil/water system of milk and can prevent the homogenized milk fat from creaming too quickly, e.g., in mixed milk drinks. Gelatine lowers the surface tension of the aqueous phase and surrounds the fat droplets of the milk with an extremely thin film that renders them hydrophilic. As these thin films have the same electrical charge, they repel each other, and the emulsion is stabilized. The thicker the film, the more resistant it is to mechanical



Fig. 3.41 Gelatine gives many dairy products their unique character.

stress and temperature and the more stable it becomes. For this reason, high-Bloom gelatines with a pH that is adjusted to the IEP are particularly suitable for the stabilization of emulsions (see Section 2.1).

Gelatine not only replaces the emulsifier casein, but it also functions as a protective colloid and suspension stabilizer, binds the whey, and provides texture. However, if a casein gel is destroyed by stirring, as happens in the case of fruit yogurts or yogurt drinks, it does not reconstitute itself at normal warehouse temperatures. Instead, a protein suspension is formed. Then, during storage, this suspension agglomerates, and sedimentation takes place such that the product separates into protein, fat and whey. This effect occurs immediately during the pasteurization of a sour casein gel if no protective colloid such as gelatine is used. In this case, the heat causes the casein to contract, whey is produced, the proteins flocculate, and the entire slurry takes on a coarse structure. Therefore, in the case of stirred and heat-treated fermented milk products, the casein fraction must be stabilized. Only by providing such colloidal protection do pasteurized fermented milk products become smoother, develop the desired texture, and not tend to exhibit syneresis.

3.2.2.2 Stabilization Against Syneresis

Syneresis is the exudation of the liquid component of a gel. In the case of milk-based products, it is the process whereby whey is expelled from the casein gel (see Fig. 3.42).

This is caused by the shrinkage tension that occurs as a result of temperature fluctuations during extended storage or subsequent pasteurization. This tension can be influenced only to a certain extent by adjusting the process parameters. However, gelatine can essentially prevent whey from being expelled if such tensions occur. This property of gelatine is utilized in the preparation of yogurt (see Table 3.32 and Fig. 3.43), curds and cream cheeses where it binds and stabilizes the whey.

The added gelatine molecules form a sort of lattice in the casein gel during the gelling process, and this is stabilized by hydrogen bonding. This prevents the protein from clumping and expelling the whey.



Fig. 3.42 Yogurt with (left) and without (right) syneresis.

Table 3.32 BASIC RECIPE – Yogurt (natural or thermally treated).**Ingredients for skimmed milk yogurt with 1.5% or 3.5% fat content:**

Yogurt milk, with adjusted fat content	97.7–85.5%
Gelatine, 200–250 Bloom	0.3–0.5%
Yogurt culture	2.0–4.0%

Process:*Preparation of the yogurt base*

- The gelatine is stirred into cold milk and heated to 60 °C.
- The solution is homogenized in 1 or 2 steps at 150–200 bar.
- The temperature is maintained for 10 min at 90 °C.
- The mixture is cooled to an incubation temperature of 42–40 °C.
- The yogurt culture is added.

Setting the yogurt

- The mass is filled into cups.
- The yogurt is incubated until pH 4.2–4.0 is obtained.
- The yogurt is cooled to 4 °C.

Thermally treated yogurt:

- The yogurt is incubated until pH 4.2–4.0 is obtained.
- The yogurt is heated to 60–62 °C.
- The yogurt is filled into cups.
- The yogurt is cooled to 4 °C.

Variations:*Production of fruit yogurt*

After placing the yogurt in a vessel, it is mixed with fruit preparations and filled into cups under aseptic conditions. Fruit preparations can be mixed with yogurt and then filled into beakers in a hot filling process.

Possible additional ingredients

Skimmed milk powder, caseinate, and starches can be added to the cold milk with stirring before the homogenization process. Stirring is continued until all the ingredients are dissolved. Sugar can also be added at the same time or when a stirred yogurt is required before the heating process starts.

Because of the nature of the gelatine/casein lattice structure and its melting point, a very high-Bloom gelatine is ideal. Both A and B types are equally suitable for this use. The viscosity should be high and the pH should be greater than 4.5, otherwise flocculation may occur during the dissolution process, at least to some extent. The concentration of the gelatine should be approximately 0.2–0.8%, depending on the dry substance concentration and acidity of the product to be produced. For every percentage point of milk powder added, or for every 10%

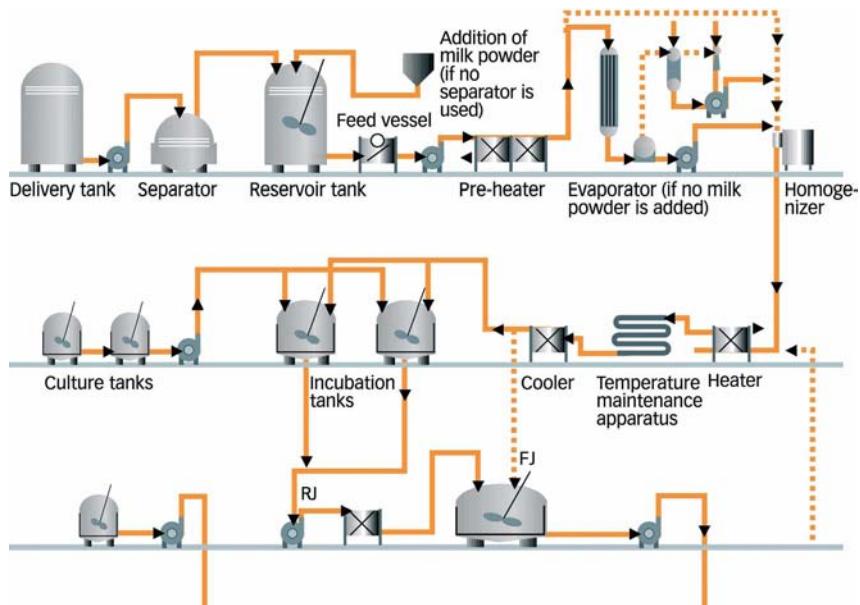


Fig. 3.43 Production flow chart for stirred or spoonable yoghurt.

concentration gained by evaporation, about 0.1% less gelatine may be used. This is because enrichment of the dry protein increases the firmness of the casein gel.

3.2.2.3 Fermented Milk Drinks

Stabilization of the suspension in fermented milk drinks – dilute stirred casein gels – or sweet milk drinks is achieved by the protective colloid effect and the increase in viscosity of the whey protein phase. The protective colloid effect enables the beverage to be pasteurized without the suspended casein agglomerating. The higher viscosity slows down sedimentation of the protein or cocoa particles in a sweet milk-cocoa drink. The gelatine should not increase the viscosity too much if the product in question is a beverage and high viscosities are not required in order to achieve a creamy and full mouth feeling. When gelatine is used as an emulsifier, it also prevents the milk fat from creaming.

Between 0.1 and 0.3% gelatine is usually added to a fermented milk drink. The gelatine is either dissolved in the milk prior to fermentation and coagulation or afterwards together with other ingredients such as fruit or cream. Of course, gelatine can also be added to whey or buttermilk to improve stability and mouth feeling. It can also prevent syneresis in sour cream.

3.2.2.4 Ice Cream and Whipped Desserts

The second most important property of gelatine is its ability to generate and stabilize foams. This property is utilized in the production of foamed milk-based desserts such as yogurt, curds, ice cream, and mousse (see Tables 3.33 and 3.34).

Table 3.33 BASIC RECIPE – Ice cream.**Ingredients:**

Sugar	14.5%
Gelatine, 125 Bloom	0.5%
Butter fat	10.5%
Water	63.4%
Milk solids, non-fat	10.8%
Emulsifier	0.3%
Colorants and flavors	as required
Total solids content	36.6%
Recommended overrun	130%

Process:

- The dry ingredients are added to warm water (30–40 °C).
 The melted (30–40 °C) and mixed butterfat and emulsifier are added.
 The mixture is pasteurized.
 The mixture is homogenized.
 The mass is cooled.
 The mass is aged and fat-crystallized.
 The mass is whipped and frozen.
 The product is packaged.

Table 3.34 BASIC RECIPE – Mousse au chocolat.**Ingredients:**

A: Gelatine type A, 260 Bloom	1.1%
Sucrose	16.0%
Cocoa powder	3.8%
Vegetable fat	10.0%
Citric acid	0.1%
B: Milk (1.5% fat content)	69.0%

Process:

- A is mixed intensively.
 B is heated to 75 °C.
 A is stirred into B and then hydrated for 15 min.
 After this step the mixture is heated to 80 °C and then homogenized for 2 min.
 The mass is cooled to 16–20 °C and whipped for 5 min.
 It is then filled into cups and stored in a refrigerator until set.

These products are three-phase emulsions of air, oil, and water. Gelatine decreases the surface tension of the water, enabling a foam to be generated by mechanical whipping or by the injection of gas. In the foam, the gelatine binds the water during the gelling process and surrounds the fat globules with a thin film, thereby enclosing the fine distribution of air bubbles within a lattice. In ice cream, the gelatine also influences the size and distribution of the ice crystals that are formed. Even if the temperature fluctuates, the water remains bound and the ice crystals are prevented from proliferating in an uncontrolled manner and a pleasant mouth feeling is maintained. The mouth feeling is enhanced by the gelatine melting in the mouth and enhancing the creamy consistency without requiring extremely fatty components to generate the same taste impression. Another advantage is that gelatine is highly compatible with modern production processes. For example, an ice cream mass, because of its low viscosity, can be easily processed using heat exchangers and pasteurization equipment. Gelatine, of course, is only one of several colloids that can be used for the stabilization of ice cream.

In foamy desserts, a high to very high-Bloom gelatine, primarily type A with very good foamability, is used. For aerated desserts with a standard dry substance content, a gelatine concentration of approximately 0.3–1.0% is adequate. In the production of ice cream the rule of thumb is that the more dry substance included the less stabilization is required. For ice cream products with a dry substance content of 30–40% and with 260-Bloom gelatine, the gelatine concentration should be 0.4–0.8%. If other hydrocolloids are used, the gelatine concentration can be reduced to 0.2–0.5%. Today, however, in many cases, gelatines of about 200 Bloom at concentrations of 0.5–1.0% are used in combination with other hydrocolloids.

Additional applications for gelatine in the sector of whipped milk products are yogurt or curds containing fruit and fruit glazes.

3.2.2.5 Stabilization of Cream

If whipped cream is to be used as a topping or cake filling, it must first be stabilized. This is the only way of preventing it from collapsing; if this happens, water will escape and the cake will become soft and wet. Medium-to-high-Bloom gelatine is predominantly used for this application, where concentrations are approximately 0.3–0.5%. The use of instant gelatine enables cold mixtures to be processed.

The fat content of cream has no great influence on the technological behavior of gelatine. Cream toppings with a fat content of less than 20% can just as easily be whipped and stabilized with gelatine as a natural cream containing more than 30% fat. Other low-fat cream products can be prepared by mixing ready-to-use foams – which also contain gelatine and other ingredients – into liquid or whipped creams. Especially in the case of low-fat products, the additional ability of gelatine to provide the consumer with a full mouth feeling is a factor of some importance (see Section 3.2.2.6).

Table 3.35 BASIC RECIPES – Icing with gelatine.*1. Icing for cakes and tarts***Ingredients:**

Icing sugar	80.45%
Gelatine, 220–240 Bloom	1.15%
Water	18.40%
Flavors and colorants	as required

Process:

The gelatine is dissolved in hot water.

When cool, the icing sugar is added gradually and stirred until a homogeneous smooth consistency is obtained.

Flavors and colorants are added as desired.

*2. Honey icing for doughnuts***Ingredients:**

Water	18.0%
Honey powder	4.0%
Gelatine, 240–260 Bloom	1.0%
Vanilla flavor	0.3%
Icing sugar	77.0%

Process:

The honey powder and the gelatine are placed in cold water and allowed to swell for 15 min. The solution is heated to 60 °C and stirred until the gelatine and the honey powder are dissolved.

The icing sugar and vanilla flavor are added and mixed until a smooth consistency is obtained.

The temperature is kept between 60 and 70 °C and the hot doughnuts are dipped into the icing.

*3. Instant icing***Ingredients:**

Icing sugar	79.0%
Gelatine hydrolysate	2.0%
Instant gelatine, Type 800	1.0%
Water	18.0%

Process:

The icing sugar, gelatine hydrolysate, and instant gelatine are mixed.

The water is added and stirred until a homogeneous creamy smooth paste is formed.

Gelatine also provides dairy products with the desired texture. Sweet milk and cream desserts such as "Creme Bavaroise" or "Panna Cotta" may still be spooned at higher concentrations; at lower concentrations, the texture is pleasantly creamy. The textural body of the product also increases with the amount of gelatine it contains. The consistency of sour cream can be improved by adding gelatine dissolved in milk when adjusting for a lower fat content.

In the case of cream-filled cakes, the cream filling is rendered sliceable by the gelatine but still remains feathery and voluminous. The prevention of syneresis is another important goal to be achieved. In preparing the cream, the fruit powder is added to the dissolved gelatine first. Some whipped cream is next stirred in, and then the remainder is mixed in rapidly. The cream is incorporated into the final product before it begins to set. Gelatine plays a similar role in cream cheese-cake, prepared by processing cream cheese at a slightly acidic pH.

Besides this classical application as a filling, gelatine is also used in the actual baking process. Especially in the case of low-fat cookies and cakes, gelatine is used to bind the ingredients, thus facilitating processing of the dough. At the same time, gelatine also minimizes textural changes brought about by the lower fat content. Gelatine also improves the water binding capacity of baked goods; the finished product then tastes fresh longer. It can also be used as an alternative to egg yolk for glazing (see Table 3.35).

3.2.2.6 Sandwich Spreads and Cheeses

In view of the worldwide trend toward more balanced diets, dairies are making every effort to provide low-fat sandwich spreads. To achieve this goal, the fat content of butter is being reduced or fresh cheese is being used as an alternative. Low-fat margarine is another product that is available. As the fat normally contained in these products is replaced by water, they must be effectively stabilized to prevent phase separation during storage. During the setting process, gelatine immobilizes the water or the whey; this prevents syneresis. Gelatine, however, is a fat emulsifier, and this also improves consistency and enhances structure. It also improves the spreadability of sandwich spreads.

For the production of low-fat butter or margarine, the gelatine concentrations are approximately 0.5–1.5% (see Table 3.36). In these cases, high-Bloom type A gelatine is particularly suitable. Gelatine helps to keep low-fat spreads stable (see Fig. 3.44). During the production of low-fat sandwich spreads, the ability of gelatine to provide a foam is also frequently used; because of the increase in volume, the amount of fat consumed per portion is further reduced.

Cheese can also benefit from gelatine by replacing most of the fat present by water without influencing taste and overall enjoyment in a significant way. This has been shown clearly in tests carried out on Camembert, Feta and special pizza cheese. The fat content was reduced to only 6% using water stabilized with gelatine. In comparison, hard cheese contains in excess of 30% fat and soft cheese between 20 and 25%. In a blind trial, consumers and a sensory panel assessed the low-fat cheeses as being typically creamy and assumed they were evaluating cheeses with normal fat content. The gelatine also improved the melting proper-

Table 3.36 BASIC RECIPE – Low-fat butter.**Ingredients:**

A: Butter fat or fat blend	39.50%
Emulsifier	0.50%
B: Gelatine, 240 bloom	0.50–1.50%
Skimmed milk powder	1.00%
Salt	0.40%
Potassium sorbate	0.12%
Beta-carotene	as required
Water	56.98–57.98%

C: Citric acid to adjust pH to 5.1–5.3

Process:

The fat is melted and mixed with the emulsifier at a temperature of approx. 55–65 °C.

The powder ingredients of B are mixed with the water and pasteurized.

On complete dissolution, the pH is adjusted to 5.1–5.3 by the addition of citric acid.

The mixture is cooled using a scraped-surface heat exchanger and mixed to crystallize the fat phase.

The product is packed.



Fig. 3.44 Low-fat spreads with gelatine (top) are more stable than those without gelatine (bottom).

Table 3.37 BASIC RECIPE – Low-fat fresh and soft cheeses containing gelatine.**Ingredients:**

Micro-filtered skimmed milk concentrate containing 28–30% total solids, without whey drainage.

Process:

The skimmed milk concentrate is adjusted to the desired fat content.
The milk concentrate is heated to 60 °C and homogenized at 50 bar.
The temperature is increased to 85 °C and maintained for 10 min.
0.5% gelatine is swollen in 2–3 parts cold milk and added.
The solution is cooled to 32 °C and 1% mesophilic culture added.
1 mL rennin (1:15 000) per 1000 L is added.
For Camembert, *Penicillium candidum* is added.
The product is filled into boxes.
The product is incubated at 22 °C for 18 h.
For fresh cheese, the product is salted for 5–10 min. in a salt bath at 18° BE and 4.8 pH.
The finished product is packaged.

ties of the pizza cheese. One of the preconditions for using gelatine in these cases is to use ultrafiltration for the adjustment of the dry substance of the cheese. This process guarantees that the gelatine remains in the cheese rather than escaping with the whey. Such low-fat cheeses, produced with gelatine (see Table 3.37), are already being successfully marketed in France.

Positive effects can be achieved with low-fat hard cheeses as well. In a patented process (European Patent No. 0 796 045 B1), gelatine is, for example, added to the milk before the addition of rennet or to the curd after the whey has been wholly or partly drawn off. This addition of gelatine gives the hard cheese a smoother consistency in comparison with the reference low-fat product, and the aroma of the cheese is brought out more clearly. This makes it possible to produce a hard cheese with a fat content of approx. 8% with a pleasant taste and mouth feeling. At the same time, the yield increases by up to 14%, depending on the gelatine added and the cheese-making technique employed. The concentration and the gel strength of the gelatine determine the quality of the end product also. These parameters can vary in the range 100–280 Bloom and 0.1–5% by weight. The process should therefore be optimized for each individual type of hard cheese.

3.2.2.7 Powdered Dairy Products

Dried dairy products are produced using skimmed milk powder, cream powder, or freeze-dried yogurt or curds. They are available on the market as powders or as ready mixes and are dissolved in milk, cream, or water immediately before use. In these products, gelatine fulfills a number of functions such as foam for-

mation and stabilization as well as its texturizing effects. Instant gelatines can be processed cold into products that subsequently set.

The USA has a long tradition of using ready mixes containing milk powder, flavors, and gelatine. They are used, for example, in preparing cream cheeses for “cold-baked” cakes and “whip-and-chill” desserts.

3.2.2.8 Gelatine in Combination with other Hydrocolloids

Improvement of the consistency and stabilization of dairy and pastry products can also be achieved with hydrocolloids other than gelatine; this, however, is often problematic. For example, the addition of carraganeen to fermented milk products can readily lead to flocculation and syneresis, the relatively large amounts of starch required for stabilization can give rise to a floury structure, agar-agar can cause some degree of brittleness, and many of the alginates are not capable of completely carrying out the functions of gelatine because of the thermal irreversibility of their gels.

Pectins are also restricted in their use: at pH values in excess of 5 and under thermal stress, they lose their gelling and stabilizing properties. In fermented milk products, the pectin must be carefully selected if the desired results are to be obtained. Aspects to be taken into account in this case are its degree of esterification and its raw material source. Highly esterified pectins from apples are used in fermented milk drinks when the product is intended to be highly viscous. If a lower-viscosity product is desired, highly esterified citrus pectins are the more suitable choice. In contrast, in the case of yogurts, pectins or amidated pectins of low esterification are used in order to achieve the desired degree of firmness. If the maximum concentration is exceeded, the neutral milk may curdle in both cases, leading to a product with a rough texture. Most importantly, pectin can only be added at the beginning of the production process; addition after the fermentation stage would destroy the casein gel because of mechanical stress.

On the other hand, blends containing gelatine can result in improved product properties in certain applications or render new product ideas feasible.

Developing the desired texture in yogurt can be accomplished by adding skimmed milk powder. If whey powder – which has a different protein composition – is used instead, any single hydrocolloid will not be able to stabilize the more highly concentrated whey powder to such an extent that the viscosity will be high enough to use a spoon. Only gelatine combined with starch can be used to produce a yogurt with an acceptable consistency, even if the whey concentration is as high as 45%.

The combination of gelatine and modified starch has also proven to be attractive for thermally treated fermented milk products from both technical and economical viewpoints. Together, they effectively prevent casein from shrinking in the acid range at the commonly used pasteurization temperatures of 70–85 °C. The casein does not curdle and the product remains smooth. Gelatine is essential in rebuilding the desired consistency in the finished product after the cooling process and also counteracts syneresis. The combination of gelatine and pectin has similar effects, and in this case syneresis can also be prevented.

Table 3.38 Common defects found in dairy products, with suggested causes and remedies.

Problem	Cause	Remedy
Product does not thicken or set	Poor gelatine dissolution Gelatine Bloom too low Gelatine level too low Damage to gelatine	Review process to ensure that conditions are adequate for gelatine dissolution Consider using a finer mesh product if necessary Increase gelatine Bloom Increase gelatine Bloom Increase gelatine level Review process to ensure that gelatine has not been subjected to excessive heating particularly in acidic conditions
Product is exhibiting syneresis	Poor gelatine dissolution Gelatine Bloom too low Gelatine level too low Damage to gelatine	Review process to ensure that conditions are adequate for gelatine dissolution Consider using a finer mesh product if necessary Increase gelatine Bloom Increase gelatine level Review process to ensure that gelatine has not been subjected to excessive heating, particularly in acidic conditions
Product is too firm	Gelatine Bloom too high Gelatine level too high	Decrease gelatine Bloom Decrease gelatine level
Foam stability is poor	Poor gelatine dissolution Gelatine level too low Whipping temperature may be too high	Review process to ensure that conditions are adequate for gelatine dissolution Consider using a finer mesh product if necessary Increase gelatine level Reduce temperature for whipping

The compatibility of hydrocolloids is, in many cases, very dependent on pH, the types of hydrocolloids used, and their ratio in the formulation. This often renders the use of mixtures a complex affair.

One example is the combination of gelatine and carraganeen, primarily used for stabilizing creams. This is because the synergistic effects of both hydrocolloids together lead to a stronger thickening effect than if they were used individually. In an acidic yogurt matrix, increasing the carraganeen content initially reduces both viscosity and body before they increase again. The texture that results, however,

Info Box 3.7**Also suitable for milk substitute products**

Milk substitute products are becoming increasingly important. They are based primarily on aqueous suspensions of soy protein. If, in the processing of soy milk, the technological requirements of customers such as shelf life, sedimentation stability, and turbidity are to be optimally fulfilled as in benchmark dairy products, gelatine can also serve as a suitable ingredient. The technology is comparable with both neutral and acid dairy products, as the isoelectric points of soy protein and casein are very similar.

is not very satisfactory from the sensory point of view. Gels produced using both gelatine and carraganeen exhibit syneresis and a strong degree of turbidity. The observed flocculations are the result of the colloidal-chemical phenomenon of phase separation or coacervation (see Section 3.2.9).

For individual applications, trials should be run to clarify whether it is better to process using a single hydrocolloid or a mixture and whether this is economical. Considerations must also include the handling of the hydrocolloid during the production process. Gelatine processing is very similar to the processes used in the dairy industry. During manufacturing, for example, a normal heating or pasteurization process is sufficient to bring the gelatine into solution; A separate swelling process is unnecessary. Gelatine can also be stirred into the milk together with the other ingredients prior to the heating process. And, as gelatine does not react with milk, it can be used in dairy products at all stages of production, including milk while it is in the vat, while it is being maintained at a higher temperature, or after incubation.

3.2.3

Meat and Delicatessen Products

Meat products, with their numerous concentrated nutrients, are important components of a balanced diet. Meat is a rich source of protein, iron, zinc, and valuable vitamins. In industrialized countries in particular, many consumers demand not only positive nutritional and physiological qualities as well as enjoyment, but they also expect increasing product diversity to meet the requirements of their nutritional habits and life styles. Gelatine provides the meat processing industry with many interesting possibilities to enable it to meet these requirements.

All aspic products are characterized by a unique visual quality. They become even more attractive within the scope of low-calorie diets, since native protein replaces part of the fat of the meat. There are, however, other applications for gelatine and gelatine hydrolysates in the meat processing industry. The technological effects of the gelatine hydrocolloid are also important, e.g., its ability to bind



Fig. 3.45 Gelatine provides the meat processing industry with many interesting possibilities for appetizing products.

water and meat juice in the package when being thawed or during cooking, and its texturizing and taste-enhancing properties. Furthermore, gelatine and gelatine hydrolysates can be used in a meaningful way to supplement meat proteins nutritionally and physiologically. All of these qualities will retain their importance well into the future.

3.2.3.1 Aspic Products

Aspic products are prepared by embedding ready-to-eat foods in a spicy jelly made from edible gelatine (see Tables 3.39–3.42). The aspic solution itself, once it has set, is transparent and can be sliced. Meat, fish, other seafoods, vegetables, and fruits are the foodstuffs usually used for this purpose (see Fig. 3.46). Aspic products garnished with mayonnaise, eggs, vegetables, and fruit, are known as delicatessen (see Fig. 3.46a).

Traditionally, aspic products have always been more popular in central Europe. However, food recipes tend to be shared worldwide, and it can therefore be as-



Fig. 3.46 Aspic products are a very attractive part of modern low-calorie diets.



Fig. 3.46a (continued)

sumed that aspic products will follow the example of fruit gummies, which have become successfully established on all continents.

3.2.3.1.1 Selection of Gelatine

Aspic products are stored and consumed, often sliced, at various temperatures. This has to be taken into account when formulating the recipe, especially when selecting the gelatine to be used.

Fresh aspic products are normally kept in a refrigerator and consumed relatively soon after removal. At refrigerated temperatures ranging between 6 and 8 °C, this means that the goods are typically consumed at approximately 10 °C. Canned aspic products, on the other hand, can be stored at room temperature as long as they are closed. Therefore, they are normally consumed at 20–25 °C. Sausage like meat in aspic (see Fig. 3.47) but prepared in sterile casings is usually sold sliced. Here, additional sales aspects have to be taken into account. For example, at the point of sale the goods should still be sliceable at a temperature of approximately 15 °C.

For all aspic products, therefore, a spiced aspic gelatine solution of the necessary concentration is required that, on setting, can still be sliced at the serving



Fig. 3.47 Sausage-like meat in aspic is very popular in central Europe.

Table 3.39 BASIC RECIPE – Ham in Aspic with Mushrooms.**Ingredients:**

52%	Cooked ham, cubed, without fat and skin
8%	Mushrooms, top quality (small, whole)
40%	Aspic solution (13% gelatine solution, 240 Bloom)

Process:*Preparation of the ham and mushroom mix*

The cooked ham is cut into cubes of 2 cm size.

These are mixed with the whole mushrooms.

The mixture is rinsed with hot water, then with cold water, and allowed to drain.

Preparation of the aspic solution

Gelatine (240 Bloom) is dissolved in 1 L of hot water to give a 13% solution.

Spice extract of high clarity is added.

If a sour taste is desired, 2–5% wine vinegar (10% acid) is added. The taste can be enhanced by adding lemon extract.

1.8–2.0% common salt per liter of aspic solution is added.

The process temperature is 50 °C max.

Preparation of the finished product

Casings of 90–135 mm diameter are filled. First, the dry material (65%) is filled into the casings.

The spiced aspic solution (35%) is then added very carefully and any air bubbles expelled.

The filled casings are placed in metal boxes for setting. To prevent the cooling process from taking too long, the boxes should not be packed together too tightly.

Storage of aspic-sausage: 4–6 °C.

temperature. Besides the concentration, the primary criterion is the Bloom value of the gelatine, i.e. the gel firmness. The higher the Bloom value, the higher is the melting temperature of the gel at the same concentration. High-Bloom gelatines in a 10% solution have a melting temperature of approximately 35 °C depending on the degree of acidity of the aspic to be prepared. In the case of medium- and low-Bloom gelatines of identical concentration, the melting points are 27 and 23 °C respectively (see Fig. 3.48).

For this reason, the concentration of gelatine required for a specified degree of firmness at serving temperature depends on the Bloom value; the higher the Bloom, the lower is the gelatine concentration required. At a serving temperature of 10 °C, for example, and assuming the same firmness, a standard gel would require about 80% more gelatine when the Bloom is 100 than it would when the Bloom is 260 (see Fig. 3.49). If the firmness is to be identical at, say, 26 °C, the amount required for a 100-Bloom gelatine increases to 226% of that required for a 260-Bloom gelatine. Thus, the use of high-Bloom gelatine is usually the more

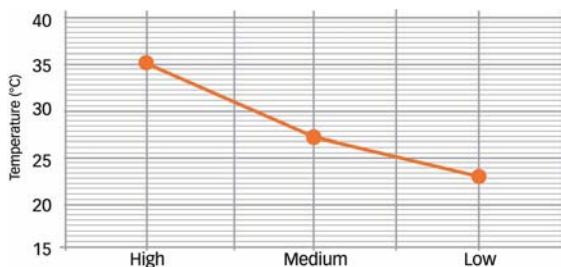


Fig. 3.48 Melting point as a function of Bloom value with identical gelatine concentrations.

economical solution even if the price per kilogram is significantly higher. Moreover, a low-Bloom gelatine, because of the increased quantity required, could possibly result in a product with a more rubber-like, viscous consistency and more intense coloring.

Table 3.40 BASIC RECIPE – Beef in Aspic with Vegetable Garnishing.

Ingredients:

55%	Lean beef, pickled and cooked
10%	Cucumbers and other vegetables (for garnishing)
35%	Aspic solution (15% gelatine solution, 180 Bloom)

Process:

Preparation of the beef

The beef is placed in a 10% brine solution overnight.

After moderate cooking (boiler temperature max. 78 °C, oven 80 °C), the beef is cooled and cut into cubes.

Preparation of the aspic solution

Gelatine (240 Bloom) is dissolved in 1 L of hot water to give a 13% solution.

Spice extract of high clarity is added.

If a sour taste is desired, 2–5% wine vinegar (10% acid) is added. The taste can be enhanced by adding lemon extract.

1.8–2.0% common salt per liter of aspic solution is added.

The process temperature is 50 °C max.

Preparation of the finished product

Casings of 90–135 mm diameter are filled. First, the dry material (65%) is filled into the casings.

The spiced aspic solution (35%) is then added very carefully and any air bubbles expelled.

The filled casings are placed in metal boxes for setting. To prevent the cooling process from taking too long, the boxes should not be packed together too tightly.

Storage of aspic-sausage: 4–6 °C.

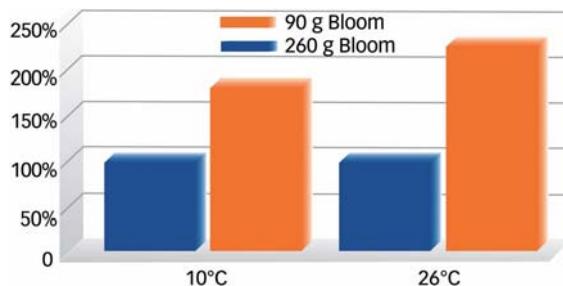


Fig. 3.49 Necessary gelatine concentration for the same gel firmness using gelatines of different Bloom values at various temperatures.

There are a few other reasons why a high-Bloom gelatine should be used. One is the fact that viscosity increases with increasing Bloom. This is desirable, as a highly viscous liquid facilitates suspending the meat or vegetables in the aspic solution prior to its setting.

3.2.3.1.2 Some Aspects of Proper Processing

The firmness of an aspic product is not just dependent on the Bloom value and quantity of the gelatine used. Appropriate processing is also important, because an acid pH and a high degree of thermal stress can render the gel less firm. This is especially important for products preserved at higher temperature or in sterile casings, or for cans or glasses sterilized for long-term stability. In such cases, the process should be designed in such a way that the gelling power of the gelatine decreases as little as possible. Close cooperation with the gelatine manufacturer is very helpful if optimal results are to be obtained.

First of all, a short sterilization period at high temperature is favorable if the gelling power is to be maintained. The product should achieve the core temperature rapidly and, once the sterilization period has been completed, should be cooled to a temperature below the less critical 80 °C as quickly as possible.

Secondly, acids such as vinegar, normally used to enhance the taste, should always be added just before the warm aspic solution is processed. In these cases too, the use of a high-Bloom gelatine is recommended, even if it tends to lose more gel firmness than a low-Bloom type upon heating in an acid medium. Practice has shown in most cases that, in spite of this, high-Bloom gelatines are more economical for use in the production of thermally stabilized products.

Thirdly, the aspic products should not be cooled too rapidly. If such cooling shock takes place, the molecules tend to become fixed very quickly because of the increased viscosity. Therefore, they will not arrange themselves optimally and the maximum firmness of the aspic will not be achieved.

Aside from gel firmness, the clarity and light color of aspic products are very important quality criteria for the consumer. Turbidity and discoloration can have many causes but can be prevented by appropriate process design. In order to pre-

Table 3.41 BASIC RECIPE – Poultry in Aspic with Filled Olives.**Ingredients:**

65%	Poultry meat (cockerel or turkey), pickled and scalded
5%	Olives
30%	Aspic solution (13% gelatine solution, 240 Bloom)

Process:*Preparation of the meat*

After cooking and cooling, the poultry meat is cut into cubes or broken into pieces. It is rinsed with hot water, subsequently with cold water and allowed to drain. The filled olives are mixed into the other materials.

Preparation of the aspic solution

Gelatine (240 Bloom) is dissolved in 1 L of hot water to give a 13% solution. Spice extract of high clarity is added. If a sour taste is desired, 2–5% wine vinegar (10% acid) is added. The taste can be enhanced by adding lemon extract. 1.8–2.0% common salt per liter of aspic solution is added. The process temperature is 50 °C max.

Preparation of the finished product

Casings of 90–135 mm diameter are filled. First, the dry material (65%) is filled into the casings. The spiced aspic solution (35%) is then added very carefully and any air bubbles expelled. The filled casings are placed in metal boxes for setting. To prevent the cooling process from taking too long, the boxes should not be packed together too tightly. Storage of aspic-sausage: 4–6 °C.

vent turbidity in the finished product, brought about by abrasion of the meat or by fat particles, all of the ingredients must be carefully mixed with the aspic solution. Therefore, a gentle mechanical process should be used, not only for the filling stage but also for the entire process from the preparation of the ingredients to the setting of the gel.

3.2.3.1.3 Fully Sterilized Aspic Products

Fully sterilized aspic products are frequently stored and served at room temperature. Such canned products can be produced using special technology whereby the gelatine gel only loses a minimum of firmness.

The principle of the process is based on powder gelatine ground coarsely and dry-mixed into the meat material to be preserved, followed by the addition of the spice solution.

Experiments carried out under practical conditions show that a 20% gelatine starting solution (processed as a dry granulate) at pH 4.8 exhibited the same degree of firmness as a 24% gelatine solution.

This can be explained by the fact that, during the sterilization process, the gelatine dissolves in a stepwise manner. It is only the gelatine in solution, however, that reacts to heat; thus, the potentially damaging effect of high-temperature treatment cannot exert its full effect on the firmness of the gel. This in turn enables lower concentrations of gelatine to be used, which provides an economic advantage. It must be taken into account, however, that at such high temperatures there will be more juice lost (drip loss) during cooking, thus necessitating a higher gelatine concentration than in the case of sausage type aspics, which are heated at lower temperatures and over a shorter time.

3.2.3.1.4 Production of Stable Frozen Aspic Products

Special gelatines can be used to prepare aspic that can be frozen. The process concentration must be between 22 and 23% and the pH of the aspic solution higher than 4.9 if the product is to be thinly sliced for sale. This particular restric-

Table 3.42 BASIC RECIPE – Veal with Mixed Pickles in Wine Aspic.

Ingredients:

60%	Veal, free of connective tissue, pickled, scalded, cubed
6%	Mixed pickles
4%	Dry white wine
30%	Aspic solution (13% gelatine solution, 180–240 Bloom)

Process:

Preparation of the meat

The veal, free of connective tissue, is salted (by injection) and cooked carefully. On cooling, it is cut into cubes of 1.5 cm size. It is rinsed with hot water, subsequently with cold water and allowed to drain.

Preparation of the aspic solution

Gelatine (240 Bloom) is dissolved in 1 L of hot water to give a 13% solution. Spice extract of high clarity is added. If a sour taste is desired, 2–5% wine vinegar (10% acid) is added. The taste can be enhanced by adding lemon extract. 1.8–2.0% common salt per liter of aspic solution is added. The process temperature is 50 °C max.

Preparation of the finished product

Casings of 90–135 mm diameter are filled. First, the dry material (65%) is filled into the casings.

The spiced aspic solution (35%) is then added very carefully and any air bubbles expelled. The filled casings are placed in metal boxes for setting. To prevent the cooling process from taking too long, the boxes should not be packed together too tightly. Storage of aspic-sausage: 4–6 °C.

tion does not apply to any other aspic products, as they remain sufficiently compactly bound at a pH of 4.0.

These special gelatines are processed in the same way as classical gelatine types: they are dissolved in water at 80–85 °C under constant stirring, and the aspic solution is subsequently spiced according to the recipe. The process temperature of the solution should not be allowed to fall below 55–60 °C.

Before the aspic products can be frozen, they must first be allowed to set at a temperature of +5 to +10 °C over a period of 10 to 12 h. After storage in a frozen condition, the products should be slowly and gently thawed at a temperature of +5 to +10 °C.

3.2.3.2 Gelatine Glazing and Dipping Masses

Gelatine glazing and dipping masses are used in meat processing, in the manufacture of delicatessen products, and in catering. The gelatine solution enables the pastries that have been baked or cooked in dishes to be embedded. This protects the sensitive products from drying out and losing a considerable amount of weight by excluding air. Taste and color also remain fresh over a longer period when products are sealed with gelatine. A further application area is pastries and pies enveloped in dough and filled with a gelatine solution. The space formed during cooking, when the filling shrinks, is filled with a solution of gelatine through a small hole in the surface of the dough. The gelatine solution serves as a link between the pastry itself and the filling. A suitable solution is one containing approximately 20% highly viscous gelatine of 240 Bloom. In addition, the jellies can be aromatically spiced. In France, for example, the use of Madeira wine for this purpose is very popular.

In the case of edible dipping masses, e.g. raw sausage meat or raw bacon, the same criteria apply to the gelatine solution used in this application as for pastries and the like. They serve to improve the visual impression given by the dishes and also prevent excessive loss of water from the meat ingredients.

Besides its adhesive property, the drying out of the dipping mass itself is an important factor. This particular parameter can be considerably improved by adding a 5% solution of 85% glycerol to a 20% solution of highly viscous 240-Bloom gelatine. The glycerol acts in a neutral manner sensorially, but must conform to the food regulations in the relevant countries if used as a softener in gelatine coatings. In such cases, the glycerol is added to the gelatine solution shortly before it is processed. The optimal dipping temperature is between 40 and 45 °C. The material that is coated should be maintained at a temperature of 18–20 °C and should be dry and fat-free. After the first dipping stage, the other garnishing ingredients such as Parmesan cheese or pepper should be sprinkled on the surface immediately. Additional dipping to seal the product can be carried out approximately 30 min. later.

The white color of non-edible dipping masses, which are peeled off the product prior to consumption, is achieved using titanium dioxide. In such cases, a mixture of gelatine, starch, guar gum, and carraganeen is processed. The hydrocolloids are mixed with the powder gelatine and added successively to cold water

under vigorous stirring. The mixture is then heated to 90–95 °C and maintained at this temperature for about 10 min. It is then cooled to approximately 60 °C, and the titanium dioxide, dispersed homogeneously in glycerol, is mixed in. The solution is now ready for processing.

A special gelatine coating spray is available for catering applications. Such a spray can be used to prolong the freshness of the items for a cold buffet by approximately 25%. The gelatine coating spray comprises a highly viscous, high-Bloom powder gelatine and a gelatine hydrolysate. The mixture is processed as a 20% solution, both components having a concentration of 10%. The mixture is dissolved in water at 90 °C with stirring. Salt and spices may be added during this stage.

The ideal processing temperature for such a spray solution is approximately 85 °C. Spraying should be carried out from a distance of 60–80 cm, and the items of food to be sealed should be dry and at a temperature of about 10 °C.

It is, of course, also possible to spread a gelatine solution onto the product using a brush; this is a widely used technique in Denmark.

3.2.3.3 Binding of Cooking Juice

In the case of heated meat products such as cooked ham, which are packaged in airtight bags or other containers, cooking juice is often lost. This juice can be bound by adding gelatine. The finished product is thus covered by a firm gel film. The product can be sliced even if stored at 20–25 °C. Furthermore, the product is more attractive visually when it is removed from the packaging by the consumer.

In this application, either dry powder gelatine is sprinkled into the can or a highly concentrated gelatine solution is added. The latter application is preferred if the many spaces that can potentially arise within the product during sterilization are to be avoided.

The amount of gelatine solution that can be added to a package is limited by the geometry of the actual container; in the case of canned goods the dosage is approximately 4.5 mL per 100 g net weight. At a pasteurization temperature of 105 °C maintained for 40 min, 12–15% cooking juice develops. Therefore, it is recommended that a 40% gelatine solution made from gelatine of at least 240 Bloom be used; in this way, all the factors capable of reducing gel firmness can be compensated for and the firmness can be maintained at an adequate level.

The process temperature for such a highly concentrated gelatine solution is 60–65 °C. In this way it can remain thin enough to be pumped for dosing without creating additional problems. The pH of the highly concentrated (40%) working solution should be at least 5.5. If at all possible it should be even higher, as at such concentrations it can influence the overall pH of the finished product, e.g., by reducing the water-binding capacity of the meat when the pH decreases.

In vacuum packs, neither powder gelatine nor gelatine solution can be used to bind any juice released during cooking, as both gelatine forms would be removed from the package during the vacuum process. Leaf gelatine is the ideal product for this application. In the case of scalded frying sausage, drip loss during a storage period of three weeks can be reduced by 80%. Depending on the size of the

package, either a half or the whole of a gelatine leaf is placed in the package and the product is placed on top. One leaf of gelatine is sufficient for 850 g of packaged sausages. The sealed package is then briefly heated. The gel that then forms is clear – it is practically invisible on examining the package – and seals in the juice, the taste, and the flavor.

3.2.3.3.1 Corned Beef

Gelatine is used by the meat industry in canned products such as corned beef, its main purpose being to absorb the meat juice released during the process of sterilizing the product. This is a very important function because of the fine structure of the meat fibers in this type of product. Gelatine enhances taste and improves slicing. In canned meat products, the principal purpose of gelatine is to hold the individual pieces of meat together. It also helps to maintain the protein balance of the product, as the gelatine has a high protein content. High-Bloom gelatine (220–250) is used to gel the juices lost during processing. It is normally used in concentrations of up to 2%, though some products can contain up to 5% gelatine. The concentrations used depend on the sterilization conditions, can dimensions, and quality of the meat (presence or absence of tendons, ligaments, etc.) being processed. Process temperature and processing time can also have an affect on gel strength and loss of viscosity; however, these can be compensated for by the concentration of gelatine used.

3.2.3.3.2 Frozen Cooked Beef

In frozen cooked beef, gelatine is added in powder form to the pieces of cooked meat before heat treatment. Gelatine helps to maintain the product structure by acting as a binding agent so that the final product is firm, consistent, easy to slice, and does not exude water. The meat is normally placed in casings in such a way that the meat layers alternate with the powder gelatine. Gelatine of medium Bloom (180–200) is used for this purpose at a concentration of 1%.

3.2.3.4 Water Binding in Fresh Meat

In fresh meat, a special protein, actomyosin, is principally responsible for binding the water. Actomyosin is a long, fibrous protein found in the cells of muscle tissue. When the pH of the meat is reduced, the protein releases water; the most unfavorable pH range in this respect is 5.0–5.2, as this is precisely the isoelectric point of actomyosin.

Immediately after slaughter, the pH of the meat, and therefore its water-binding capacity, is reduced; both increase again as the meat begins to age. The extent of water binding depends on the type of meat and the way it is processed. The following general rule can be used: low-grade and poorly processed meat tend to lose more water. Furthermore, mechanical stress brought about by the pressure generated on the lower layers as a result of the stacking of soft packages can force water out of the meat.

These processes cause liquid to collect in the package, an aspect that tends to be somewhat unsatisfactory to the consumer. Drip loss can have a qualitative effect

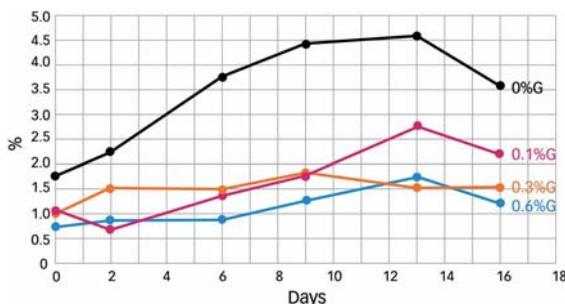


Fig. 3.50 Drip loss of juice (sliced meat) in % of the total weight in as a function of dusting with gelatine.

too, in that the meat tastes less juicy once cooked. On the side of the meat where the liquid has collected, discoloration can also occur, and the aroma may also be affected. Drip loss is also undesirable for economic reasons.

Drip loss is highest in the case of sliced meat. A conventional slice of veal can lose up to 4.0% of its weight within 7 days (see Fig. 3.50). However, if it is sprinkled with 6 g kg⁻¹ of extremely finely granulated gelatine, this figure is reduced to 1.0% (European Patent No. 0008829). Treatment with gelatine has been shown to have a positive effect on most products tested, although the efficiency is variable. This can be explained by the variation in storage time and the heterogeneous types of meat matrices involved, as the specific surface area, among other factors, may well have an effect on the drip loss.

The results obtained from sensory tests also showed that treatment with gelatine had a consistent and positive effect on the color, texture, aroma, and taste of the samples tested.

Gelatine is also suitable for reducing drip loss in deep-frozen and re-thawed meat. In slices of minced meat for example, the drip loss can be reduced by 50%. This value can be achieved both by sprinkling the outside of the product with 0.6% gelatine or by processing the same amount into the meat. Comparative tests have shown that gelatine is more effective in this application than, for example, carraganeen, although this latter ingredient is often recommended in the literature.

3.2.3.5 Pickled Products

In the production of pickled products using the conventional injection curing process, the weight of the finished product can be more than that of the original because of the injected pickling solution. This difference can be compensated for, i.e. the deficit in protein made up, by adding gelatine hydrolysate. The gelatine hydrolysate solution can either be added directly to the meat by injecting along with the pickling solution or processed into the meat by applying a vacuum. The gelatine hydrolysate binds the water, thus preventing drip loss into the package or onto the sliced product. At the same time it produces a very juicy taste. This ap-

plication of gelatine hydrolysate is not permitted by the food regulatory authorities in all countries. It is generally recommended that, when using gelatine hydrolysate, a protein of animal origin rather than carraganeen is co-processed, as carraganeen is a hydrocolloid derived from a different species. Other observed effects are an intensification and stabilization of the color generated by the nitrite in the brine.

3.2.3.6 Reduction of Baking, Frying, and Grilling Losses

The addition of gelatine to meat can reduce drip loss brought about by baking, frying, and grilling. This is an important economic factor for the meat processor but also enhances the quality for the consumer. Water binding is extremely important in low-fat meat products, as there is more water to be stabilized. Furthermore, gelatine also enhances the mouth feeling generated by fat.

If the product, e.g., a minced meat roast, is to be subjected to a prolonged heating process in order to dissolve the gelatine, conventional powder gelatine is ideal for the purpose. The powder gelatine is added to the minced meat, where it binds the juice released as a result of the meat proteins becoming denatured upon heating. On cooling, the meat juice becomes increasingly viscous because of the gelatine; as a result, an enjoyable, fat-like mouth feeling is generated. Once cold, the juice is embedded in the gel structure and cannot be released into the packaging. As a result, the meat is juicier when it is prepared by the consumer.

Similar results can be obtained by processing cold water-soluble gelatine hydrolysate into the product. The only exceptions here are products where gel formation, such as that which takes place in the setting of cooking juice using standard gelatine, is technologically required for the process.

The addition of 2–3% gelatine hydrolysate improves the softness and spreadability of meat products prepared from cooked chopped meat and fat tissue that are emulsified and subsequently homogenized. This also applies to low-fat sandwich spreads. In these recipes, fat is replaced by a vegetable mixture. The ingredients of the mixture are chopped in a mincer and subsequently homogenized and whipped along with hydrolyzed gelatine in a continuous cutter. The proportion of meat (or the main source of flavor) is added to the finely chopped and whipped vegetable mixture and is homogenized and then deposited into casings, cans, or glasses and cooked.

Hydrolyzed gelatine has excellent whipping properties and a stabilizing effect on emulsions and suspensions, and improves flavor, aroma, and color. Tasty and soft “light sandwich spreads” can be prepared in numerous ways (see Tables 3.43 and 3.44). Because of their low meat content, their fat content is below 10%. Depending on the product, the calorie content is between 450 and 750 kJ/100 g.

Gelatine hydrolysate also demonstrates its stabilizing effect in maintaining the binding capacity of sauces and soups. As a result, these products have a smoother and creamier consistency and enhanced gloss. Adding 2–3% gelatine hydrolysate also increases the consistency of roasts and chopped meats in which binding is generated by the pre-digestion of the muscle fiber proteins of the meat. In the manufacture of canned meat products and pre-prepared meals, these effects re-

Table 3.43 BASIC RECIPE – Light Sandwich Spread with Herbal Mixture (Low-fat, Low-calorie).**Ingredients:**

	%		kJ/100 g
Vegetable mixture comprising (cooked and finely chopped)	13.3	Potatoes	38
	26.6	Diced asparagus	13
	5.0	Onions	8
	2.0	Hydrolyzed gelatine as whipping agent	33
Basic meat mass comprising (cooked and finely chopped)	27.0	Pork	318
	6.0	Herbal mixture	25
Cooking broth	20.0	:	42
			477 kJ in 100 g of final product

Spices and other ingredients:

1% salt, 0.5% deli-liver sausage spice mixture, 0.15% sodium glutamate, 0.6% herbal mixture (chives, garlic, thyme, parsley, tarragon, oregano, rosemary, basil).
 If the aspic is molded into boxes they do not have to be tied up very tightly to achieve an exact shape.

Aroma:

Natural aroma

duce jelly and fat deposits, thereby increasing the net weight of homogenized products such as balls of liver and meat. The improvements achieved can be as much as 30% in individual cases.

The improved homogeneity of the binding of the sausage meat and its enhanced smoothness brought about by the addition of gelatine hydrolysate can considerably improve the skin formation of hot dogs as well as their peelability. Moreover, gloss and color are improved, curing and smoking times are shortened, and fewer sausages tend to burst during sterilization.

A second interesting application, wet canning, is the result of the fact that canned sausages are subject to both osmotic exchange and diffusion between their soluble components and the pickling solution. For this reason, there is often a migration of soluble meat protein into the pickling solution. This loss of protein can be reduced by adding gelatine hydrolysate to the pickling solution. This compensates for the osmotic gradient, which in turn increases production reliability and provides for a more accurate business calculation.

Table 3.44 BASIC RECIPE – Light Mushroom Spread (Low-fat, Low-calorie).**Ingredients:**

	%		kJ/100 g
Mushroom mixture comprising (cooked and finely chopped)	40.0	(Mushroom/vegetable mix 1:1)	63
	5.0	onions	8
	2.0	Hydrolyzed gelatine as whipping agent	33
Basic meat mass comprising (cooked and finely chopped)	30.0	Pork	352
Cooking broth	23.0	Cooking broth	48
			504 kJ in 100 g of final product

Spices and other ingredients:

1% salt, 0.6% deli-liver sausage mixture, 0.15% sodium glutamate, 0.2% parsley.

If the aspic is molded into boxes they do not have to be tied up very tightly to achieve an exact shape.

Aroma suggestion:

Mushroom dry aroma.

3.2.3.7 Mayonnaise and Salad Dressings

Sauces like vinaigrette, tartar sauce, chip sauce, mayonnaise, and salad dressings are emulsified semi-solid foods that contain an oil, an acidifying agent, egg yolk and, in some cases, starches, in addition to the specific spices, salts, and other flavoring agents that characterize each of them.

The need for an emulsifier and/or a stabilizing agent in this class of products is determined by the amount of fat in the formulation. Products with fat levels higher than 80% are generally emulsified by the egg yolk with no need for any another agent.

Products with fat levels lower than this will require an emulsifier, a stabilizer, or a combination of both; this is because the emulsifying power of a formulation decreases with the oil and the egg content, whereas the proportion of the aqueous phase increases.

As these are oil-in-water emulsions, stabilization of the system is achieved by avoiding the two occurrences responsible for emulsion breakdown: decanting and coalescence.

To avoid complete separation of the two phases and hence to ensure stability of the system, the surface tension between the two phases can be adjusted by using an emulsifier, and/or the viscosity of the continuous phase can be adjusted.

The emulsifying power of proteins has been extensively studied, and gelatine has been shown to be an important agent for stabilizing such substances because of its protective colloid property. In emulsified products, it has the ability to form a monomolecular layer of protein around the oil droplets, thus stabilizing the emulsion (see Section 2.1.1).

Stabilization can be achieved by increasing the viscosity of the oil-in-water emulsion; this can be done by increasing the disperse phase or by thickening the aqueous phase. This technique is used for emulsified sauces containing less than 80% oil. Gelatine is the first choice as a thickener because of its ability to absorb up to 10 times its own weight in water, therefore behaving as an effective water-binding agent.

In this respect, one advantage of gelatine is that the increase in viscosity occurs after several hours and does not jeopardize the packaging step of the process.

For some of the most common emulsified dressings and sauces, the following gelatine levels, preferably high Bloom, are recommended:

- Mayonnaise – 0.2%
- Ketchup – 0.25%
- Salad dressing – 0.45%.

3.2.3.8 Other Aspects

Comprehensive sensory testing of meat products and pre-prepared meals by consumers has shown that the addition of gelatine hydrolysate significantly enhanced the salty taste and aroma of these products. The aromas in question were the actual natural meat aromas and those of the spices added. Gelatine hydrolysate is thus a promising ingredient for reducing the salt content of products naturally and is being increasingly demanded in the interest of healthy nutrition (German Patent DE 3620150).

At the same time, the nutritional and physiological values of the products are enhanced by the increase in the content of protein. The improvement of the amino acid composition of the mixture of muscle and connective tissue proteins also significantly increases their biological value. The addition of gelatine hydrolysate is facilitated by its solubility in cold water and by the fact that it is more neutral in taste than products such as soy or milk protein. In addition, it has a significantly lower allergenic potential.

3.2.4

Beverages

The object of fining a beverage is to produce a product that is near perfect in terms of taste, color, aroma, and clarity. This involves the removal of unwanted color, haze, bitterness, excessive astringency, off-flavors, unpleasant odors, etc. Gelatine is also used in the production of beer, fruit juices, and wine, not just

for clarification and the precipitation of substances causing turbidity, but also for reducing the concentration of polyphenols such as tannins and anthocyanogens. Once again, gelatine exercises a number of different properties here in one single process: it prevents unwanted flavor, color, and odor by specifically removing the substances that cause these; and, gelatine fining improves the filtration properties of the beverage by ensuring practically complete pre-clarification beforehand.

Conversely, in juices with fruit pulp, a special type of gelatine hydrolysate can add protein value while still keeping the system stabilized, as in such products it's desirable to have the particles in suspension (pulp), what will give the natural aspect to the product.

The treatment of wine with gelatine has a very long tradition extending back to Roman times. Two mechanisms are responsible for the clarification and stabilization effects:

- The positively charged gelatine molecules in beer, wine, and fruit juices react with the negatively charged polyphenols and anthocyanogens present by forming hydrogen bonds – these render the gelatine insoluble – and by taking part in the electrical discharging processes. The complexes thus formed precipitate, and in doing so they adsorb other turbidity-forming substances causing them to co-precipitate. These all sediment at the bottom of the tank.
- A parallel reaction takes place: the formation of complexes between the natural proteins contained in the beverage and the added gelatine. These natural proteins are formed as a result of the enzymatic processes that take place during the production of the beverage. Colloidal protein particles are formed that are initially soluble but become insoluble over a longer period of time and may precipitate in the bottle if they are not previously removed.



Fig. 3.51 The use of Gelatine in the production of beer, fruit juices and wine has a very long tradition extending back to Roman times.

These reactions are primarily electrical discharge reactions; the positively charged gelatine molecules neutralize the negatively charged colloidal protein particles. As a result, the repelling effect between the uniformly charged colloidal particles that keeps them in suspension is neutralized. As a result, they form complexes with the gelatine and precipitate. The precipitate then binds other turbidity-forming substances and co-precipitates these.

3.2.4.1 Selecting the Most Suitable Type of Fining Gelatine

Fining reactions are influenced primarily by the iso-electric point (IEP) of the gelatine and the pH of the beverage. The IEP of type A gelatine is 8–9 and that of type B approximately 5 (see Section 2.1). If the pH of the beverage is lower than the IEP of the gelatine, it will be positively charged. As wines and juices normally have a pH of approximately 3.5 and beers around 4.5, all types of gelatine are positively charged in such beverages; the greater the difference between the pH of the beverage and the IEP of the gelatine, the stronger is the positive charge. Thus, gelatines of type A are normally used for fining if they are available.

As the reaction between gelatine and polyphenols and tannins is a hardening reaction – the cross-linking involved renders gelatine insoluble in water – a high-Bloom gelatine would appear to be of particular advantage, at least theoretically. This would ensure the rapid formation of a precipitate of high molecular weight and large surface area; this in turn would result in a short clarification process. On the other hand, the higher the Bloom value, the higher the risk of setting once the gelatine solution is cooled to the temperature of the beverage. This could be counteracted by diluting the gelatine solution more; however, this would mean that much more water would be brought into the beverage during the fining process. It should be taken into account that, in the case of high-Bloom gelatines, the alcohol of the wine can also bring about precipitation.

Table 3.45 Quantities of individual types of gelatine for optimal fining.^a

Gelatine type/ Bloom strength	Optimum usage rate g hL ⁻¹
A-267	90–100
A-210	80–90
A-195	80
A-141	50–70
A-120	40–60
A-100	30–60
A-080	30–90
A-060	25–100

^a Source: Wucherpfennig, K., Possmann, Ph., Kettern, W., & Scherpe, W. The effect of gelatine type on fining in white wines. Wein und Rebe, Wissenschaft, Forschung, Praxis. 55, 920–937.

Table 3.46 Gelatine fining tests on 1982 Stein, using Type B gelatine at 3 g hL⁻¹.^a

Determination	Bentonite (g hL ⁻¹)	100 Bloom	125 Bloom	150 Bloom	175 Bloom	200 Bloom	225 Bloom	250 Bloom	275 Bloom	Control
Sediment (%)	20	4.2	4.4	4.4	4.6	4.8	4.6	4.7	4.6	3.2
	40	5.4	5.3	5.4	5.5	5.2	5.4	5.3	5.6	4.4
	60	6.4	6.5	6.4	6.5	6.6	6.7	6.5	8.8	5.4
	80	7.4	7.3	7.4	7.5	7.4	7.5	7.4	7.6	6.2
Clarity (%T @ 520 nm)	20	91	92	91	92	92	91	91	91	88
	40	92	91	92	91	91	91	92	91	89
	60	92	91	91	91	92	91	91	92	89
	80	91	91	91	92	91	92	92	91	88
Protein stability	20	—	—	—	—	—	—	—	—	—
+ = stable	40	+	+	+	+	+	+	+	+	+
– = unstable	60	+	+	+	+	+	+	+	+	+
	80	+	+	+	+	+	+	+	+	+

^a Source: Bestbier, W. 1983. Ondersoek na die brei-effekt van gelastien met verskillende Bloom-getalle. Die Wynboer 621, 61–62.

Tests have shown that acid-conditioned gelatines with a Bloom value of 100 deliver the best results in practice (see Table 3.45).

Other studies using type B gelatines have shown no difference in the clarification effect achieved by using different gel strengths (see Table 3.46).

A very high degree of fining efficiency has been demonstrated by using special blends of gelatine of low and high Bloom but with a total Bloom value within the low-Bloom range of about 100. These special gelatines do not show the typical molecular weight distribution of, say, an 80–100-Bloom gelatine; rather, a higher proportion of the blend has a higher molecular weight than would normally be the case for the same Bloom value. The blend, however, combines the advantages of both the low- and high-Bloom types as far as this is possible in one type.

Fining gelatines are thus special products; but they must have a standard composition as only then can they have a reproducible spectrum of properties and effects. Close cooperation with the gelatine manufacturer for the supply of gelatines of consistent quality according to the specification is thus highly recommended.

3.2.4.2 Determining the Optimal Quantity of Gelatine

The optimal fining concentration must be determined by carrying out a series of pre-tests, if only gelatine is used as a fining agent. Having determined the optimal dosage, all tanning agents and substances causing turbidity are precipitated, and the gelatine collects completely at the bottom of the tank. In most cases, a concentration between 5 and 30 g per hectoliter is adequate.

If the amount of gelatine added is too low or if fining is incomplete, precipitation will be inadequate; it will not be quick enough and, once formed, the sediment at the bottom of the tank will be too loose. Such incomplete fining often produces a beverage that is even more difficult to filter than an untreated one.

Over-fining should also be avoided. Increasing the dosage of gelatine as determined in the pre-tests does not automatically result in more precipitate. Thus, such a course is not technologically meaningful. On the contrary, increasing the gelatine dosage by too much can result in the excess gelatine colloids giving rise to turbidity once the beverage is bottled. This is especially the case when no subsequent protein stabilization step is included in the process.

3.2.4.3 Combined Gelatine-Silicic Acid/Bentonite Fining

Today, the most popular fining method used is a combination of gelatine and silicic acid or bentonite. The negatively charged silicic acid or bentonite enhances the fining effect of the gelatine and accelerates precipitation and sedimentation. Furthermore, complete precipitation of all residual proteins – including gelatine itself – can be achieved without difficulty. This also prevents any excess fining.

Thus, fining can be carried out without the need for time-consuming pre-tests to determine the optimal concentration of gelatine. A standard dosage of gelatine is added to the beverage, and subsequently the proteins are stabilized with bentonite or silicic acid. Over-fining with gelatine should still be avoided. Although there is no danger of subsequent precipitation in the bottle, it can, for example in the case of red wine, lighten the color considerably.

3.2.4.4 Procedure for Fining with Gelatine

The amount of powder gelatine required for fining should be dissolved as described in Section 3.1.2. The gelatine should be processed within a period of 5 h if at all possible, as the risk of microbiological contamination increases considerably, especially in warm weather.

A very simple technical procedure allows cold water-soluble gelatine hydrolysate in powder form or a ready-made gelatine solution of fining gelatine with the specified concentration to be used. The liquid gelatine solution can be directly added from the can or the bottle used for delivery, hence eliminating weighing and dissolution procedures. Those ready to use gelatine solutions are normally stabilized with sulfur dioxide.

In the case of cold water-soluble gelatine hydrolysates, the preparatory procedures of cold swelling and warm dissolution are not necessary; the powdered gelatine hydrolysate can be directly added to the cold red wine mash. An alternative is the use of a highly concentrated solution containing 20–50% gelatine hydrolysate. In contrast to the classical 5% gelatine solution, this enables less water to be added to the beverage.

When using gelatine hydrolysates, combination with bentonite or silicic acid is particularly important. This is because the lower molecular weight of the hydrolysate does not always result in direct precipitation during the clarification process. As a result, if there is no direct protein stabilization, there will be an in-

creased risk of sedimentation in the bottle, as these substances only develop the molecular weight necessary for precipitation during storage.

3.2.4.5 Dosage of Gelatine

Independently of the type of gelatine selected and the technical process employed, effective fining of the beverage requires the gelatine to be well and uniformly mixed. Before adding the gelatine, the tank contents should be homogeneous. Once this is the case, the gelatine solution can be continuously added under stirring. Stirring should continue slowly for a few minutes after the solution has been added in order to ensure homogeneous distribution of the gelatine in the tank. If the gelatine is placed in the empty tank or if the entire solution is added too quickly, local areas of over-concentration may occur. In such a case the gelatine will start to set and to precipitate without having bound the polyphenols or anthocyanogens. Standing tanks with a height-to-diameter ratio of approximately 1:1.5–2.5 are to be preferred to horizontal tanks.

In some breweries, the gelatine solution (1–5%) is added to the beer on-line, between the fermentation and the storage tanks (see Fig. 3.52).

It is important that the gelatine be dispersed rapidly in order to avoid localized over-fining. This is the main reason for using such dilute solutions. Addition of the gelatine at or near the carbonation stage under pressure will assist in dispersion without causing the gelatine to float. The level of gelatine required and the temperature of addition need to be established by trials, but typically a level of 30–40 mg L⁻¹ of beer is required. The solution should be added at a temperature of around 4 °C followed by storage at around 0 °C until the required sedimenta-

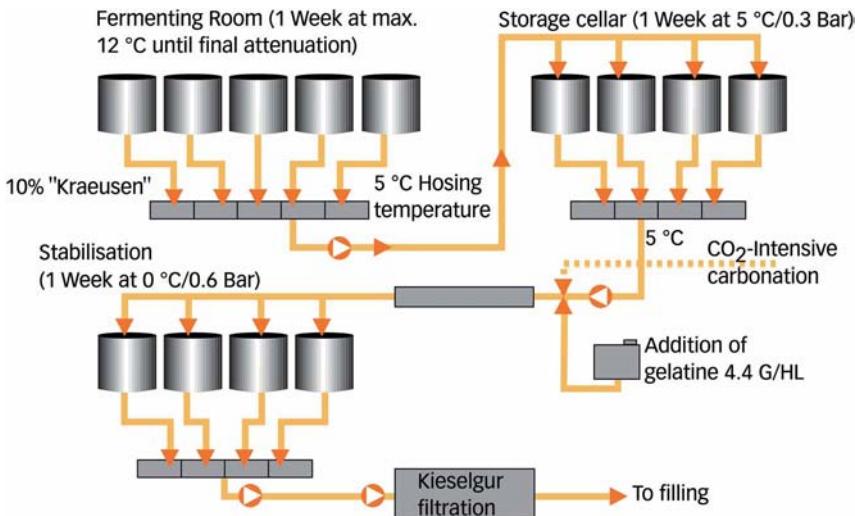


Fig. 3.52 Modern gelatine clarification: here in a brewery.

tion has occurred. Once again, the ideal temperatures for a specific process need to be identified by trials.

When carrying out combined gelatine-silicic acid/bentonite fining, the sequence of adding the components to the beverage is important. The time between the dosing operations is however not of importance.

If fining is intended primarily to reduce the content of polyphenols, i.e. to stabilize and smoothen juices or wines, the gelatine solution should be added first. This has the advantage that the silicic acid or bentonite added later then precipitates any possible excess gelatine present. This minimizes the risk of over-fining.

If the intention is to clarify the beverage – including removing any polyphenols present – the silicic acid or bentonite should be added before the gelatine. Using this procedure, the gelatine solution, when added, has an adequate amount of immediate reaction partner available. Precipitation and sedimentation then proceed more spontaneously and effectively.

3.2.4.6 Factors that Influence Fining Efficiency

It is not possible to give precise dosing data for fining procedures using gelatine.

This is because the correct ratio of fining agent to the substances to be precipitated is dependent not only on the specific type of gelatine used but also on the chemical composition of the beverage to be fined (see Info Box 3.8) and this of course can fluctuate considerably. Approximate figures are given in Table 3.47.

Other important factors are temperature, mechanical factors, and the geometry of the tanks used. Other particles in the beverage, e.g., yeast particles, also exert an influence on the fining efficiency. Thus, beers brewed using powdered yeast are difficult to pre-clarify as these very fine and extremely light particles hinder the charge equilibrium and destabilization procedures brought about by the positively charged gelatine molecules. Generally speaking, the fining of beer and wine

Info Box 3.8

Chemical factors that influence fining efficiency in wine

Acidity: The weaker the actual acidity, the poorer is the flocculation and subsequent clarification.

Level of gums and mucilages contained in wines (gums, pectins and dextrins): These act as protective colloids and can influence the effectiveness of cationic fining agents such as gelatine.

Selective trivalent ions such as Fe^{+3} catalyze initiate flocculations and clarifications. They can contribute to higher-temperature flocculation tolerances.

Tannin levels: Wines with higher tannin levels display greater fining reactivities with gelatine. For this reason, gelatine is more widely used in the fining of red wine than it is in white wine.

Table 3.47 Common dosage levels of fining agents.

Beverage	Gelatine g hL ⁻¹	Bentonite g hL ⁻¹	Kieselsol 15% ml hL ⁻¹
White wine	5–10	30–100	25–50
Red wine	10–25	20–80	10–25
Cider	10–50	30–120	10–35
Apple juice	15–50	—	—

using gelatine should take place after the main fermentation step, when most of the turbidity-causing particles have been removed.

3.2.4.7 Hot Fining of Fruit Juices

To obtain optimal fining, the temperature of the beverage is crucial. In principle, the cooler the beverage the better is the fining. In the case of wines and fruit juices, temperatures over 20 °C may lead to poor results. In the case of beer, temperatures below 2 °C should be used if possible.

One exception is the hot fining of fruit juices, which is carried out at temperatures between 40 and 50 °C. In these cases, any starches (e.g., in the case of apple juice) or pectins that may be present must be denatured enzymatically, as otherwise precipitation and sedimentation will be delayed.

Only when this step has been carried out can the gelatine solution be added. The juice can then be completely clarified within 2–3 hours. The use of silicic acid or bentonite as a reaction partner for gelatine is indispensable in this hot fining process.

3.2.4.8 Pre-fermentation Fining with Liquid Gelatine Hydrolysates

Apart from its ease of use, another advantage of using liquid gelatine hydrolysates over traditional gelatine is in pre-fermentation fining. While many vintners prefer to assess their finings requirements after fermentation, others have shown increased yields from the application of finings to the unfermented grape juice because of the compact sediment which is obtained. It is not possible to use gelatine in this way because of the gel formation which can occur in cool conditions.

After fining, it is important to test that there is no excess gelatine in solution. This is done by taking two 5 mL aliquots of the fined juice, placing them in test tubes and adding 5–10 drops of 1% gelatine solution to one tube and 5–10 drops of 1% tannin solution to the other tube. Shake the tubes well and observe which tube becomes cloudy. Cloudiness in the gelatine tube indicates under-fining, cloudiness in the tannin tube indicated over-fining (excess gelatine), and cloudiness in neither tube indicates optimum fining.



Fig. 3.53 Gelatine is the ideal ingredient for modern health-promoting nutritional and dietary products.

3.2.5

The Traditional and Modern Nutritional Science of Gelatine

In many applications, the technological properties of gelatine are, for good reasons, the main focus of attention. Although this may be justified, its nutritional value is also important. Gelatine is a highly concentrated source of protein; it contains no sugar, cholesterol, or other fats. It is also highly digestible and is readily absorbed by the body. In addition, in comparison with other proteins, its allergenic potential is extremely low, and its physiological properties make it highly suitable for use as a component of modern health-promoting nutritional and dietary products.

3.2.5.1 Gelatine and Nutrition – a Historical Review

Gelatine has been known in principle by man since he started cooking meat. However, this knowledge was only incorporated into nutritional textbooks at a much later date. At the beginning of the 19th century, the Napoleonic Wars were raging in Europe, and food was not always in plentiful supply. France in particular was in great need of large quantities of alternative sources of protein – and discovered gelatine. This decision was surely helped by Papin's "Digestor" (see Fig. 3.54), which made it possible to manufacture gelatine economically (see Section 1.1).

At this time, gelatine had become a focus for nutritional scientists in much the same way that vitamins or plant-derived substances are today. One of the major researchers was D'Arcet (see Fig. 3.55), a French scientist, who, around 1800, established that gelatine could easily replace 75% of the meat necessary for preparing a broth of high nutritive quality. D'Arcet realized even then that gelatine was only capable of replacing part of the total food intake; his broth thus also contained meat and vegetables.

For some decades, gelatine broth then became the main protein source for the poor and the sick. Furthermore, it was also the major dietary component for armies and mariners, as it was not only able to replace meat, but was easy to transport and, most importantly, was less perishable. The French army, for example, prior to the Algerian Campaign in 1830, purchased some 400 000 biscuits containing gelatine that had been prepared using a D'Arcet recipe (see Fig. 3.56). In fact, attempts were made to replace not only meat, but also all other dietary com-



Fig. 3.54 At the beginning of the 19th century, Papin's "Digestor" made it possible to manufacture gelatine economically as a food protein.



Fig. 3.55 Around 1899, the French scientist D'Arcet established that gelatine could easily replace 75% of the meat necessary for preparing a broth of high nutritive quality.

ponents with gelatine. As a result of this massive effort, the population became somewhat averse to gelatine – understandably so, as neither taste nor quality was comparable to today's standards. Furthermore, by the middle of the nineteenth century, scientists were increasingly of the opinion that gelatine *per se* was unsuitable as the sole source of protein. Experiments had shown that gelatine and dry



Fig. 3.56 The French army purchased some 400,000 biscuits containing gelatine that had been prepared using a D'Arcet recipe for the Algerian Campaign in 1830.

bread were insufficient for the maintenance of good health. Consequently, gelatine was regarded as being unsuitable as the primary daily basis of food. The scientists at the time, however, had no knowledge of amino acids or other essential food components such as vitamins and trace elements.

The research work of D'Arcet – which never actually supported gelatine as the main source of nourishment – hence became less important over the years. In addition, the results obtained by other scientists were not regarded as being of much significance, e.g., the results obtained in 1831 showing that gelatine could improve a diet based on potatoes. It was only at the end of the nineteenth and the beginning of the twentieth centuries, with the establishment of the science of modern nutrition and the development of amino acid analysis, that scientists rediscovered gelatine, this time as a food additive. In 1916, the results of one study showed that just 3.5% gelatine, because of its high concentration of lysine, was able to increase the biological value of wheat protein considerably. This observation remains as valid today as it was then and is of practical importance. In many developing nations, people are still very dependent on grain with a low lysine content for their food.

During the course of the 20th century, gelatine was repeatedly subjected to intensive scientific study. Its role in the nutrition of children, in dietetics, and in the prevention of osteoarthritis was investigated. At the same time, the mode of action of the individual amino acids in human metabolism became better understood. And, in many of these studies, it was impressively demonstrated that gelatine – as it always had been and always will be – is an interesting source of protein in human nutrition and one with numerous unique and valuable attributes.

3.2.5.2 Protein Requirement and Biological Value

Proteins are one of the basic building blocks required by the body (see Fig. 3.57). They are indispensable for all the body's processes and are continuously being used up: they are excreted as urea via the kidneys, are lost along with growing

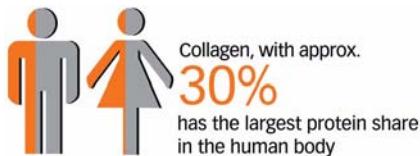


Fig. 3.57 Proteins are one of the basic building blocks required by the body.

nails and hair, and serve as sources of energy if they are not required for the formation, restructuring, or maintenance of the body's cells. Their energy content is equivalent to that of carbohydrates.

This utilization of protein must be compensated for by the intake of new protein in the form of food. The recommended daily intake of protein for an adult is usually given as 0.8 g per kg of body weight. Manual workers, athletes, and children require more. However, one gram of protein is not always equal to a gram of another protein. The biological value of a specific protein is dependent on its amino acid composition. The more this corresponds to body protein – especially regarding the content of essential amino acids – the higher is its biological value. The most critical factor is the amount of the particular essential amino acid present that is lowest compared to the ideal concentration required by the body. The lower the biological value of a particular protein, the more that protein must be taken in with the diet so that the total requirement of the limiting essential amino acids can be met. Chicken egg protein has the highest biological value of all individual substances and is hence given the reference value 100. Animal proteins in meat have a general value of over 90. Native plant proteins have values between 60 and 70 (see Fig. 3.58). The biological value of an individual protein is only relevant when it represents the exclusive source of nutrition; this, how-

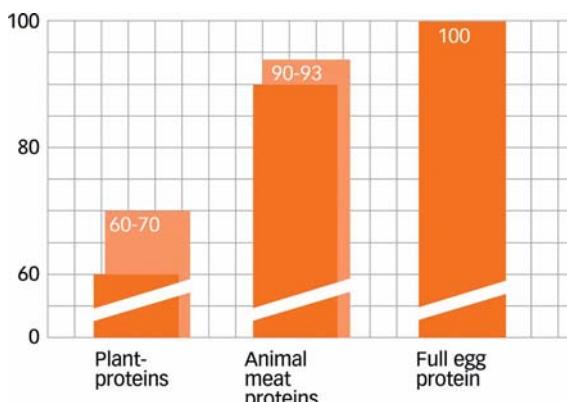


Fig. 3.58 The biological value of some proteins.

ever, is rarely the case. Food is always a mixture of various proteins, the amino acid compositions of which complement each other.

The proteins ingested as food are broken down during digestion into fragments of peptides of various sizes and ultimately to amino acids, their basic building blocks. The amino acids are then recombined by the body into the individual proteins that are required by the body. Mathematically, there are 10^{15} possible combinations involving the protein building blocks that occur in nature. Liver proteins are completely renewed every 10 days and those in leukocytes every 3 to 8 days. Thus, over a period of about 80 days, the entire protein of the body is renewed. As the organs of the body are made up of very different protein molecules, the body requires the various amino acids in differing amounts at different times. External influences also have considerable influence on protein metabolism. For example, an illness probably increases cell regeneration and hence the requirement of total protein and essential amino acids. Also, psychological stress increases the excretion of nitrogen in urine, hence requiring readjustment of the amino acid balance.

3.2.5.3 Nutritional and Physiological Importance of Gelatine

Gelatine is composed of approximately 90% protein. It contains all the essential amino acids with one exception – tryptophan (see Fig. 3.59). Furthermore, the sulfur-containing amino acids cysteine and methionine are present in low concentrations only. Therefore, gelatine is not suitable as a sole source of protein for human nutrition. But who would try to use gelatine as the only source of their daily food intake? It is highly interesting, though, to consider the importance of those amino acids that are present in relatively high concentrations in gelatine.

Of the essential amino acids, lysine in particular is present in gelatine. For the build-up of muscle mass, which characteristically requires large amounts of lysine, proteins containing high concentrations of this amino acid are recommended. In this context, the high content of arginine in gelatine is also of great value. According to a number of scientists, this at least semi-essential amino acid is required in creatine synthesis. This metabolite in turn, in its phosphate form, plays a major role in the energy metabolism of muscle cells. The oral administration of L-lysine and L-arginine increases the production of insulin, which in turn triggers increased secretion of growth hormones.

Glutamic acid, present in gelatine at approximately the same concentration as arginine, is particularly relevant for athletes participating in endurance sports, as it improves the regeneration process. One hour after a marathon, the glutamic acid level in plasma is reduced by about 20%. Sports drinks containing a high concentration of glutamic acid can reduce or even prevent this occurrence; the body can then recover more quickly. Simultaneously, glutamic acid supports the immune system, and these athletes are therefore less susceptible to infection.

The amino acids glycine and proline, present in gelatine at 10- to 20-fold the concentration found in other proteins, are also of value. In order to ingest the same amount of glycine that is contained in 10 g of gelatine, one would have to consume about 2.8 L of milk or 160 g of meat (see Fig. 3.60). In the case of proline, the equivalent amounts are 0.4 L and 110 g respectively.

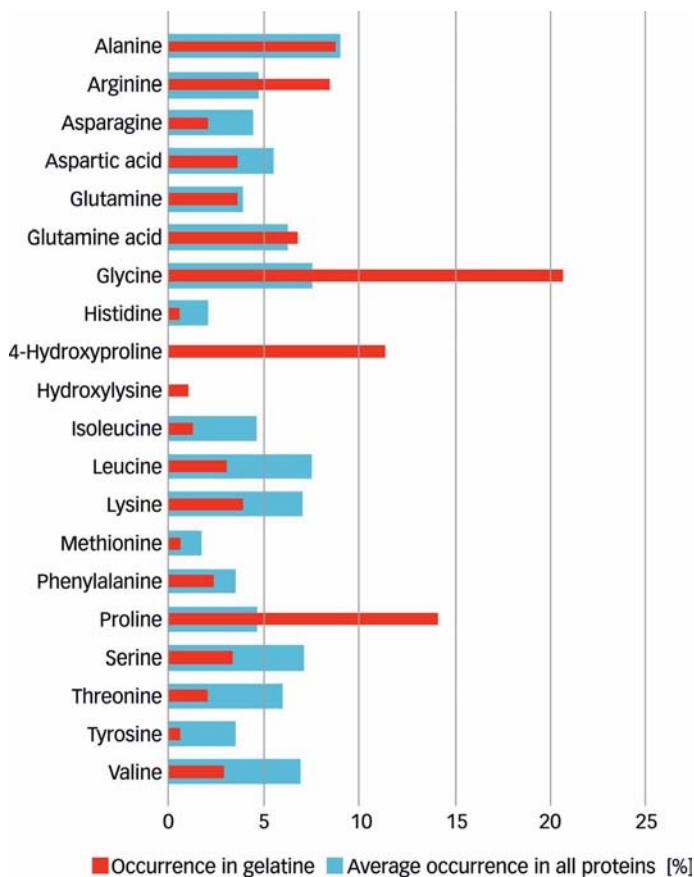


Fig. 3.59 Comparison of the amino acid spectrum of gelatine with that of the average of all proteins. Source: Special print: Collagen Hydrolysate and its Relationship to Joint Health, GELITA Health Initiative, 2005, 2nd revised edition.

The same amount of the amino acid glycine is contained in:



Fig. 3.60 Gelatine is a highly concentrated source of the important amino acid glycine.

It is often claimed that the non-essential amino acids proline and glycine can be synthesized by the body itself. However, the body preferentially utilizes proline and glycine building blocks, as is unequivocally shown by the example of cartilage metabolism (see Chapter 4). The reason for this is straightforward: the body requires proline and glycine for the formation of collagen, but it cannot always produce enough to meet demands at any specific time. For example, the proline level in plasma decreases by 20–30% if the body is faced with a diet low in proline.

In the case of glycine as well, the amounts required by the body would tend to exceed those provided by synthesis alone: glycine is not only critical for collagen metabolism, it is also a component of the amino acid pool that is used for the synthesis of other amino acids as well as for other proteins such as hemoglobin and DNA. Glycine is also utilized by the liver during detoxifying processes; it helps during digestion by regulating the secretion of acid in the stomach and is involved in many other bodily processes. Therefore, the requirement is correspondingly high and the body must obtain it from foodstuffs.

Gelatine also contains hydroxyproline that is readily absorbable. This is significant, as, during the synthesis of collagen, proline has to be partially converted into hydroxyproline. This reaction requires the enzyme proline hydroxylase, and if it is to function properly, both vitamin C and iron are required. If these are not available in adequate amounts, the reaction will not proceed. In extreme cases, this gives rise to the deficiency disease scurvy.

Sometimes less can mean more in terms of nutrition. The intake of gelatine does not necessarily increase the content of methionine and cysteine proportionately; the sulfur-containing fragments produced by their decomposition have less influence on the acid-base balance in the body.

The biological value of a protein reflects its real quality to a limited extent only. Today, many scientists tend to assess the value of a protein according to how well it supplies specific groups of persons with the amino acids that happen to be in increased demand. Lysine, for example, is not just required by athletes requiring power and strength in industrialized countries; it is also needed for people in many developing countries where foodstuffs are primarily based on starch. Lysine occurs in limited quantities in rye, wheat, rice, and corn (see Fig. 3.61); in diets that are primarily carbohydrate-oriented, deficiencies tend to occur. Improvement of the amino acid composition is thus one of the major goals of plant cultivators.

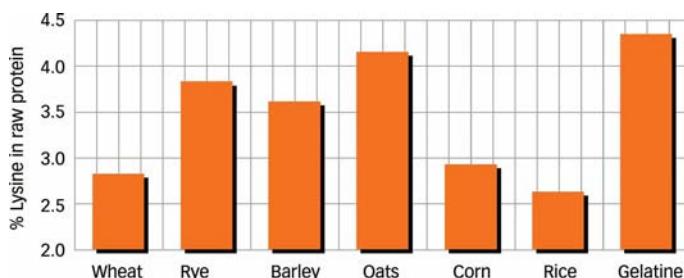


Fig. 3.61 Lysine content of various types of grain compared to that of gelatine.

This could have been achieved more rapidly if gelatine, with its relatively high content of lysine and hydroxylysine, had been added to diets, as proposed as early as 1916 (see Section 3.2.5.1).

Meat is another example. Meat protein has a biological value of 92. In contrast, a combination of 83% of the same meat and 17% gelatine has a value of 99. Meat in aspic, therefore, has a higher biological value than the meat on its own.

Apart from the amino acid composition of a protein, its real value is influenced by other factors: proteins in particular must be readily digestible. Of the amino acids in gelatine, lysine is utilized up to 95% by the body. Gelatine is not only metabolized well, it also acts as an emulsifier and as a protective colloid, hence improving the digestibility of other proteins ingested with food. In dairy products, for example, gelatine not only emulsifies the fat, but also, in its function as a protective colloid, regulates the clotting mechanism of casein. This in turn increases overall digestibility.

Furthermore, gelatine has for many decades been an ingredient in bland diets suitable for use in conditions affecting the stomach and the intestine: one of the foremost benefits of gelatine in this application is that it behaves like a "solid liquid." The patient has a chewable alternative to the mostly pasty dietetic foods available. This feature alone brings about an increase in appetite and in addition, as gelatine melts at body temperature, it is resorbed and digested by the body just like a liquid. Gelatine as an ingredient in foodstuffs also provides for a very fine distribution of the nutrients in food. This reduces the amount of degradative work that has to be done by the digestive organs and prevents the unnecessary secretion of gastric juice. It is of interest to note that hundreds of years ago, gelatine, in the form of jellied fruits, was often served after sumptuous meals. It was likely recognized then that gelatine was able to soothe digestive stress after such an event (see Fig. 3.62).



Fig. 3.62 Gelatine as an ingredient in foodstuffs reduces the amount of degradative work that has to be done by the digestive organs and prevents unnecessary secretion of gastric juice.

Gelatine is also a valuable ingredient in other types of diets. Foodstuffs containing no carbohydrates, sugar-free bars, vitamin tablets, and cold water-soluble instant teas are only a few examples of what can be done for diabetics using gelatine, a carbohydrate-free hydrocolloid. Using gelatine, cream dishes can be produced without having to bind and lighten with eggs and cream; they then become more digestible for people with gall bladder problems. For those suffering from certain types of kidney disease, the overall protein content, including gelatine, must be restricted.

3.2.5.4 Gelatine for Modern, Health-promoting Foodstuffs (Low-fat, Low-carb, Low-calorie)

“Low-fat,” “low-carb,” and “low-calorie” are phrases frequently used in describing foodstuffs today. A product with these nutritional qualities can only become successful if it is consistent with a number of other customer desires. In brief, the nutritional benefits required by the consumer must be incorporated in a product in such a way that it is natural, versatile, easy to prepare, and appetizing – most importantly, it must taste good. For the development and manufacture of such health-oriented foodstuffs, gelatine possesses the necessary technological and physiological properties to a great extent.

Gelatine is primarily an excellent source of protein. As such, it can optimize the biological value of the total protein contained in protein bars, protein pastries, and cold-water-soluble protein beverages, hence improving their compatibility and digestibility (see Section 3.2.5.2).

Gelatine also provides secondary benefits such as the reduction of sugar through the use of gelatine hydrolysate as a binding agent in cereal bars (see Section 3.2.1.3 and Fig. 3.63). It also reduces calories by replacing fat – the protein contained in gelatine and the water bound by it have fewer calories than fat.



Fig. 3.63 Gelatine hydrolysate as a binding agent enables the sugar content of bars to be reduced.



Fig. 3.64 A 50:50 mixture of meat and aspic has the same biological value as that of the meat alone – but it contains less fat.

The classical method of reducing fat using gelatine is by the use of aspic products (see Fig. 3.64). Here, the meat, and hence the fat, is replaced by jellied meat broth and vegetables. Despite this, because of the amino acid composition of gelatine, the biological value of the total protein of such an aspic product is very high; even a 50:50 mixture of meat and aspic has the same biological value as that of the meat alone.

In low-fat margarine (see Fig. 3.65) fat is replaced by water, which is bound by the gelatine. As an excellent emulsifier and stabilizer, gelatine guarantees the spreading properties and consistency required by the consumer. In desserts and ice cream, gelatine compensates for the loss of mouth feeling that is often associated with reduced-fat products: gelatine melts in the mouth, transforming itself into a viscous liquid. This behavior is similar to that of fat and hence provides a comparable taste and mouth feeling.

Spicy sandwich spreads can be replaced by homogenized vegetables that have been whipped to a foam using gelatine hydrolysate (see Fig. 3.66). In this way, the fat content can be reduced to under 10% and the calories to 461–754 kJ/100 g. Meat products such as sausage spread contain a minimum of 20% fat and have a caloric value of at least 1250 kJ/100 g.

In cheese, too, gelatine can be used to replace most of the fat with water (see Fig. 3.67). In this way, cheese varieties, such as Camembert, Feta and pizza



Fig. 3.65 In low-fat margarine, fat is replaced by water, which is emulsified and bound by the gelatine. At the same time, gelatine guarantees the spreading properties and consistency required by the consumer.



Fig. 3.66 With gelatine hydrolysate, the fat content of a sandwich spread can be reduced to under 10%. In such products, meat is replaced by homogenized vegetables that have been whipped to a foam using gelatine hydrolysate.



Fig. 3.67 Gelatine can be used in soft and hard cheese to replace most of the fat with water. In sensory tests, consumers and experts assumed they were sampling cheeses of normal fat content.

cheese could be reduced in fat content to approximately 6% in absolute terms. In comparison, hard cheese contains about 30% fat, and soft cheese between 20 and 25%. In spite of these significant fat reductions, in sensory tests consumers and experts have described these products as being typically creamy; they assumed they were sampling cheeses of normal fat content. In addition, gelatine significantly improves the melting properties of pizza cheese. The technological precondition for the manufacture of such products is the use of ultrafiltration by the cheese producer; this guarantees that the gelatine remains in the cheese and is not separated with the whey.

From the point of view of healthy living, reducing the salt content of food is also of great importance. Sensory tests carried out on sausage and soup products have shown that the use of gelatine hydrolysate significantly intensifies the salty taste. This synergistic reaction affects not only the salty taste, but also the meat flavor and the spices contained, especially pepper. Depending on the water content, this effect can vary; however, it is always statistically significant except for those products containing very little water. It is therefore possible to lower the



Fig. 3.68 Gelatine hydrolysate, when added to dough, renders bread softer and delays staling during storage. Therefore, the consumer need not shop so frequently.

salt concentration in numerous products while maintaining the taste that is expected by the consumer.

Besides its nutritional and physiological properties, the technological benefits of gelatine make it a desirable ingredient for modern foodstuffs. Gelatine hydrolysate when added to dough renders bread softer and delays staling during storage (see Fig. 3.68). As a result, the bread tastes fresh longer, and therefore the consumer need not shop so frequently. For many consumers this is a valuable benefit, as time is a precious commodity in the modern world. This is also reflected in eating habits: on a worldwide basis, the office and the train compartment have become the dining rooms of our mobile society, and the microwave has replaced the traditional oven.

This does not mean, of course, that people must necessarily forego their favorite dishes – they just have to adapt to the actual situation. With the help of gelatine hydrolysate and instant gelatine, a light and delicious mousse can be prepared when traveling (see Fig. 3.69). The cup contains a pre-mixed powder; this is dissolved in cold water and the sodium bicarbonate contained in the powder creates the necessary foam. Gelatine enhances the foam and provides the creamy texture. If sugar is then replaced by a sweetener, the product becomes both fat- and carbohydrate-free, as well as low-calorie. For the consumer, a real benefit is that such powder products can be stored longer term without the need for refrigeration. Other variations on this theme include powdered fruit yogurts that simply require water and stirring to prepare, a jam that can be sliced and subsequently melts on toast, an “ice cream lollipop” that need not be kept in the freezer, fruit and vegetable foams that can be used as aperitifs, or desserts sprayed out of a dispenser like cream as a side dish – gelatine provides the product developer with numerous options.

In addition to the nutritional, physiological, and technological properties, the unique functional properties of gelatine are also of importance. Collagen hydrolysate has been shown to have a favorable effect on skin, hair, bones, and joints.



Fig. 3.69 With the help of gelatine hydrolysate and instant gelatine, a light and delicious mousse can be prepared easily “on the go” – the consumer needs only to add cold water.

This protective effect brought about by higher dosages of collagen hydrolysate in “joint and bone health” is a valuable product benefit. Furthermore, its functional properties clearly establish gelatine as a link between “nutrition, wellness, and beauty”, another market sector destined for enormous growth according to market researchers.

Info Box 3.9

Collagen hydrolysate may help overweight individuals in their dietary efforts to lose weight

As preliminary data generated in a clinical study suggest*, collagen hydrolysate may exert metabolic effects resulting in the central nervous system registering a sensation of satiety. When individuals ingest food, hormones are secreted in the gastro-intestinal tract; these exert a feed-back mechanism on the brain, i.e. the brain itself starts secreting hormones that generate a feeling of satiety in the human body. Results of a clinical trial that was carried out on obese women suggest that collagen hydrolysate may actually induce the secretion of that particular hormone. The clinical implications that one can conclude from these results is that collagen hydrolysate may fulfill the role of an active agent that may ultimately help overweight individuals in their dietary efforts to lose weight.

*Source: Nogueira de Almeida et al, Poster presentation annual Congress of Associação Brasileira de Nutrologia, 2005



Fig. 3.70 Gelatine us an extremely important and versatile excipient for pharmaceutical and medical applications.

3.2.6

Pharmaceuticals and Medicine

Because of its unique technological and biopharmaceutical properties, gelatine is an extremely important and versatile excipient for pharmaceutical applications. Gelatine has been listed in the various pharmacopeias for decades as an excipient for the manufacture of capsules and rectal and vaginal suppositories. It is also used in the manufacture of numerous pharmaceutical products, e.g., as a thickener in liquid dosage forms, as an agent for increasing the adhesiveness and viscosity of products for sugar-coated tablets, as a gel-forming component in dental pharmaceuticals, as a protective ointment for the mucous membranes of the mouth, and as an excipient in the manufacture of granules and tablets. The excellent physiological compatibility of gelatine is also used in numerous medical applications. It is an important component of blood plasma substitutes based on gelatine that is frequently used in emergency medicine as well as in major surgical operations. It is also used in innovative applications such as in regenerative medicine and minimal invasive surgery. To date, no other natural or synthetic polymer provides such versatility in medical and pharmaceutical applications.

3.2.6.1 Gelatine in the Pharmacopoeias

In view of its considerable importance in pharmaceutical technology, gelatine is listed in all major pharmacopoeias. In the current American version (USP XIX/NF 24), it is described as “a product obtained by the partial hydrolysis of collagen derived from the skin, white connective tissue, and bones of animals”. A similar listing is found in the Japanese Pharmacopoeia. The current version of the European Pharmacopoeia (EP V 2005) additionally and explicitly lists raw materials obtained from poultry and fish; and in addition to the gelling gelatines, hydrolyzed non-gelling types are also listed.

In general, the pharmacopoeias limit the information given on quality parameters to identity, pH, moisture, arsenic, peroxide (European Pharmacopoeia), SO₂, ash, conductivity, heavy metals (more detailed in the European Pharmacopoeia) and microbiological status (see Section 2.3).

Technologically relevant parameters such as isoelectric point, viscosity, and gelling behavior are not listed. Important quality parameters such as gel strength are only mentioned in the European Pharmacopoeia (standard value of Certificate of Analysis ± 20% of the labelled nominal value).

As a result, customer specifications with respect to product and application tend to be much more comprehensive; only if this is the case can optimal performance be achieved for the application in question. One good example is the viscosity of a 30% hard shell capsule gelatine solution at 50 °C – an important criterion in the production of hard shell capsules. The thermal stability of capsule gelatine solutions during unavoidable storage at temperatures between 50 and 60 °C also plays a major role (“viscosity breakdown”).

3.2.6.2 Gelatine Capsules

Approximately 90% of all pharmaceutical gelatine produced is processed to capsules. Gelatine capsules are single-dose solid drug forms. The capsule shell is made of gelatine suitable for the application intended. Gelatine capsules protect their contents to a very large extent against the affects of light, atmospheric oxygen, contamination, and microbial growth. There are two types of capsule – soft and hard; they differ in the composition of the capsule shell, the type of drug they contain, and the manufacturing method used.

3.2.6.2.1 Hard Shell Capsules

Hard shell capsules consist of two cylindrical shells, each closed off at one end (see Fig. 3.71). The upper part, the cap, has a somewhat larger diameter than the lower part, the body, which is usually a little longer. The two parts fit each other perfectly to form a hermetically closed unit. Hard shell capsules are normally supplied empty to manufacturers of pharmaceutical, health and nutritional products, where they are then traditionally filled with powdered products. In order to be able to fill hard shell capsules with liquids and pastes, and in the interests of drug safety, methods have been developed for sealing and subsequently packag-



Fig. 3.71 Gelatine hard shell capsules are produced in a wide variety of sizes and colors.



Fig. 3.72 Modern high-performance hard shell capsule machine.

ing the capsules. Hard shell capsules can thus be used in some cases for the same purpose as soft shell capsules.

A modern, high-performance hard shell capsule machine can be described briefly as follows: polished stainless steel pins are dipped in a warm solution consisting of 28–35% gelatine, colorants, and other additives. The film that is formed when the pins are withdrawn from the solution sets within seconds to form empty gelatine bodies; these are subsequently dried under defined conditions. In this way, some 40 000 capsules per hour can be produced (see Fig. 3.72).

The speed at which the pins are withdrawn and the viscosity of the gelatine solution determine the thickness of the capsule walls: if the viscosity is too high and the speed of withdrawal of the pins too fast, the capsule walls will be too thick. Generally, the viscosity, which is about 750–1000 mPas at a temperature of 50 °C, and the temperature of the gelatine mass in the dipping tank are somewhat lower for bodies than for caps. This ensures that the caps and bodies fit perfectly after drying. The wall thickness of dried hard capsules is not uniform over the length of the capsule. It is thinnest (80–120 µm) at the shoulder and thickest (130–150 µm) at the rounded ends or domes. The mid-sections are normally 100–130 µm thick (see Fig. 3.73).

During the initial drying step, the temperature is set at 22–28 °C. At the beginning of the process, the capsules dry very slowly, in the middle a little more quickly, and at the end again slowly. This enables the gelatine to achieve the intended structure and at the same time increases the elasticity of the finished capsules. If the drying process is too fast and the temperature is over 30 °C, the capsules may become brittle and have a rough surface.

At the end of the drying process, the moisture content of the capsules is between 14 and 16%. This increased water content facilitates removal of the capsules from the pins. After drying, the gelatine capsules on the pins are longer than required. Also, because of the dipping and drying processes used, the ends have different thicknesses. The capsules are then standardized by trimming with a rotating blade.

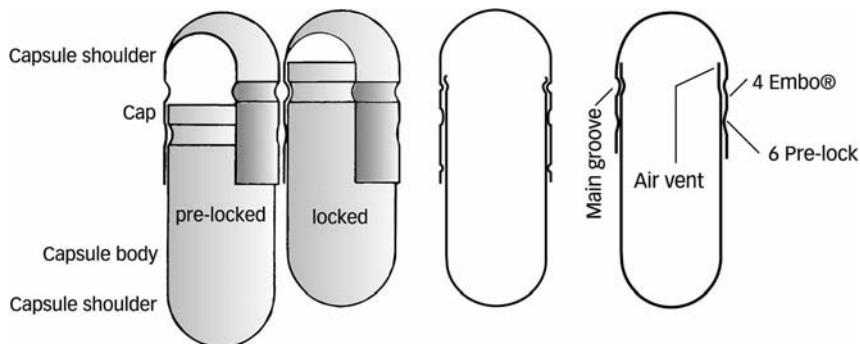


Fig. 3.73 Various systems for hard shell capsule pre-locks and final locks.

In a final step, the bodies and caps from the two parts of the machine are joined and collected. Specially designed grooves and notches are placed around the body and cap which allow temporary closure, the so called “pre-lock”, during transportation but can easily be opened by the filling machine. To facilitate the separation of the empty capsules and to make the subsequent filling and closure processes more efficient, the upper edges of the bodies are often flattened. Specially designed body and cap ends at the overlap areas facilitate air being exuded during the closure process (see Fig. 3.73). The capsules are then dried in climate chambers set at about 22 °C and 50% rel. humidity. The final residual moisture content is about 13%.

Both hard and soft shell capsules can be manufactured as single- or dual-color products. Synthetic water-soluble colorants or pigments that have been approved for pharmaceutical applications are used for the purpose. Insoluble pigments such as iron oxides are widely used. Such coloration is used not only for identification purposes; it also provides protection for contents that may be sensitive to light. To increase product safety and to prevent counterfeiting, the capsules are frequently printed with special product codes.

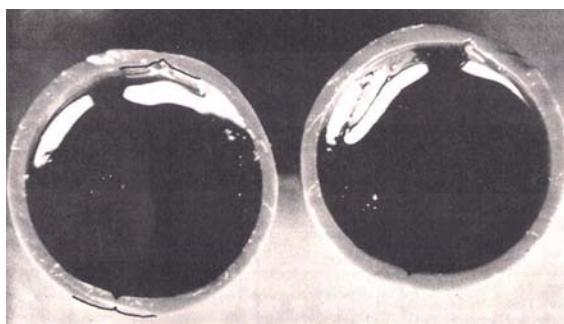


Fig. 3.74 Cross-section of the central part of a soft shell capsule.

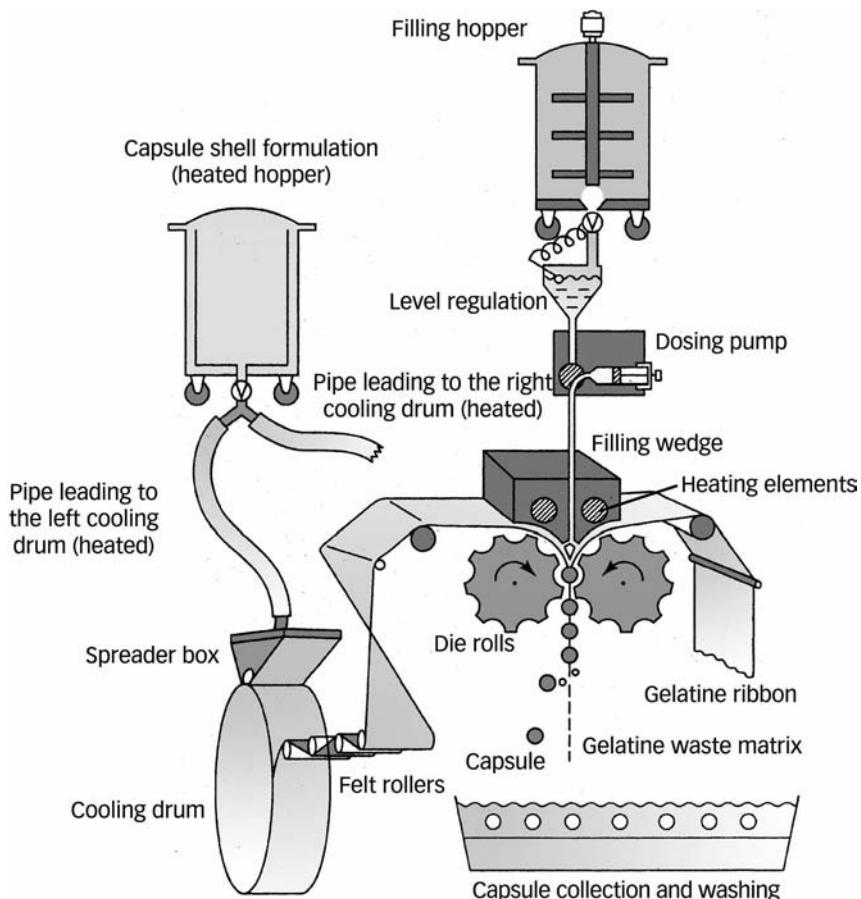


Fig. 3.75 The vast majority of soft shell capsules are manufactured today using the Rotary Die Process.

The solubility of hard shell capsules depends very much on the type of gelatine employed in manufacture. Tests carried out on dried gelatine films have shown that films produced from ossein gelatine dissolve quickest while hide split gelatine dissolves slowest. Because of electrostatic effects, gelatine films made of mixtures of ossein and pigskin also dissolve slowly; however, all the films dissolve completely within 30 min.

3.2.6.2.2 Soft Shell Capsules

Soft shell capsules are completely closed units. They are either seamless (Globex Process, see Fig. 3.76) or are provided with a longitudinal seam (Rotary Die Process, see Fig. 3.75). They are produced, filled, and sealed in one production step and are used predominantly for non-aqueous liquids and pastes. The main advantages of soft shell capsules are their dosing accuracy and the possibility of includ-

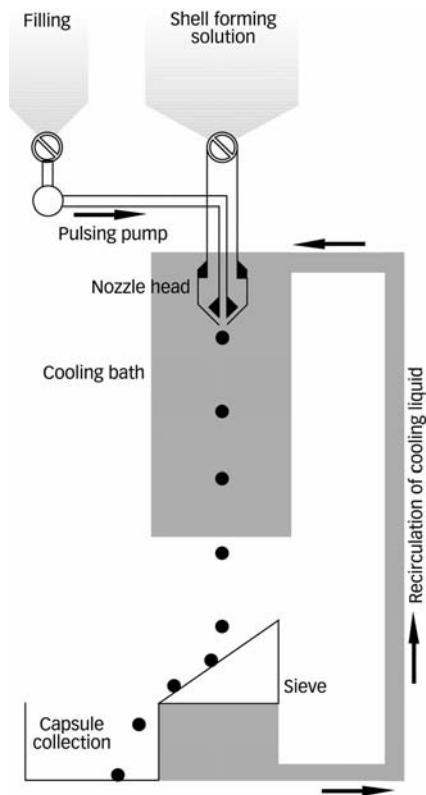


Fig. 3.76 Globex Process for the production of seamless soft shell capsules.

ing various active substances that may normally be incompatible by dispersing them in an oil-based formulation.

The designation soft shell capsules does not necessarily mean that the texture is soft; it simply indicates that, in addition to gelatine, the shell contains plasticizers. Such plasticizers ensure that the capsules retain their elasticity during the drying process and subsequent storage, i.e. they do not become brittle. Water loss during drying causes the gelatine gel to shrink somewhat, a process that leads to tension within the capsule shell. As a result, toward the end of the drying process or if the capsules are subjected to mechanical stress at or around the seam (which is only about one third of the normal capsule wall thickness), cracks may appear and cause the capsule to burst (see Fig. 3.74).

The selection and concentration of the plasticizer together with the residual moisture and the thickness of the shell (normally 250–500 µm) determine the hardness and mechanical stability of the capsule. The plasticizer should not interfere with the formation of the stable three-dimensional gelatine network, nor should it affect the form stability of the finished capsule. Furthermore, there



Fig. 3.77 Soft shell capsules are produced, filled and sealed in one production step. They are completely closed units in different forms and colors. On the right a modern Scherer Rotary Die machine.

should be no interaction between the plasticizer and the active substances contained in the capsule; the chemical, hygroscopic, and other properties of the active substances as well as the excipients used should be taken into account to avoid this. The following polyalcohols are mostly used as plasticizers in soft gelatine capsule production:

- Glycerol (in 85–87% or 98% grades)
- Sorbitol (normally 70%, non-crystalline grade)
- Combinations of glycerol and sorbitol.

Glycerol is generally more effective than sorbitol; for certain active substances, however, its dissolution capacity is rather too high so that its use is limited. In such cases sorbitol is the preferred choice. Depending on the manufacturing process used, non-crystallizing sorbitol may contain variable amounts of starch degradation products such as glucose oligomers, cyclic compounds, and mannitol; these can influence the property profile of the soft gelatine capsules. In general, these capsules have a lower dissolution capacity for most active substances; they also demonstrate rather slow interaction with atmospheric moisture. One disadvantage of capsules containing sorbitol, however, is that they are much more brittle.

Today, worldwide, the vast majority of soft gelatine capsules are manufactured using the Rotary Die Process developed by Robert Pauli Scherer in 1930 in Detroit, USA. Depending on the size and shape of the capsules and the length of the die rolls used, such capsule machines can produce between 80 000 and 160 000 capsules per hour.

In the Rotary Die Process, a gelatine mass stored in heated stainless steel tanks maintained at about 60 °C is spread (by so-called spreader boxes) over highly pol-

ished air- or water-cooled stainless steel drums to form two continuous elastic-like films. Depending on the capsule size selected, the thickness of the films is 500–800 µm. To prevent the films and the capsules from sticking to each other, a fine coating of lubricant (e.g., paraffin oil, lecithin, or stearate) is applied to both sides of the films. The two gelatine films are then directed at an angle of 180° to two counter-rotating die rolls in opposite directions. A special filling device is located between the rollers; this fills the capsule being formed with the designated substance (see Fig. 3.77).

Liquids can generally be encapsulated directly or dissolved in an inert, water-free, lipophilic or hydrophilic diluent. Solids in contrast must be dissolved or suspended in suitable liquids. Much care has to be taken when formulating the contents of soft shell capsules. The active substance and any excipients required must be selected for each product according to stability and biopharmaceutical requirements, and possible interaction with the gelatine shell must also be taken into account. Many of the stability problems that occur with soft shell capsules result from interactions of hydrolysis-sensitive active substances with the residual water of the shell.

The capsule-filling device is thermostatted at 40–45 °C by means of an external water circulation system. This brings about a slight degree of melting of the surfaces of the gelatine films. This, in conjunction with the mechanical pressure subsequently applied by the die rolls, is a precondition for the hermetic sealing of the filled capsules.

The filled, sealed, and separated capsules are then fed onto a conveyor belt via a vibrating chute. This can be fitted with a washing device for removing any residual lubricant from the surfaces of the capsules. In a subsequent drying stage lasting some 2 h, atmospheric air at 25 °C and 25% rel. humidity is used to remove about half of the original 40–50% water content. Drying to a final moisture content of 6–8% takes place over a period of 3–8 days in air-circulation drying chambers at 20–25 °C and 20–30% rel. humidity.

After the encapsulation and drying steps, a variety of product modifications can be carried out if desired. Enteric-coated capsules (for contents that can become unstable at the acid pH of the stomach) can be prepared using the following methods:

- Subsequent hardening of the gelatine capsule shells with aldehydes (e.g., formaldehyde) or reducing sugars
- Coating the finished capsules with a gastric juice-resistant film (e.g., polymethacrylate dispersions or cellulose acetate/phthalate)
- Processing gastric juice-resistant substances into the gelatine shell or using alternative shell materials.

Soft shell capsules administered orally generally release their contents within 2–10 min. The specific effect, timing, and duration can be determined by altering the formulation of the content and the capsule shell.

Soft shell capsules can also be used for rectal and vaginal applications. Special capsules for chewing and biting have also been developed for resorption via the mucous membranes in the mouth. On biting, the capsule content is immediately released. One well-known example of this type is the capsule containing nitroglycerine preparations for use in acute coronary conditions. A further form of soft gelatine capsule is the tubular form; these are used for topical applications. In the 1960s and 1970s, cigarette lighter fuel was also packaged in tubular capsules. Regardless of the form of the capsule required, the optimal gelatine type can be selected.

3.2.6.2.3 Property Profile of Capsule Gelatine

Besides the minimal requirements specified by the various pharmacopoeias, other criteria are important if soft gelatine capsules are to be produced continuously and economically: apart from being able to form a mechanically stable and quick-setting film of constant thickness, it is important that the film itself is elastic enough to enable it to survive the individual process steps without becoming damaged. For example, the cast and set film must be able to be removed from the cooling drum and it must be able to form a stable seam within the required temperature range during the production and filling processes. The freshly formed soft gelatine capsules must also be mechanically stable enough to retain their shape and to be dried within a defined period of time.

If all of these requirements are to be fulfilled, the gelatine for soft shell capsules used must have the following minimum profile parameters:

- The mean gel strength must be within the range 150–200 Bloom depending on the capsule type, whereby the ratio between high- and low-Bloom components must be in special balance. Long-chain gelatine structures are essential for the mechanical stability of the film, especially during production and storage; short-chain components on the other hand allow the short-term melting of the plasticized gelatine film when the seam is being formed.
- The viscosity, depending on the type of gelatine, should, in a 6.66% solution at 60 °C, be 2.5–4.5 mPas. The viscosity of the soft shell capsule gelatine is crucial for the setting performance of the gelatine mass used.
- The thermal degradation behavior of soft shell capsule gelatine is economically decisive for the entire production process. The “window” between manufacture of the gelatine/plasticizer/water mass and final processing in the capsule machine can be as much as 24–36 h in practice; however, hydrolytic degradation brought about by storage temperatures between 60 and 65 °C should not exceed a certain limiting level, otherwise the mechanical properties of the cast and set film and finished capsule may be negatively affected. This process

causes high molecular weight components of the gelatine ($\geq 400 \text{ g mol}^{-1}$) to be split into medium-sized and small fragments. Some soft capsule manufacturers use this “aging” effect to deliberately reduce the viscosity of highly concentrated gelatine formulations. Here, the concentration of the gelatine employed is generally more than 44%.

- The particle size distribution of the gelatine used is also of major importance with respect to dissolving the gelatine: depending on the technical possibilities open to the customer, too high a proportion of gelatine particles $< 500 \mu\text{m}$ can lead to the formation of lumps and increased foaming during vacuum debubbling of the gel mass (see Section 3.1.2).

The gelatine types mostly used for the production of soft shell capsules, including viscosity and Bloom ranges, are summarized in Table 3.48.

The selection of the specific type of gelatine to be used is dependent on technological properties such as the type and composition of the plasticizer system, the formulation of the filling material to be encapsulated, the cost of the gelatine, and specific customer requirements. For pharmaceutical and food additive applications, medium-Bloom bone and hide gelatines are frequently used. 200-Bloom acid bone and pigskin gelatine types are preferred for the encapsulation of hygroscopic and water-sensitive active substances. These gelatine types, because of their favorable Bloom/viscosity ratios, can be used for formulations containing less water; in addition, they can be dried more quickly. Blends of gelatine of less than 100 Bloom with medium-Bloom types are more suitable for the formulation of chewable soft gelatine capsules.

In addition to the soft capsule gelatine types listed in table 1, certain types of gelatine obtained from poultry or warm water fish can be used; these are specifically listed in the European Pharmacopoeia (EPV 2005) as pharmaceutical gelat-

Table 3.48 Physical-chemical properties of pharmaceutical soft shell capsule gelatine.

Gelatine type	Raw material	Type	Bloom range (10 °C/6.67%/7 h)	Viscosity range (60 °C/6.67%)
160 LB	Bone*	B	155–185	3.4–4.2
160 LH	Bovine hide	B	150–170	3.5–4.2
160 LB/LH	Bone*/bovine hide	B	150–170	3.5–4.2
200 AB	Bone*	A	180–210	2.7–3.2
200 PS	Pigskin	A	190–210	2.5–3.1

*Can be bovine and/or porcine bone.

Blends of alkaline- and acid-conditioned gelatine can also be used for certain types of capsules.

tines. As an alternative for customers who wish to avoid using gelatine of bovine or porcine origin, poultry and fish gelatines have a similar technological profile to those of mammalian origin. The higher price, limited availability, and to a certain extent differing technological properties (e.g., cold water fish gelatine) have to date restricted their use.

The same applies to biotechnologically produced gelatine: because of the extremely high costs involved, its unclear regulatory status, and inadequate gelling and setting profile, it is still not a real alternative for capsule manufacture.

Modified gelatines, in contrast, have established themselves on the market. A number of international pharmaceutical customers are using succinylated pigskin gelatine of 185–215 Bloom and a viscosity of 3.30–4.10 mPas. This special gelatine is produced by reacting pharmaceutical pigskin gelatine with succinic acid anhydride. In this reaction, the side chain amino groups of peptide-bound lysine residues are completely blocked. They are thus no longer available for cross-linking reactions with the reactive groups of the capsule contents, e.g., traces of aldehyde present in natural product extracts. These undesired “hardening reactions” otherwise lead to increased brittleness when such soft shell capsule products are stored; in fact, they sometimes become completely insoluble and present problems in releasing the active ingredient.

The regulatory status of hard shell capsule gelatine corresponds more or less to that of soft gelatine; the only exception is in the case of USP/NF – that approves the use of up to 1500 ppm SO₂ for hard capsule gelatine.

A high degree of thermostability is expected of hard shell capsule gelatine solutions during storage, as the dipping process is practically continuous. Fresh gelatine solution is continuously taken from a reservoir subjected to temperature and viscosity monitoring and pumped into the dipping tank. Here it may have to remain for some considerable time until used up. If the gelatine were to lose too much quality, the physical data would be altered and quality fluctuation would result.

The decisive quality criteria for hard capsule gelatine are uniform flow during the dipping process to ensure constant capsule thickness, reproducible setting of the thin gelatine film around the metal cracking pins of the capsule machine, excellent drying, and a high degree of capsule elasticity to prevent splintering during the final cutting process.

To determine the loss in viscosity of the gelatine used, the decrease in viscosity of a 12.5% gelatine solution is measured after storing for 18 h at 60 °C. Depending on the customer specification and the type of gelatine used, the loss of viscosity should not exceed the range 18–24%.

Because of the increased use of fully automatic high-performance hard capsule filling machines with capacities of 100 000–200 000 capsules per hour, the requirement profile with respect to surface properties of the empty hard shell capsules has increased drastically. In order to improve the gliding properties of the hard shell capsules during the filling process and hence to prevent blockages and automatic shutdown of the machine, lubricants such as sodium lauryl sulfate (SLS) are added to the gelatine mass.

The titanium dioxide added for the production of opaque hard shell capsule formulations reduces the electrostatic charge on the capsule surfaces; this also contributes toward improved gliding properties. In general, the dose used, based on the weight of gelatine, is 1000–2000 ppm. As an alternative, the natural fat content of the gelatine can be increased by altering the process steps during production.

The elasticity of the gelatine after drying is a decisive factor when the capsule ends are being cut. The natural elasticity of the capsule after drying is highest in limed bone gelatine; this is followed by hide and pigskin gelatines. Industrial practice has shown that hard gelatine capsules made from limed bone gelatine retain their initial elasticity best on storage over longer periods if the moisture content is kept between 13 and 14%. Capsules made of 100% pigskin gelatine lose a considerable amount of their elasticity after a period of 3 months even if stored under the recommended conditions for hard shell capsules of 15–25 °C and 35–65% relative humidity. They also tend to become somewhat brittle. Hard shell capsules made of hide split gelatine or blends containing some pigskin gelatine are much less brittle. There is as yet no sound scientific explanation for the increased brittleness of pure pigskin gelatine hard shell capsules.

The elasticity of empty hard shell gelatine capsules and encapsulated products can be improved for storage purposes by adding highly disperse silica to the gelatine mass. The dosages are approximately 1000 ppm for clear capsules and up to 3000 ppm for opaque capsules.

Table 3.49 lists the main characteristics of the most important hard shell capsule gelatine types.

The capsule industry often uses pre-prepared gelatine blends of different types and origins, and in some cases these ready-made blends are obtained from gelatine manufacturers. As a result of the implementation of more stringent conditions regarding the stability testing of pharmaceutical products such as gelatine capsules or gelatine-coated tablets, an increase in the number of problems connected with solubility has been reported. The tests, carried out according to ICH guidelines, involve storing empty or filled capsules at 40 °C and 75% relative humidity for at least 6 months. Often, however, the release rates of the active ingredients in water at 37 °C, as required by the authorities and documented in the dossiers, cannot be achieved. The main reason for this is cross-linked and hence

Table 3.49 Physical-chemical properties of pharmaceutical hard shell capsule gelatine.

Gelatine type	Raw material	Type	Bloom range (10 °C/6.67%/17 h) [g]	Viscosity range (60 °C/6.67%) [mPa s]
LB	Bovine and/or porcine bone	B	220–260	4.4–5.0
PS	Pigskin	A	240–280	4.2–4.8
LH	Bovine hide	B	200–270	4.2–5.0

water-insoluble gelatine that has formed under the influence of temperature and high humidity. Reactive components present in trace amounts in the active ingredient and the excipients used favor such reactions.

In almost all cases, the so-called “two-tier test” (a test using release medium with added pepsin or trypsin) that has been approved by the United States regulatory authorities produces the desired results; the capsules thus provide the required fast release of the contents. *In-vivo* tests carried out on stress-stored selected products also resulted in acceptable release rates.

3.2.6.2.4 Alternative Capsule Materials

Alternative capsule materials have been sought since the 19th century. The initial reason for the search was to find a way around the manufacturing patent for gelatine capsules. Today, the pharmaceutical industry is simply attempting to expand its product range in order to meet the requirements of new target groups of customers such as vegetarians who refuse to consume products of animal origin. Another reason is the fact that customary gelatine capsules produced using complex filling formulations sometimes give rise to stability problems or incompatibilities.

If a substitute product for gelatine is to be used in conjunction with current technology, it must possess two basic properties: it must be an excellent film-forming polymer and have good gel-forming properties.

The first gelatine-free capsules to be manufactured on a larger scale were made from methyl cellulose (MC). MC can be processed to hard shell capsules on standard machines; however, the temperature must be adjusted, as it is different from that required by gelatine. The pins used with the polymer solution must be thermostatted so that they can be dipped at room temperature; in this way, the polymer sets on warming when the pins are withdrawn from the solution. In comparison, in the production of gelatine hard capsules, the pins are dipped in the warm gelatine solution at room temperature and the gelatine sets on cooling once the pins are withdrawn.

Methyl cellulose hard shell capsules manufactured using this method were on the market for a number of years. However, their *in-vivo* dissolution properties proved most unsatisfactory; in some cases, the capsules were excreted from the body still intact. Consequently, manufacture ceased.

Using this modified MC process, hydroxypropylmethyl cellulose (HPMC) capsules were also produced. One disadvantage encountered, however, was that, even with the same wall thickness as gelatine capsules, the mechanical stability proved inadequate. This particular problem was essentially solved by doubling the thickness of the capsule wall and tackling a few other technical problems connected with the dipping and drying processes. However, production of these capsules is still on a low level.

An alternative route is the blending of HPMC with other hydrocolloids such as gellan gum (International Patent PCT No. 98/27 151; European Patent No. 1 057862) or with kappa carrageenan (US Patent No. 5 756 123, 1998) along with the additives required for gelation. In this case, the process is similar to that using gelatine, i.e. the cold metal pins are dipped in the warm solution (see Fig. 3.78).

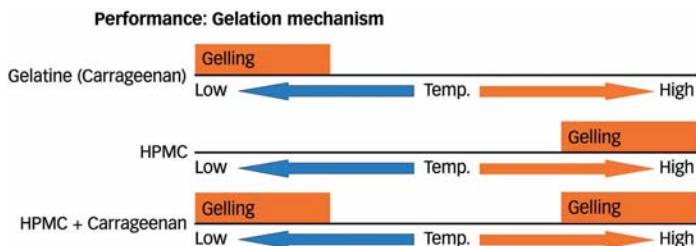


Fig. 3.78 Gelling behavior of alternative capsule materials.

Capsules produced by this method have the same dimensions and similar filling characteristics to gelatine hard shell capsules. HPMC capsules cannot always be used for prescription medicines for a number of biopharmaceutical reasons: capsules containing gellan gum, for example, have a limited release profile in acid media and hence in the stomach of the patient. The release kinetics of active ingredients from HPMC capsules is dependent on the electrolyte balance; for example, the potassium ions that occur in high concentrations in certain types of fruit result in the slow dissolution of HPMC/kappa carrageenan capsules shells.

Furthermore, the oxygen permeability of HPMC capsules is much higher than that of gelatine capsules. Capsules made of substances based on cellulose and starch are thus unsuitable for use with active substances and excipients that are susceptible to oxidation.

Pullulan capsules in contrast have better oxygen barrier properties; however, the reduced bioavailability at acid pH and in the presence of potassium is similar to that of HPMC capsules. Pullulan is a film-forming extra-cellular polysaccharide based on polymaltotriose that is formed by fermentation of a certain species of yeast. Kappa carrageenan is used as a gel-forming polymer, and potassium chloride as an accelerator. This type of hard shell capsule formulation can be processed with currently available hard capsule machines.

The manufacturing costs of “non-gelatine hard shell capsules” are much higher than those for classical gelatine capsules because of the very much higher material costs and the slower machine speeds. Even the costly development of starch hard shell capsules using the high-pressure extrusion method did not result in a marketable product; this was mainly because the mechanical stability and dimensional accuracy were inadequate for subsequent filling and packaging. The high degree of precision required of capsule dimensions can only be perfectly fulfilled today by gelatine capsules.

A number of systems were also developed for the production of gelatine-free soft shell capsules. One example was based on native and modified starches, plasticizers, and excipients; these were processed to a semi-opaque plasticized product and subsequently extruded as a thin film. As in the case of gelatine, the starch films are run onto two oppositely rotating dies and simultaneously injection-filled with product. The contents, as in the classical Rotary Die process, have to be non-aqueous liquids or paste. As the capsule shell is essentially free of water, the fin-

ished capsules can be filled and packed without the need for an additional drying step.

In a second process, the capsule shell is made of hydroxypropyl starch as the film-forming component, iota carrageenan/sodium phosphate as gelling agents, and glycerol as the plasticizer. Film formation and encapsulation take place at temperatures in excess of approximately 90 °C because of the high melting point of the capsule wall material. This presents a problem with some capsule contents. Subsequent drying is carried out until a certain degree of capsule hardness is attained.

The performance profile of soft starch capsules such as the absorption of moisture, oxygen permeability, and long-term chemical stability is described as being “close to gelatine” by manufacturers. Subsequent to swelling in gastric juice, the soft gelatine capsules are opened by breaking the capsule seam.

For technical (e.g., paint balls) and cosmetic applications, a further method for the production of starch-free soft shell capsules from pre-processed plasticized film material was developed. The capsule material selected was polyvinyl alcohol with glycerol as plasticizer or HPMC/PEG. However, as these materials have either not yet or only to a restricted extent been approved for pharmaceutical applications, this particular product concept is little used.

In summary, it can be said that all alternative capsule materials have a combined market share well below 10%. This is because the advantages offered by gelatine have not been attained.

3.2.6.3 Plasmas Substitutes

Plasma substitutes based on gelatine have been used in emergency medicine and major surgery for decades. The main application of these gelatine-based products is replacing lost blood until such time as the body can regenerate itself or adequate amounts of suitable whole blood are available for transfusion.

As aqueous gelatine solutions, even in low concentrations of around 1%, begin to gel at room temperature, the chemical structure of the gelatine used must be modified for this particular application. In a first step, the mole mass distribution of the gelatine – in general high-Bloom limed bone gelatine with a molecular weight of 160–180 000 g mol⁻¹ – is reduced by thermal treatment to approximately 10 000 g mol⁻¹. It is then chemically modified using a number of reactive substances; these convert the chain-like molecular structure to a more globular one with a molecular weight of approximately 30 000 g mol⁻¹. Depending on the manufacturer, this can be achieved using a number of compounds:

- Glyoxal (reaction with the amino side chains of lysine)
- Succinic acid anhydride (formation of carboxylic acid amides by reaction of the amino groups of lysine and succinate)
- Phenyl-diisocyanate (cross-linking of peptides with the formation of urea structures).

In commercially available products, the proportion of modified gelatine is 3.0–5.5%. The solution is supplemented with sodium, potassium, calcium, chloride, phosphate, and sulfate ions in order to obtain an isotonic solution and hence the

correct osmotic pressure. All the products have a gelation point under 3 °C; they can be kept at room or refrigerator temperature for at least 7 years.

Because of the conversion from a linear to a globular structure, the gelatine diffuses more slowly through the arterial walls. In animal studies, a half-life value of 4–5 h was established; after a period of 24 h, 3–8% and after 48 hours 0–3% of the product was detectable. Most of the degradation products are excreted with the urine. In contrast to products containing gelatine, those based on dextran, hydroxyethyl starch or polyvinylpyrrolidone (PVP) often produce allergic reactions in patients; furthermore, they are retained longer in the body and sometimes accumulate in various organs.

3.2.6.4 Vitamin Coating

The fine dosing of oily substances such as vitamins A and E, long-chain fatty acids and carotenoids for food, animal feed, and pharmaceutical applications is a special challenge. By embedding these products in a gelatine matrix they can be converted into easily dosable free-flowing powders; at the same time they are protected from the damaging influence of light and atmospheric oxygen. Unsaturated fatty acids in foods and pharmaceuticals for example do not become rancid when processed or stored if they are processed in this way.

Starting with a highly concentrated emulsion of gelatine, various sugars and up to 25% oily vitamin substance, the manufacturer can produce a powdery product by carrying out a double-emulsion process (US Patent 3 143 475) followed by spray- or fluid bed drying. For protection purposes and in order to increase mechanical stability, such pharmaceutical and food products are coated with starch; animal feed products are coated with highly disperse silica. Primarily, type A and type B gelatines of 90–140 Bloom are used for this purpose; however, for cold-water-soluble vitamin preparations, gelatine hydrolysates and, for special applications, high-Bloom gelatines can be used. The size of the drops of oily substance in such a gelatine/sugar matrix is approximately 1 µm; the overall particle size is 200–300 µm (see Fig. 3.79). Such powdered products are extremely stable; they can be converted into tablet form without disintegrating.

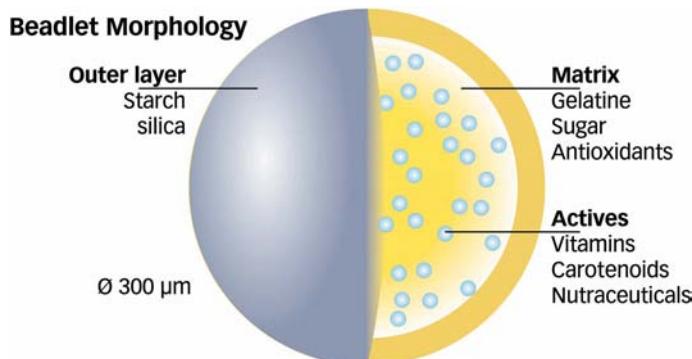


Fig. 3.79 Model structure of spray-dried and coated vitamin powder based on a gelatine matrix.

3.2.6.5 Other Gelatine Applications in Pharmaceutical Technology

Gelatine has also been used for many years in the wet granulation of numerous pharmaceutical products. Normally, an aqueous solution of medium-Bloom gelatine of 1–10% concentration (based on mass of powder) is used. The granulates can subsequently be processed to tablets or filled into hard shell capsules.

In the manufacture of pastilles, gelatine can be used to improve the binding power between the various components; it also facilitates resorption without accompanying irritation.

In the production of sugar-coated tablets, a thin coating of gelatine is applied to the active ingredient core; this improves the binding properties of the outer sugar coating.

Gelatine and gelatine hydrolysate are also being increasingly used in the formulation of new vaccines. The mode of action is based on their stabilizing the vaccine via protein-protein interaction. The specification required for this application is extremely high; among other requirements, it must be pyrogen-free, otherwise increased temperature could occur in the patient.

A more traditional use of gelatine is in the production of globules or of Unna's paste dressings. Several cosmetic products contain gelatine as a gel-forming or thickening agent.

3.2.6.6 Medical Applications

Gelatine is regarded as an innovative excipient in modern medical technology. Among its numerous applications, it is used as an adhesive in the implantation of heart valves in microsurgery. The adhesive in question is a dual-component product comprising a gelatine/resorcinol solution and a hardener (www.berlinheart.de). Both are contained in a dual-chamber syringe that is available for use at short notice. The special gelatine selected for this particular application has a very high specification, e.g., it must have the lowest possible endotoxin content.

A second surgical example is in the treatment of intestinal obstruction. In this application, a probe is inserted into the stomach via the mouth and ultimately into the small intestine. In contrast to the traditional balloon probes, this type of gelatine-headed probe reaches its destination without any problems.

The head of the probe is made of soft gelatine, while the shaft is of hard gelatine; both are connected by a silicone tube through which medication can flow or intestinal splinting carried out (see Fig. 3.80). The gelatine head is warmed immediately prior to the operation to optimize its lubricating properties. After 40–60 min, the head dissolves completely inside the body. Thanks to its optimal bioavailability, the gelatine does not attack the highly sensitive intestinal mucous membrane. In Germany alone, some 70 hospitals are working with this new technique.

Gelatine sponges (see Fig. 3.81), also used in surgical and dental applications, remain in the body to be resorbed after use. These extremely safe hemostatic agents have also been in use for decades. They are used to absorb blood and other body fluids and can absorb up to 50 times their own weight of fluid. Generally, they can stanch blood flow within minutes by adhesion and aggregation of the

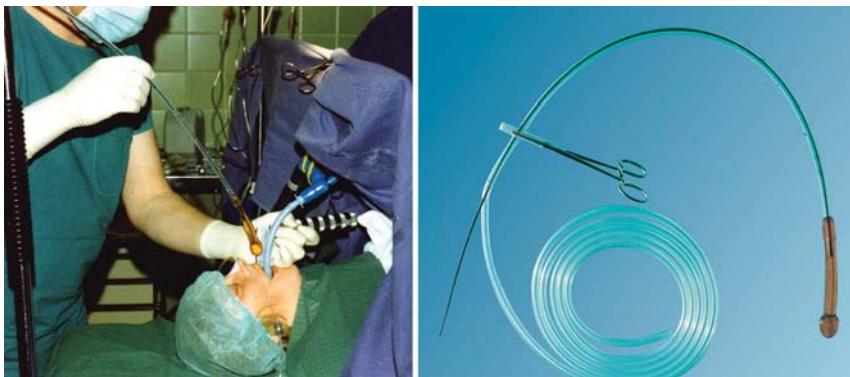


Fig. 3.80 A modern surgical application of gelatine is in the treatment of intestinal obstruction. After 40–60 minutes, the gelatine head of the probe dissolves completely within the body.



Fig. 3.81 Gelatine sponges for surgical and dental applications.

blood platelets. The sponges are also completely absorbed by the body, and the surrounding tissues do not react by encapsulating the foreign material. Such encapsulation processes, which frequently occur when other types of hemostatics are used, present a considerable problem when treating a wound after an operation.

Gelatine sponges, apart from their blood-stanching properties, also facilitate the migration of new tissue cells, hence accelerating the healing process. The sponges are produced by foaming aqueous pharmaceutical gelatine solutions. The pore structure is determined by selecting the correct process parameters such as concentration, speed of the foaming equipment and temperature. The normal pore diameters are approximately 350 µm. The degree of cross-linking selected determines the amount of time they remain in the body until completely dissolved. This degradation rate corresponds to the specifications of the various pharmacopoeias for hemostatic sponges; using a special digestive cocktail con-

taining 1% pepsin at pH1, the sponges dissolve within 75 min. The dissolution time can be widely varied depending on the specific application. Highly cross-linked sponges can thus be prepared that remain stable for up to 6 months *in vitro* without losing its good biocompatibility. Hemostatic gelatine sponges can be impregnated with antibiotics, thrombin, or chemotherapeutic substances whilst retaining their blood-stanching properties.

Smaller gelatine sponge particles on a millimeter scale can also be used in minimally invasive techniques, such as the treatment of uterine myomas that cannot be removed surgically; instead, the blood and oxygen supply are interrupted, thus “starving” the tumor. Currently, polystyrene and polyvinyl beads are used for this purpose and are brought by arterial catheter directly to the location of the tumor. These synthetic polymers, however, degrade very slowly and can lead to problems; these can be avoided by using gelatine sponge particles.

For the future, researchers have great expectations of making further progress, especially in regenerative medicine. Regenerative medicine is based on the reproduction of the patient’s own cells in the laboratory; these can then later be implanted at the location of the damaged tissues. There is indeed a very high demand for suitable carrier matrices for regenerative medicine, as most human cells require a matrix onto which they can adhere and grow. The best possible matrix would be human collagen. However, as this is not available, numerous attempts have been made over the past few decades to find suitable bio-compatible materials for the purpose.

These materials can be roughly divided into three groups: natural biopolymers, processed biopolymers, and synthetic polymers (see Table 3.50).

Most of the biomaterials used currently originate from animal connective tissue, as this represents a known surface for the cells. The main disadvantage of such materials is the fact that the product properties are difficult to control; also, the source of the material is frequently uncertain. In contrast, the product param-

Table 3.50 Selection of polymers used for the development of carrier material.

Polymers for matrix systems		
Biopolymers	Processed biopolymers	Synthetic polymers
Collagen	–	Polylactate
Hyaluronic acid	–	Polycaprolactone
Alginates	–	Polyurethane
–	–	Polyethylene terephthalate
–	Chitosan	–
–	Oxycellulose	–
–	Gelatine	–

Table 3.51 Advantages of gelatine.

-
- Well established as a pharmaceutical excipient
 - Well tolerated in food
 - GRAS status
 - Excellent cell compatibility
 - Highly reproducible production
 - Highly purified, no risk of contamination from natural sources
 - Minimized immunogenicity
 - Well-controllable physical parameters
 - Variety of types/qualities available
 - Amphoteric biopolymer
 - Engineerable biopolymer.
-

eters of synthetic polymers can be precisely and reproducibly determined. Availability is also rarely a problem. On the other hand, such synthetic polymers often give rise to local incompatibilities; critical and even toxic reactions can take place brought about by residual monomers and incompatible degradation products.

Thus, processed biopolymers that can combine the positive properties of natural and synthetic biopolymers have a distinct advantage.

Gelatine belongs to the group of “processed biopolymers”. It is produced on a large scale and in reproducible quality by the chemical hydrolysis of collagen. Its properties can thus be controlled in a similar way to those used for synthetic polymers, and its primary sequence of peptide chains is essentially the same as that of native collagen.

Thus, from the point of view of the developer of medical products, gelatine offers decisive advantages (see Table 3.51).

The first successful human trials on the use of a gelatine matrix were carried out on patients suffering from Parkinson's disease. In this study, cells were isolated from the retinas of donors. These are the cells that produce dopamine, the absence of which gives rise to Parkinson's disease. The cells were then implanted into the brains of the volunteers in a matrix of gelatine particles. The patients' symptoms significantly improved. This new cell transplant therapy using gelatine in the form of microcarriers is now verified in a multi-center study, phase II, promoted by an international pharmaceutical group (www.schering.de/scripts/en/30rd/areas/neuro/parkin.php).

A further example of possible future application of biodegradable matrices is in the development of protective nerve sheaths. In Germany each year, some 400 000 injuries to the peripheral nervous system are treated using neurosurgery. To date, treatment has been less than optimal, as nerves that have been severed tend not to fuse together again because of the formation of scar tissue. The problem to be

solved is that the surrounding tissue grows more rapidly than the remaining ends of the nerve cells. In addition, no commands can be given by these nerves as to the direction of growth. One possible solution would be the implantation of protective nerve sheaths, a sort of growth tunnel that would enable the nerve endings to grow without being disturbed by the surrounding tissue. Materials such as synthetic plastic used to date have proven only partially successful, mainly because the sheaths have to remain in the body after the operation. Thus, the search has been intensified for biodegradable materials that can be left in the body. The first *in-vitro* experiments with very fine gelatine sheaths have shown that they possess the required mechanical stability for the duration of the healing process. In addition, the supply of nutrients is guaranteed.

The most modern aspect of regenerative medicine is tissue engineering. In this technique, the body's own tissue is used to prepare a tissue transplant; in this way, tissue rejection is avoided. The cells taken from the body are reproduced externally and embedded in a suitable carrier material. Once the tissue grows, it is implanted in the patient together with the carrier matrix. The applications extend from replacing burnt skin to replacement parts for the skeletal system.

In Europe today, some 25 000 people are living with implanted skin, cartilage, and bone cells; heart valves, blood vessels, ears, and teeth are planned to follow. Scientists, using a step-by-step technique, have already grown complete mandibles including bones and gums (www.wga.dmz.uni-wh.de). In addition, the organic molecules in dental enamel can be replaced by gelatine (www.cpf.s.mpg.de). In this technique, various gelatine layers containing calcium, phosphate, and fluoride ions are coated onto the teeth. Once the ions come together, they form parallel apatite crystals along the gelatine fibers; these behave in the same way as natural dentine and are just as hard. An international company is already planning medium term to market a corresponding toothpaste.

3.2.7

Photography and Ink-jet Printing

Gelatine is an indispensable coating agent in analog photography. Gelatine solutions are transparent and colorless – essential preconditions for photographic applications. They act as binding agents and also prevent the light-sensitive silver halides from coagulating. Interaction with the halides enables the required highly sensitive photographic emulsions to be formed. Furthermore, gelatine is an important component for stabilizing oil/water emulsions (see also Section 2.1.2.6) of dyes and color couplers essential for the image-forming layers in color photography. Because of its property of forming thermoreversible gels, gelatine enables photographic emulsions to be permanently coated onto supports such as transparent film and photographic paper. Just as important is its ability to swell in a controlled manner, hence making the reproducible development of photos possible. The fine grain quality, the color density, and the color permanence made possible by gelatine are today's standards. This combination of properties inherent in

this one substance still remains unequalled, even by the newer complex synthetic polymers.

3.2.7.1 Characteristics of Photographic Gelatine

Based on its photographic behavior, gelatine is designated as inert, semi-inert, or active. The reason for this classification is that certain components of gelatine can influence the ripening process of modern silver halide emulsions in a positive or negative way. In the past, only ossein-derived type B gelatine was photographically neutral in behavior because of the intensive and time-consuming processing it had to undergo. Hide gelatine on the other hand sometimes contains thiosulfate and other compounds that can lead to undesirable side reactions. Today, however, the thiosulfate can be neutralized using a special process, so that this type of gelatine can also be used for inert photographic coatings. The presence of calcium ions also has to be taken into account. Depending on the production process involved for photographic emulsions, calcium may be required in concentrations ranging from 0 to several thousand mg kg⁻¹. Today's technology, combined with sophisticated process controls, allows the production of photographic gelatines with precisely defined salt levels, particularly calcium, required for the photographic application.

Classical photographic gelatine is characterized by a Bloom value of approximately 260–280 g and a standard viscosity greater than 5 mPas. This specification is optimal for stabilizing emulsions and producing the required quality of film.

The setting behavior and swelling properties of gelatine are additional important parameters that characterize photographic gelatine. While the setting time is of fundamental importance for the production of modern photographic products, excellent swelling properties have a positive effect on the processing speed in the photographic laboratory.

These properties can be optimized by the selection of raw materials, the methods used for processing and modification, and the physical-chemical parameters specified for the application in question. Photographic gelatine with a Bloom value less than 200 can now be used for photographic materials that have been produced in part using other hydrocolloids and additives.

3.2.7.2 The Photographic Process

Photographic materials comprise a support such as paper or synthetic film onto which the silver halide crystals in a gelatine emulsion are coated in layers. Color films, for example, consist of up to 16 individual coatings containing gelatine, 8 or 9 at most of which are light-sensitive (see Fig. 3.82). The remaining layers are auxiliary and protective in nature; they optimize the color and sharpness of the final image, prevent the colors from mixing during the coating process, and protect the final surface. In both color and black-and-white films, a layer of pure gelatine is coated onto the rear side in order to minimize unwanted curling. X-ray films, in principle the same as black-and-white films, are coated on both sides with a photographic gelatine emulsion.

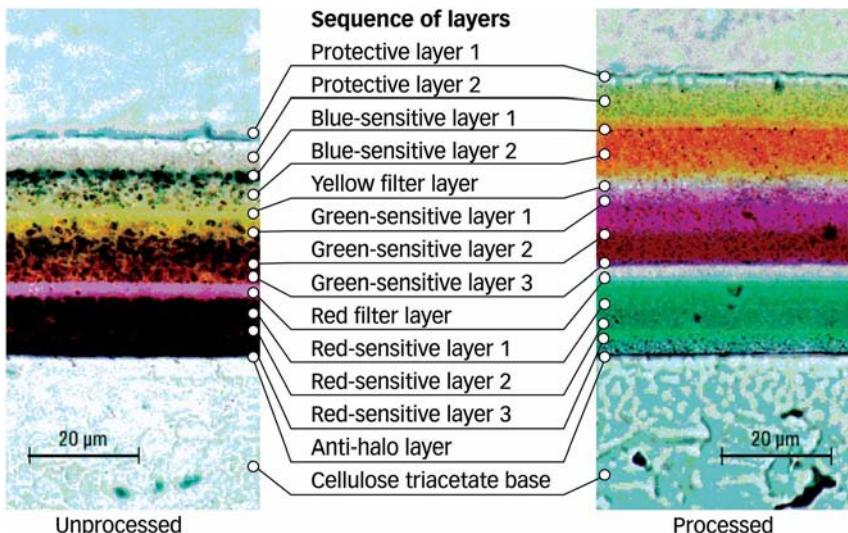


Fig. 3.82 Thin sections through a color-negative film (swollen in water; light microscope). Source: Folienserie “Fotografie”, Fonds der Chemischen Industrie Frankfurt, Germany.

3.2.7.2.1 The Emulsion

The tiny silver halide crystals embedded in the gelatine act as light detectors. Here, gelatine functions as a protective colloid (see also Section 2.1.2.8) by stabilizing the silver halide crystals and hence preventing them from agglomerating. This allows for controlled growth of the crystals (ripening) and also stabilizes the emulsion by preventing sedimentation of the crystals.

3.2.7.2.2 Exposure

During the exposure process, a latent image consisting of tiny particles of elemental silver, initially invisible to the naked eye, forms on the light-sensitive crystals.

This first step in the creation of a latent image (Ag_n) is the absorption of a photon of energy ($h\nu$) by the silver halide crystal (see Fig. 3.83). A photoelectron is released from a halide ion in the crystal lattice; this is then able to move freely within the crystal. The free electron position remaining after release of the electron from the halide ion is called a defect electron. Chemically, it corresponds to a halogen radical.

In a reverse process, defect electrons can react with the photoelectrons but can also attack, and destroy, the existing latent image elements. The gelatine surrounding the silver halide crystals prevents this undesired process; it reacts with the defect electrons that diffuse to the surfaces of the crystals, thereby neutraliz-

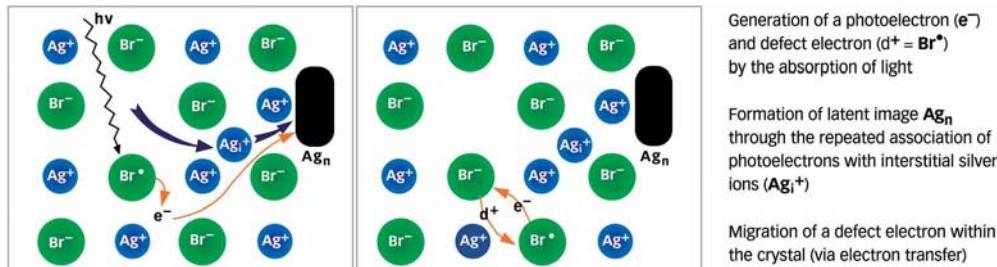


Fig. 3.83 Reactions within the silver halide crystal (exposure). Source: Folienserie "Fotografie", Fonds der Chemischen Industrie Frankfurt, Germany.

ing them. Gelatine thus enhances the photographic light sensitivity of the process. The simple change from collodion to gelatine as a binding agent for the silver halide crystals at the end of the 19th century shortened the exposure time required for a photograph from approximately 15 seconds to less than a second.

3.2.7.2.3 Development and Fixation

After exposure, the photographic image remains invisible until the development process, when it is enhanced by a factor of 10^{10} and becomes visible. During the development process, the silver halide crystals carrying latent image elements are chemically reduced to metallic silver by a reducing agent. During this process, the latent elements are supplied with electrons and silver ions from all sides by the liquid developer (see Fig. 3.84).

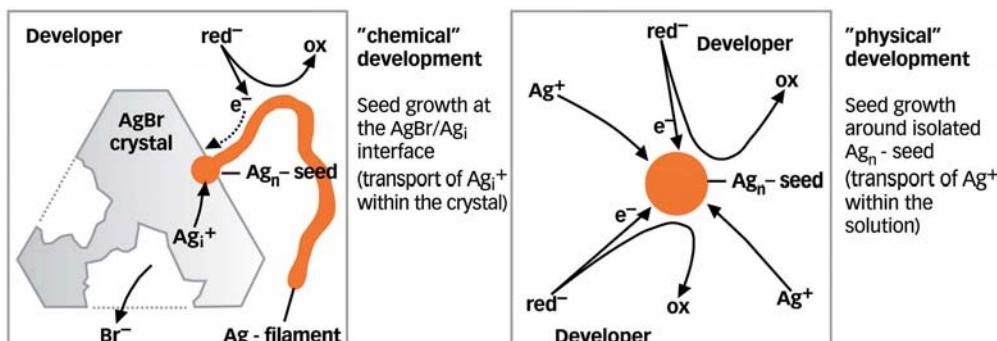


Fig. 3.84 Reactions within the silver halide crystal (development). Source: Folienserie "Fotografie", Fonds der Chemischen Industrie Frankfurt, Germany.

Black-and-white processing

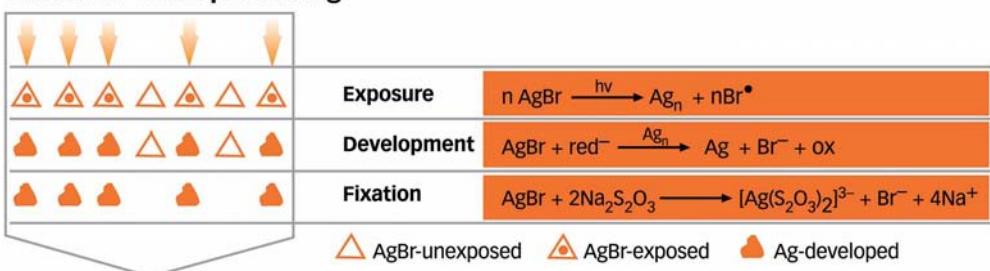


Fig. 3.85 Black-and-white processing from exposure to fixation. Source: Folienserie "Fotografie", Fonds der Chemischen Industrie Frankfurt, Germany.

The development process is then stopped at a predetermined time using a stop-bath containing, in the simplest case, dilute acetic acid. The next step is fixation by treatment with a thiosulfate solution; at this stage, any remaining unexposed silver halide is converted into a water-soluble complex (see Fig. 3.85). In the final rinsing process, the silver halide complex salts and any other residues diffuse out of the film layer. The developed silver image remains fixed in the gelatine. The critical factor in the development process is the reproducible diffusion of the chemicals onto the film. This is made possible by the swelling properties of the photographic gelatine layers.

Enlargement of the silver image to the final paper print is in principle a repetition of the exposure and development processes. Here, the negative is exposed onto photographic paper, which is also coated with a photographic gelatine emulsion. The result is a positive print of the image.

3.2.7.3 The Manufacture of Photographic Emulsions

In the manufacture of photographic film and paper, the main process steps are the preparation of the emulsion and the coating of the support material. The most important materials employed for the support material are polyesters, cellulose triacetate or, today, polyethylene-coated paper, and, for the emulsions, silver, gelatine, and special organic chemicals.

A photographic emulsion is a system comprising light-sensitive silver halide microcrystals and gelatine as a binding agent. On an industrial scale, photographic emulsions are prepared in reaction vessels of several thousand liters capacity. Using such vessels, and by precisely regulating the temperature of the reaction mixtures, vigorously stirring and precisely dosing, different emulsion formulations can be produced. pH sensors and pAg electrodes (for the measurement of the Ag^+ ion concentrations) are also employed. The reactions result in silver halide microcrystals of different sizes, shapes, and compositions with respect to the halides and other additives (see Fig. 3.86).

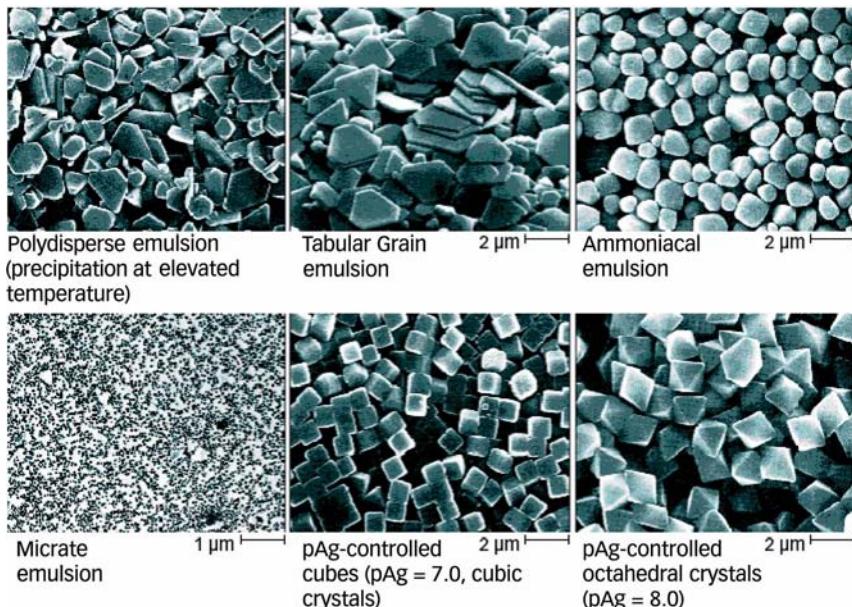


Fig. 3.86 Crystal shapes of photographic emulsions. Source: Folienserie “Fotografie”, Fonds der Chemischen Industrie Frankfurt, Germany.

Photographic characteristics such as sensitivity can be directly influenced in this way. The common steps for all types of emulsion are crystallization, the removal of soluble salts, and the physical/chemical ripening of the crystals.

3.2.7.3.1 Crystallization

When aqueous silver nitrate and alkaline halide solutions are brought together with vigorous stirring, over-saturation takes place because of the low solubility of the halides. Microcrystals form spontaneously, and these then precipitate. Precipitation takes place in an aqueous gelatine solution, which prevents agglomeration of the silver halide crystals. This protective colloid role during the precipitation of the silver halides is one of the most important functions of gelatine in the production of photographic emulsions.

The initial crystals produced are not all stable, and, if stirring is continued, the smaller ones redissolve and later recrystallize onto the larger ones. This process is due to the higher solubility of the smaller particles compared with the larger ones. Overall, during the stirring phase (the so-called “physical ripening” phase), the mean crystal size and the distribution range of the crystals increase, while the total number of crystals decreases (see Fig. 3.87). Thus, at this stage of the process, gelatine regulates not only the speed of crystal growth but also the mean crystal size.

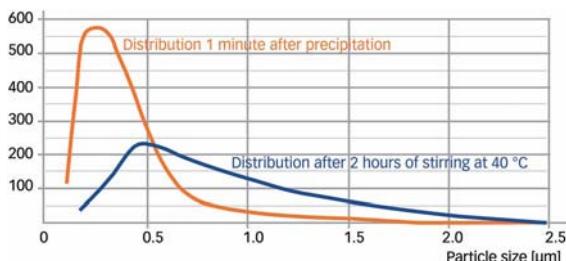


Fig. 3.87 Particle size distribution in physical ripening.

3.2.7.3.2 Removal of Soluble Salts

Residual salts such as KNO_3 that are present in high concentrations in the emulsion must be removed prior to further processing, otherwise they would crystallize after coating and drying. This would interfere with the photographic process and increase the brittleness of the photographic layers.

For this desalting reaction, the gelatine is modified by reaction or by the addition of suitable organic compounds. Alternatively, other specially modified gelatines are used so that they become practically insoluble in acid medium. They then flocculate and precipitate together with the dispersed silver halide microcrystals. The flaky precipitate is washed and decanted several times. The pH is then increased, which reconverts the precipitate into a colloidal solution.

Another modern technique for the removal of salts is ultrafiltration. This membrane-based process can separate the salts directly in the liquid phase so that the gelatine does not have to be solidified or coagulated.

3.2.7.3.3 Chemical Ripening

Photographic emulsions have a low level of sensitivity after precipitation and desalting; therefore, they must be chemically treated before being further processed. This chemical treatment of the crystal surfaces is known as chemical ripening or sensitization, and it again takes place in the gelatine solution. A combination of thiosulfate and gold(l) thiocyanate complexes has proven suitable for this process. This “gold-sulfur ripening” increases the sensitivity of the emulsion approximately 10–15-fold.

Silver halides absorb light, but only within the ultraviolet to blue range of the spectrum. Using special dyes – spectral sensitizers – the silver halide crystals can be rendered sensitive to green and red light, making them suitable for use in color film (see Fig. 3.88). The type, quantity, and specific process for absorbing the sensitizers onto the crystal surfaces varies from manufacturer to manufacturer.

The ripening and absorption processes described and the dye and coupling emulsions used in color photography are stabilized with gelatine.

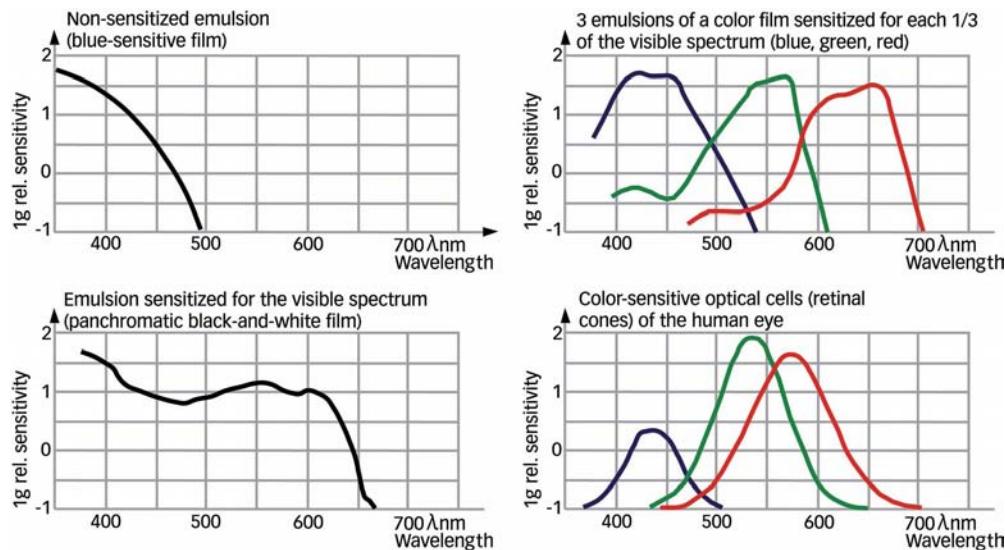


Fig. 3.88 Spectral sensitivity of AgBr emulsions and the human eye.

Source: Folienserie "Fotografie", Fonds der Chemischen Industrie Frankfurt, Germany.

3.2.7.4 Coating

Another important function of gelatine is its reversible gelling property. This ability allows emulsion layers poured successively onto each other to set quickly on cooling; the individual emulsion layers are thus securely fixed on setting.

Before the emulsion preparation is coated onto the support, an additional cross-linker may be added (see also Section 2.1.4); this helps to control the hardening process on the photographic material. The hardening process increases the viscosity of the gelatine solution and, at the same time, the solubility after drying is decreased or even eliminated. For this reason, it is important that the gelatine does not contain too many components of very low molecular weight. If this were the case, the gelatine would still remain soluble, especially as development of the films and photos takes place at about 40 °C in order to reduce the processing time. Hardening also exerts an influence on the swelling properties of the film.

The hardening agent is added to the emulsion immediately prior to its being applied to the support. Inorganic hardeners include, e.g., metal cations such as aluminum, chromium, and iron, and organic hardeners include, e.g., aldehydes, ketones, epoxides, isocyanates, and carbodiimides. Hardening by enzymatic cross-linking is another alternative.

In the past, emulsions were applied to the support material, e.g., film, layer by layer using an immersion process. The modern process involving 12 or more layers would hardly be possible using this method. Using modern cascade coat-

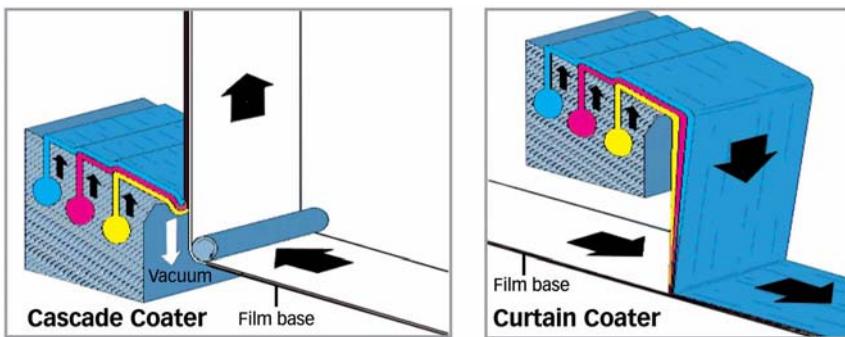


Fig. 3.89 Coating process (schematic) with cascade and curtain coater.

Source: Folienserie "Fotografie", Fonds der Chemischen Industrie Frankfurt, Germany.

ing equipment (see Fig. 3.89), several such layers can be prepared simultaneously; the layers can be coated simultaneously onto a support of up to 3.5 m wide, at a speed of 300 m min^{-1} (photographic paper) and with a coating thickness of $10 \mu\text{m}$.

A so-called curtain coater, a further development of the cascade coater, allows even higher coating speeds. Both of these processes allow precise dosing; the amount of coating per unit time is regulated precisely by dosing pumps.

In cascade coating, the coating solutions are pumped through slits onto a slanting plate where they run off by gravity. The solutions must be superimposed in a laminar fashion so that there is no mixing of the coatings. In this particular production step the viscosity of the gelatine emulsion is of major importance as it exerts considerable influence on the flow properties and prevents the different layers from mixing. Therefore, the viscosity must be kept as constant as possible over the entire coating process.

At the bottom of the cascade run-off plate, the support film to be coated runs at high speed in close proximity to the coating edge. As negative pressure exists here, some of the solution is drawn into the interstitial space, pressed firmly onto the rapidly moving film, and hence transported onwards. Because of the much higher speed of the moving film with respect to the emulsion, the latter is stretched by a factor of up to 50. In this way it is possible to produce a bundle of thin layers – the dry thickness of individual coatings is in the range of $0.5 \mu\text{m}$ – at high production speeds.

Immediately after coating, a cooling process takes place during which the emulsion sets. In this process, the setting behavior of the gelatine is an important parameter. Once set, the emulsion is dried and becomes more concentrated. Relatively dry warm air absorbs any water present in the layer. The process must be a gentle one, i.e. the temperature must not be too high as the mechanical properties of the binding agent, gelatine, are dependent on the selected drying conditions.

3.2.7.5 Ink-jet Media

Gelatine was one of the first substances used by paper manufacturers to improve the properties of their product; as early as the 13th century Italy, paper fleece was saturated with a gelatine solution. This “animal glue” enabled the absorption qualities of the paper to be controlled, with the result that the ink used for writing no longer tended to smear. At the same time, the glue improved the smoothness and the gloss of the paper as well as its firmness. All of these properties are typical of the gelatine that is used today in the industrial production of high-gloss ink-jet paper. Gelatine coatings provide the paper manufacturer with many other attractive possibilities: the available qualities can be economically incorporated to generate added value, e.g., by producing premium-grade matte photographic paper. Such paper quality enables sharp prints to be produced with living and especially durable colors.

3.2.7.5.1 High-gloss Ink-jet Paper

The worldwide growth in ink-jet technology brought about by digital photography further increased the application areas for gelatine. Special gelatine types for ink-jet applications are available today in technologically relevant areas such as rheology, swelling, surface tension, and IEP, but all are quite different in character. These special properties can be controlled during the gelatine manufacturing process and can be optimized for ink-jet applications. Gloss, color stability, and the color brilliance of the prints produced are equally good with all types of ink-jet gelatines (see Figs. 3.90 and 3.91).

Gelatine coatings are primarily used for the manufacture of premium grade high-gloss photographic paper. Gelatine forms the special ink-jet coating that absorbs the solvent contained in the ink, fixes the dye, and protects it from fading. The color permanence and high image quality produced by a gelatine matrix cannot be achieved with any other coating process. In addition, gelatine is easy to process and can be precisely hardened and modified to optimize both the water resistance and water absorption of the coating.

High-quality ink-jet paper should have a homogeneous surface after coating. There should be no cracks on the coated surface, the color should be stable and true, and the coating should not be tacky and should dry rapidly. Even the smallest of color drops should not be able to flow together and combine. Production should be economically attractive, and, if possible, the coating should be suitable for all types of ink, regardless of whether they contain organic solvents such as glycol in addition to water.

However, the swelling properties of gelatine are somewhat restricted when organic solvents are used. This can be overcome by special modifications provided for by the production of optimized ink-jet gelatines. For example, treatment with dodecenylsuccinic anhydride leads to a gelatine product with a certain degree of hydrophobicity, and this product exhibits improved swelling behavior in organic solvents. Miscibility with many polymers and additives, necessary for the production of ink-jet coating, is also improved by this method. This specific modification also lowers the surface tension (see Fig. 3.92), so that the gelatine films adhere

Gelatine

LIGHT TEST Date: 26.03.2003
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: CANON S800
Coating: Gelita Imagel MA
Paper: resin coated paper



LIGHT TEST Date: 26.03.2003
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: HP DeskJet 970 Cxi
Coating: Gelita Imagel MA
Paper: resin coated paper



LIGHT TEST Date: 26.03.2003
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: EPSON Stylus Foto 950
Coating: Gelita Imagel MA
Paper: resin coated paper

OEM Media

LIGHT TEST Date: 12.02.2004
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: CANON S800
Coating:
Paper: CANON Glossy Foto Paper GP-301



LIGHT TEST Date: 12.02.2004
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: HP DeskJet 970 Cxi
Coating:
Paper: HP Premium Plus Foto Paper Glossy



LIGHT TEST Date: 12.02.2004
Mode: Programme 1, sample quality
DGF Stoess AG / Dr. B. Köhler / P. Reiter (R & D)
Printer: EPSON Stylus Foto 950
Coating:
Paper: EPSON Glossy Paper

Fig. 3.90 Gelatine coatings are the benchmark for light-fast Inkjet paper.

well to the low-energy surfaces employed in PE-coated paper – a type widely used for photographic paper.

Coatings with a high pigment content absorb the ink via the capillary effect much more quickly than gelatine coatings; however, they can only store a limited amount of fluid. If this limit is exceeded, the ink tends to smear or even penetrate through the paper. Such “porous” paper does not produce the gloss and color density of a gelatine coating. In addition, there is no barrier to protect the dyes from gases such as oxygen and ozone. Such reactive gases can cause dye fade or color shifts on porous papers. The capillaries of the paper provide a very large surface area, hence facilitating susceptibility to these attacks. This can present a serious problem.

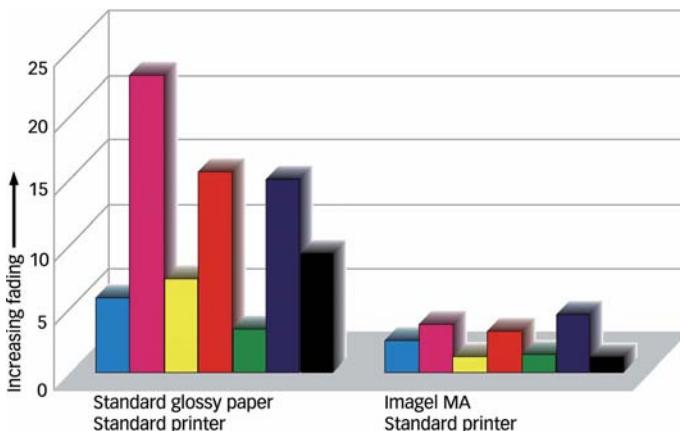


Fig. 3.91 Light stability test (72 h irradiation) with standard and gelatine-coated (right) Inkjet paper.

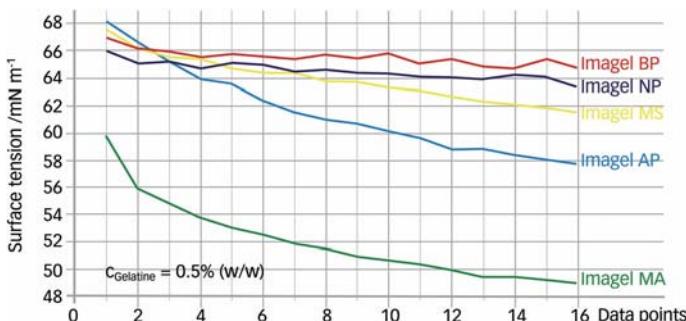


Fig. 3.92 Surface tension of different ink-jet gelatines.

Gelatine, on the other hand, forms a thin film around the dye, hence protecting it from the effects of reactive gases. The color stability is thus increased. This particular effect is also utilized in pharmaceuticals manufacture: gelatine is used to protect vitamins and other oxygen- and light-sensitive substances employed in microencapsulation techniques.

As a polyelectrolyte, gelatine can fix the color very close to the surface of the paper, so that it neither penetrates into the paper nor migrates right through it. This is presumably one of the major mechanisms that result in the high degree of brilliance of gelatine-coated paper (verifiable by analyzing the color density).

By adding special types of chitosan, a natural polymer that occurs in crustaceans, the color-fixing properties of the gelatine coating can be improved even further (see Fig. 3.93). The light stability of dyes fixed on gelatine coatings in this way remains permanently at a high level. This property is currently unique, as

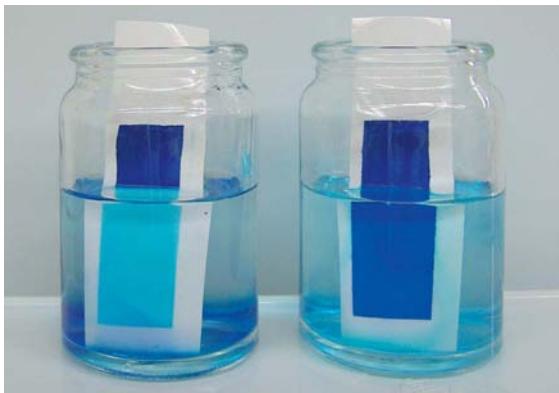


Fig. 3.93 Gelatine coatings containing chitosan (right) show improved dye fixation without affecting the image quality and light stability.

all other substances used for fixing ink-jet coatings – e.g., PolyDADMAC – reduce the light stability considerably.

3.2.7.5.2 Matt Ink-jet Paper

The interaction between gelatine and the dye can be explained by the large variety of functional side chains of the protein molecule such as amino-, hydroxyl, or carboxyl groups. Gelatine is thus also an excellent binding agent for a large number of inorganic pigments that are of interest for paper processing.

Used together with silicates, bentonites, carbonates, or zeolites, gelatine enables matt photographic and printing paper of excellent color density to be produced. The coating guarantees quick-drying prints that are mechanically very stable. Investigations carried out on the adhesiveness of the coating have shown that, with respect to kinking, firmness, resistance to smearing, and water fastness, gelatine provides the same degree of mechanical robustness and the same performance and stability as other binders. The coatings can be processed using more or less standard methods to produce different coating weights per unit area.

The major advantage of a gelatine coating is the distinct increase in color density with cyan and magenta but also with yellow and black. Thus, gelatine coatings can significantly improve the quality of the entire range from office to matt premium grade paper.

In the premium grade sector, much livelier colors can be produced on gelatine coatings with a high coating weight per unit area. Furthermore, it is of interest for the paper manufacturer to know that with gelatine, in contrast to other coatings, the desired quality can be achieved with more economically priced pigments, the gelatine providing the improved color density.

If paper is coated using less coating mass, the color density for some colors can be increased by more than 30% in comparison with standard office paper (see Fig. 3.94).

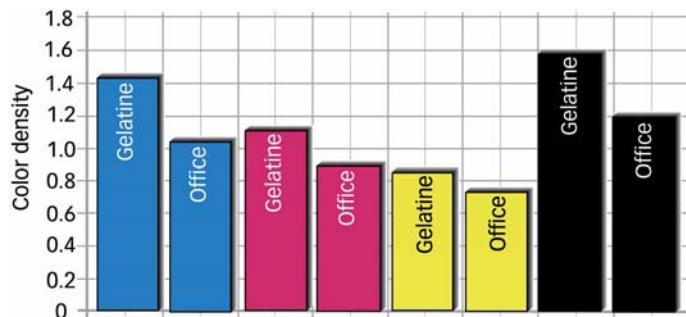


Fig. 3.94 Improvement of the color density of office paper by gelatine coating.

During the manufacturing process, such light gelatine coatings can be directly applied online with a film press, a process that reduces the overall cost of coating.

The combination of color density, film formation, gloss, and light stability also makes gelatine attractive for a wide range of other paper types, such as special offset and gift-wrapping paper.

3.2.8 Cosmetics

The health care (hygiene and beauty) market is one that has been showing one of the highest growth rates in the world. In 2004 this market was 230.4 billion US\$ and has grown about 8% year over the last five years. The largest sectors and those showing most growth were hair and skin care products. The products most in demand in these sectors are those that not only enable passive corrections to be made, e.g., color, but also actively react with the skin and hair matrices to produce positive effects – in short, products that keep the skin and hair healthy and young. Collagen and its derivatives play a major role in such products as functional ingredients.



Fig. 3.95 Collagen and its derivatives play a major role in skin and hair care cosmetics.

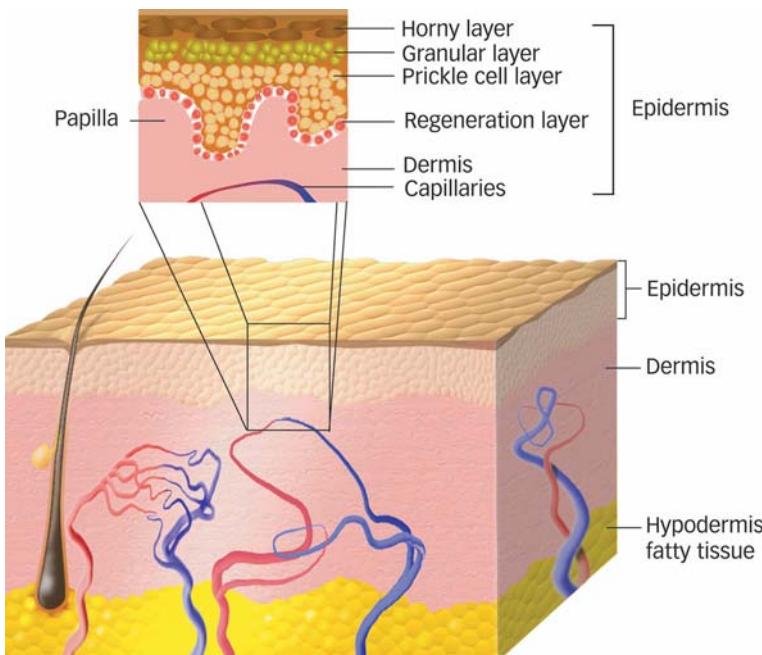


Fig. 3.96 Structure of the human skin (Source: Spektrum der Wissenschaft/Siganius).

3.2.8.1 Structure of the Skin

The skin is the largest and heaviest organ of the human body. In its function as an acidic protective surface, the skin actively prevents damaging germs from entering the body. It also protects the body against cold, heat, radiation, external pressure, physical blows, friction, and chemicals, and prevents loss of moisture and heat. One of its major functions is that of a sensory organ.

The skin (the cutis) comprises the external epidermis and, immediately below that, the dermis and the sub-cutis. Beneath the sub-cutis there is a general layer of collagen fibers that forms the base of the skin (see Fig. 3.96).

The epidermis itself has a number of sub-layers: the upper cell layers (stratum corneum) consist of flat keratinized cells. Keratin is water repellent and also provides the skin with its natural firmness. Below these keratin layers there is a spinous cell layer and the basal layer of the dermis (stratum spinosum and stratum basalis). Here, in the keratinocytes, new skin cells are permanently being produced. These new cells then migrate toward the surface of the skin; however, they become keratinized and are used to form the external layer. This continuous process is necessary because the external layer is constantly being discarded. A completely new skin layer is formed approximately every 27 days.

The dermis is elastic in nature and contains a high proportion of loosely linked connective tissue. It also consists of two main layers: the papillary layer connects

the dermis with the epidermis by interlocking itself with its cone-like protrusions. The interstitial space is the space between the cells of the papillary layer. This space is filled with a liquid called the interstitial fluid. It is a gel-like substance in which the cells can move freely.

Fewer free cells are found in the omentum of the dermis. Instead, the omentum contains a dense network of collagen fibers arranged parallel to the surface of the skin. This network is filled with elastic connective tissue made of elastin. Elastin, after collagen, is the second most frequently occurring connective tissue protein in the human body. This network structure provides the skin with the required firmness and elasticity.

The sub-cutis is made up of loose connective tissue that contains pads of fat cells. These fat cells insulate the body from the effects of heat and cold. The connective tissue is permeated by fibers that originate in the dermis and are directly connected with the strong collagen fibers located directly under the sub-cutis. Depending on the part of the body involved, muscle, bone, cartilage, and fat come next.

3.2.8.2 Aging of the Skin

The statement “People are as old as their connective tissue”, coined by Bogomol'etz in 1946, has not lost its meaning over the years – it could well be a sort of credo for modern cosmetics.

Aging describes the complex but natural biological process the skin goes through during its lifetime. The way we live can also accelerate the process, as can a number of environmental factors. Characteristic symptoms of aging skin are increased roughness, formation of wrinkles, loss of elasticity, and irregular pigmentation.

Biological aging is the result of reduced cell renewal within the layers of the skin. The epidermis of a young person has many more cell layers than that of an elderly person. Consequently, it can bind more moisture than the older and thinner skin. The more moisture skin can store, the fresher and smoother it appears (see Fig. 3.97).

The most critical changes – those that lead to the formation of deep wrinkles – take place in the dermis. With increasing age, the collagen takes increasingly



Fig. 3.97 The epidermis of a young person can bind more moisture than older skin. Consequently, it appears fresher and smoother.

longer to be formed and reformed. At a certain point in time, the loss becomes greater than the quantity renewed.

At the same time, the collagen becomes increasingly more cross-linked. As a result, its moisture-binding capacity is reduced, and some elasticity is lost. In time, the connective tissue fluid that provides the skin with its smoothness, suppleness, and tautness also gradually decreases in volume, and the skin then loses even more moisture.

In addition, a number of age-related processes develop within the sub-cutis over a period of time. Because of inadequate blood flow, the fat padding cells in the sub-cutis disappear, with the result that the skin loses its firmness and appears more wrinkled.

In addition to these biological processes, a number of external factors can influence skin aging. UV radiation, for example, can have a drastic effect: the radiation enables free radicals to be formed which can harm the skin cells. Scientific studies have also shown that sunlight accelerates the production of a collagen-denaturing enzyme (collagenase), while its inhibitor does not lose its efficacy. At the same time, the gene activity relating to the formation of type I collagen is reduced. Thus, collagen plays a major role in the skin aging process.

3.2.8.3 Structure of the Hair

Hair consists of keratinized cells that are formed within the hair follicles (see Fig. 3.98). Morphologically, there is a difference between the hair root that is located in the hair follicle and the hair stalk that is visible on the surface of the skin. This, like the skin, is multi-layered in structure. Marrow cells (medulla) that consist of long polygonal cells are located towards the center, at least in the case of thick hair. These marrow cells are surrounded by longitudinal spindle-shaped keratinized fiber cells (cortex). This layer contains the pigment melanin and is the major component of hair which determines its firmness and elasticity.

A layer of scales (cuticula) is arranged around the cortex; these are similar to the slates on a roof. The cuticula is also multi-layered, but is extremely thin and

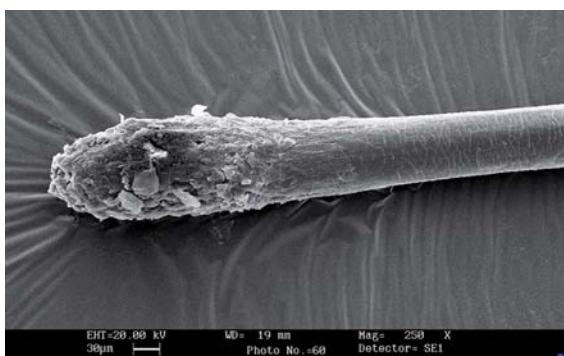


Fig. 3.98 Microscopic image of a hair follicle.

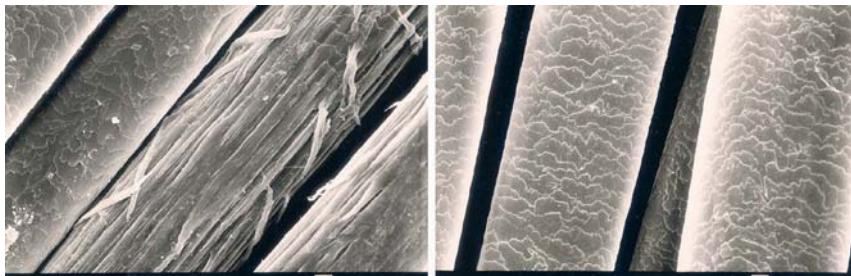


Fig. 3.99 Microscopic image of a hair damaged by external influences (left). Substances like gelatine hydrolysate that actively protect the keratin structure of the hair can counteract these negative influences (right).

transparent; as a result, the hair pigments shimmer through to provide natural color.

Hair care products are essentially produced for six different categories of hair:

- Normal hair is healthy, elastic, and glossy. The surrounding film of fat is neither too thick nor too thin. The external scaly layer is smooth and reflects light.
- Stressed hair results when it is exposed to damaging influences, e.g., dyes, bleaches, permanent waving, and hot blow-drying. As with skin, environmental factors such as too much sunlight or chlorinated water can be harmful. Stressed hair is dry, brittle, difficult to comb, and lacks gloss. Substances that actively protect the keratin structure of the hair can counteract these negative influences (see Fig. 3.99).
- Dry hair results when the protective layer of fat surrounding the individual hairs is absent. The hair loses its moisture and becomes lusterless and brittle. In such cases, substances that support the formation of the fat layer and provide moisture to the hair matrix have a positive effect.
- Thin hair lacks substance and volume and readily collapses after brushing and combing.
- Fatty hair results from an over-production of fat in the scalp. This gives the hair a stringy and greasy look.
- Dandruff results from a fungus that releases substances causing itching and infection of the scalp. The scalp reacts by producing excess cells that are then quickly discarded.

Gelatine hydrolysate has been proven to be of help in combating some of the above-mentioned conditions (see Section 3.2.8.4.4).



Fig. 3.100 It is not the oil and fat that keeps the skin young and wrinkle-free – it is the moisture stored in the cells.

3.2.8.4 Collagen in Cosmetic Applications – Direct Effects

The primary goal of skin care products is the improvement of the moisture content. Therefore, it is not the oil and fat that keeps the skin young and wrinkle-free – it is the moisture stored in the cells.

Cosmetic collagen products work in two ways – directly and indirectly. Direct product effects actively improve the condition of skin and hair through specific interaction with the cells. An indirect product effect, for example, is the skin's ability to cope with basic cosmetic substances (see Section 3.2.8.5).

3.2.8.4.1 Oral Applications

Numerous scientific studies have demonstrated the fact that a diet containing gelatine can improve the structure and appearance of skin, hair, and fingernails. In one example, based on a daily diet containing 14 g of gelatine taken over a period of at least three months, the mean hair diameter increased by an average of 10%. Increases in the size of the hair stalk and the hair density were also reported. In a three-month application study, fingernails became very much firmer and less brittle. Additionally, the oral application of gelatine enriched with glycine increased the moisture-binding capacity of the epidermis.

Scientists have explained these effects by the fact that gelatine, because of its amino acid composition, activates the synthesis of collagen and elastin in the body. Collagen proteins are produced in the fibroblasts of the dermis specifically from the amino acids that are characteristic of gelatine – principally glycine and proline. Elastin is also synthesized in the fibroblasts, and this occurs in a number of steps, similarly to collagen. Elastin, like collagen, contains proline and hydroxyproline but in much lower quantities. Overall, the proportion of non-polar amino acids in elastin is much higher than that in collagen. Elastin, where less than 10%

of the amino acids involved in the synthesis are polar in character, is a particularly hydrophobic protein.

This stimulation theory is supported by the fact that, upon stopping the administration of gelatine, the positive effects observed also essentially cease – they are directly dependent on the availability of gelatine to the organism. Another piece of evidence comes from osteoarthritis research: here, it has been demonstrated in *in-vitro* tests that collagen hydrolysate stimulates cartilage synthesis (see Chapter 4). Thus, in all probability, gelatine and gelatine hydrolysate have a similar mode of action in improving the formation of skin, hair and fingernail matrices.

3.2.8.4.2 Skin Care – Native Collagen and Elastin Hydrolysate

Native collagen and elastin have a long tradition of being used in cosmetic products for external application. Native collagen obtained from very young mammals is water-soluble even at low temperatures. It is mainly used in hydroregulatory skin care products for improving the smoothness and suppleness of the skin. Because of its molecular size, native collagen cannot penetrate deeply into the intact skin; it therefore exerts its effect on the upper layer of the skin. Its high moisture binding capacity increases the turgor of the skin and reduces wrinkle depth. The so-called turgor pressure arises because of moisture being taken up by an osmosis-like effect. The cell plasma increases in volume when moisture is absorbed and shrinks when this moisture is lost. Depending on the liquid status of the cell, the cell wall becomes more or less distended. If the degree of turgor decreases, the skin tends to sag and takes on a parchment-like feel.

Native water-soluble collagen, because of its high molecular weight of over $300\,000\text{ g mol}^{-1}$, is also a very good film former on the skin. It not only binds moisture but also, because of its film forming properties, slows down the release of moisture to the atmosphere.

The functional properties of native collagen are closely related to the retention of its natural triple-helix structure. This is ensured by the gentle process used to extract it from the skins of very young animals. Native collagen obtained in this way is a colorless, opalescent liquid with a very mild inherent odor.

If it were further processed using heat, collagen would become denatured and lose its desirable properties. This is prevented by processing it into cosmetic preparations at a temperature below $30\text{ }^\circ\text{C}$. Native collagen is also very sensitive to alkaline conditions and high concentrations of salts, alcohol, and surfactants. It should therefore be used at a pH below 6.

Native collagen is also used in cosmetic surgery. It is injected directly into the skin to eliminate wrinkles and tighten the skin. The procedure must, however, be repeated at regular intervals as the body denatures the collagen. The procedure is also regarded with some skepticism by scientists.

If elastin is to be used in a cosmetic product, the fibrous protein must first be converted into a water-soluble form. This takes place using an enzymatic hydrolysis process on connective tissue with a high content of elastin. The elastin hydrolysate obtained in this way from the raw material Ligamentum nuchae (the nuchal ligament) is a very good film former and hence moisture binder.

3.2.8.4.3 Gelatine Hydrolysate in Skin Care

In comparison with native soluble collagen, gelatine hydrolysates are short-chained polypeptides, which, depending on the production method employed, can have different molecular weights. Their functional properties can be controlled by the degree of hydrolysis they undergo. Gelatine hydrolysates are soluble in cold water, non-toxic, and dermatologically well tolerated.

The ability of gelatine hydrolysate to adsorb onto the keratin structure of skin and hair is designated as substantivity. In general, the substantivity increases with increasing molecular weight, whereas the cold-water solubility decreases. Gelatine hydrolysates having a mean molecular weight of 3000 g mol^{-1} thus have a distinctly higher substantivity than hydrolysates of lower molecular weight.

This adsorption is a vital factor in skin and hair care. It enables gelatine hydrolysates to remain active on the skin for a longer period, i.e. they are able to bind moisture during that time. Furthermore, these polypeptides contribute toward improved skin feel.

It has been scientifically proven that when gelatine hydrolysates are applied to the skin, the external skin layer takes up more moisture and is able to bind it better. The optimal type is assumed to be a partially conditioned collagenous protein of molecular weight between 600 and $12\,000\text{ g mol}^{-1}$. Hydrolysates of high molecular weight, between $12\,000$ and $18\,000\text{ g mol}^{-1}$ possess additional film-forming properties. Thus, like elastin and native collagen, they not only store moisture, but also reduce trans-epidermal moisture loss. And, of course, collagen- and elastin hydrolysates can be used in combination if specific functions are to be added.

Orally applied gelatine hydrolysates – as in the case of gelatine in general (see Section 3.2.8.4.1) – also improve skin quality. A recent clinical investigation was conducted in a Brazilian institute to evaluate the efficacy of gelatine hydrolysate on skin firmness, elasticity, and hydration. The study was conducted with three groups of female volunteers aged 35 to 60, who were given one daily dose of an artificial drink prepared from a solid compound containing one of the two gelatine hydrolysate concentrations or a placebo containing a carbohydrate instead of gelatine hydrolysate.

Instrumental evaluation was carried out at the beginning of the study (T_0) and after 60 days (T_{60}) during which time the product was ingested once a day. Results were subjected to statistical evaluation, differences being considered significant when $p < 0.05$.

On comparing the results obtained with the placebo to those with gelatine hydrolysate at both concentrations, no significant difference in skin firmness ($p > 0.05$) was observed; however, a clear trend to substantial improvement was observed over time for the products containing gelatine hydrolysate.

In the case of elasticity, however, a significant difference between T_0 and T_{60} was observed when the product containing 5 g of gelatine hydrolysate was applied (see Fig. 3.101). The results obtained for hydration for the product containing 5 g of gelatine hydrolysate, which were significantly better than those for the placebo

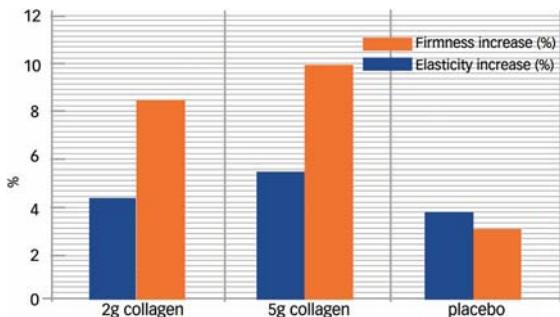


Fig. 3.101 Orally applied gelatine hydrolysates can improve skin quality (increase of firmness and elasticity after 60 days).

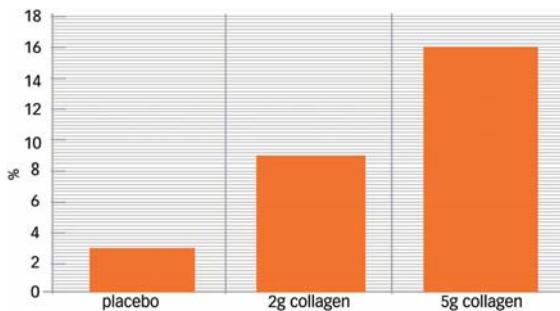


Fig. 3.102 Hydration results in % increase after 60 days.

and for the product containing 2 g gelatine hydrolysate (see Fig. 3.102), together with the firmness and elasticity observations, show that this product has a high potential for skin care applications using a simple drink to administer the daily dose.

3.2.8.4.4 Direct Effect on the Hair Matrix – Gelatine Hydrolysates

The relevant direct effects of gelatine hydrolysates on the hair matrix are substantivity, film formation, the improvement of gloss, feel, and volume, and ease of combing.

Gelatine hydrolysates adsorb onto the keratin of the hair, this effect becoming stronger when the hair is damaged. Film-forming hydrolysates also form a protective layer around the individual hairs. This interaction improves the hair structure and gloss, and facilitates combing.

Gelatine hydrolysate of mean molecular weight 3000 g mol⁻¹ is not only adsorbed onto the squamous cell layer but can also diffuse through this into the fibrous cells below. In permanent wave and hair bleaching preparations of alkaline pH, gelatine hydrolysates can prevent the extreme swelling brought about by the

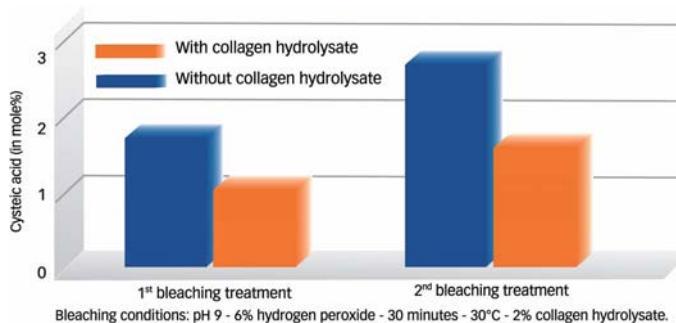


Fig. 3.103 Reduction of hair damage due to bleaching.

alkali as well as excessive chemical damage to the cystine bonds and the surface of the hair (see Fig. 3.103). Hair dyeing products containing gelatine hydrolysate enable the dye to be absorbed more uniformly.

3.2.8.5 Indirect Effects in Skin and Hair Care

Gelatine hydrolysates are not only used widely in cosmetic and dermatological preparations for their direct effects on skin and hair; they are used especially in skin and hair cleansing preparations as protective colloids to improve the tolerability of the surfactants.

In the first instance, the gelatine hydrolysate adsorbs onto the keratin, where it acts as a protective colloid, hence protecting it from the effects of the surfactants. In this way, extraction of the non-keratin components from the corneous layer – the NMF (natural moisture factor) – is reduced, and the natural pH of the skin is maintained. Gelatine hydrolysates can also help to reduce the irritation potential of surfactants. This complex formation between proteins and surfactants is based on ionic interaction. In the case of anionic surfactants, the complex formation is stronger when the surfactant ion is more polar. Thus, a weakly acidic salt is formed from the salt of a strong acid, because the carboxyl group of the polypep-

Table 3.52 BASIC RECIPE – Hair and body shampoo.

Ingredients:

MIPA – Lauryl sulfate (and) cocoamidopropyl betaine	25%
Lauryl-2	1.5%
Sodium cocoyl hydrolyzed collagen	2.5%
Hydrolyzed gelatine	0.75%
Hydrolyzed elastin	0.1%
Polyquaternium-10	0.5%
Preservative, fragrance, water	ad 100%



Fig. 3.104 Gelatine hydrolysates are used especially in skin and hair cleansing preparations as protective colloids to improve tolerability to surfactants.

tide partially becomes a functional group of the surfactant. It has also been clearly demonstrated that the mucous membrane compatibility of surfactants can be substantially improved using gelatine hydrolysate. This was determined using the Draize method on a rabbit eye; the result was a strongly reduced irritation effect.

Gelatine hydrolysates can also be used to achieve technological effects. For example, gelatine hydrolysates exert a very positive influence on the foaming behavior of surfactant formulations. The foam stability and quality can be substantially improved in this way.

3.2.8.6 Protein Surfactants

Protein surfactants produced from gelatine hydrolysate and plant fatty acids such as coconut oil combine optimal dermatological compatibility with excellent cleansing properties.

Such gelatine hydrolysate/fatty acid condensates do not give rise to irritation of the skin or the mucous membranes. Moreover, they can, as protective colloids, considerably improve both the skin and the mucous membrane compatibility of other anionic surfactants.

The mean molecular weight of such anionic surfactants, comprising the hydrophilic gelatine hydrolysate and the lipophilic fatty acid ester, is approximately 3000 g mol^{-1} . Even at low concentrations they can reduce surface tension and make excellent cleansers. In addition, with an HLB value of approximately 17, they are skin-compatible oil-water emulsifiers. Gelatine hydrolysate surfactants are particularly suitable for use in formulations containing vegetable oils as irritation-free co-emulsifiers for dermatologically compatible skin and hair care products (see Table 3.52).

The foaming ability of collagen-fatty acid condensates is essentially independent of water hardness.

As gelatine hydrolysate surfactants are made from pure natural products, they are completely biodegradable. Using the OECD Screening Test, 60% of this material was shown to have been converted to carbon dioxide and water after only 5 days.

Cold-water-soluble gelatine hydrolysate surfactants are available as standard viscous solutions. They are thus easy to process and can be blended with anionic, non-ionic, and amphoteric surfactants in any desired ratio and can be used over a wide pH range.

3.2.9

Technical Applications

In technical applications, different types of gelatine are employed depending on the area of specialization involved. The gelatines range from those demanding the highest quality, e.g., for photographic work and microencapsulation, to simple types for book binding. In this latter case, there is a gradual, stepwise, difference in quality from gelatine to glue. In contrast to glue, the typical gelatine type used for technical applications is purer and exhibits a higher overall quality. This so-called technical gelatine is different from the gelatine used for edible and pharmaceutical applications in that it does not have to conform to the stringent regulatory requirements that characterize these areas. On the other hand, however, the typical types A and B, the Bloom value, the viscosity, and the many technological properties used in technical applications are identical. These properties include gel, foam, and film formation as well as adhesion and a protective colloid effect. In an international study in which publications and patents up to the year 1984 were assessed, over 700, involving mainly technical gelatine applications, were documented. Although most of these have not achieved commercial success, several processes, including microencapsulation, are important techniques in modern industrial processing.

3.2.9.1 Microencapsulation Using Complex Coacervation

Using the technique of microencapsulation in conjunction with complex coacervation, both solids and liquids can be encapsulated within a very thin polymer film. In this way, numerous effects can be achieved (see Tab. 3.53).

The most successful application of microencapsulation was the production of carbonless paper. This type of paper is coated on the back with microcapsules containing a colorless substance that is a pre-stage of the actual dye to be used. When the paper is written on, the thin polymer walls of the microcapsules rupture due to the pressure exerted and the reactive dye is released. As a result of the special chemical reaction that takes place – whereby the components from the ruptured microcapsules on the back of the first page react with those on the top of the page below – the actual dye is formed that then shows up as text on the

Table 3.53 Advantages of microencapsulation.

-
- Protection against oxygen, light, water
 - Fixation of highly volatile substances
 - Optical effects (color, pearl luster)
 - Controlled release of active substances
 - Conversion of liquids into solids
 - Masking of taste and odor
 - Improving chemical and biological safety
 - Separation of incompatible substances
 - Improved flowability of powders
 - Reduction of dust and electrostatic charges
-

next page of paper. This type of carbonless paper is very widely used and is particularly suitable for applications where sets of forms are used.

“Scratch and sniff” applications have long been used in the perfume industry, where microencapsulated fragrances are applied to a coating substrate for advertising purposes. Today, however, the microencapsulation technique is used in a wide variety of products, e.g. agrochemicals, cosmetics, food ingredients, printing and paper, building chemicals, adhesives, textiles, and displays (see Tab. 3.54). When used for microencapsulated products in the pharmaceutical and food industries, the gelatine must of course fully comply with all relevant laws and regulatory requirements. This is of course the case, as here it is not just simple and low grade technical gelatine that is processed but very specially produced types conforming to these requirements.

3.2.9.1.1 Theory of Complex Coacervation

Complex coacervation utilizes the fact that colloidal molecules dissolved in water possess an electric charge due to the dissociation of acidic or basic groups. Below a pH of 5.0, all types of gelatine are positively charged. Gum arabic, however, is negatively charged at this pH. Because of these electrical charges, both hydrocolloids are more strongly hydrated than uncharged hydrocolloids, providing no other hydrocolloids are present. If both are slowly mixed at a high pH and then the pH of the solution is reduced to below 5.0, the hydrocolloids combine to form a complex. The opposite charges are neutralized so that there is less attraction between the water molecules. The resulting coacervate is of course less soluble; it remains solvated but is no longer miscible with the rest of the free solvent. The liquid coacervate envelopes the liquid drops or solid particles that are present in the solution, encapsulating them on a micro scale; hence the term “microencapsulation”.

Subsequently, by reducing the temperature, the wall material sets and is then hardened by cross-linking with aldehydes; it is thus rendered essentially insoluble in water. Subsequent treatment is dependent on the desired end-product. If a dry

Table 3.54 A selection of current applications of microencapsulation.**Pharmaceuticals**

- Microcapsules in hard gelatine capsules
- Microencapsulated viral vaccines
- Protection of cells foreign from the body's immune system
- Reduction of allergenic potential
- Gastric juice-resistant active substances

Foodstuffs

- Aromatic oils released after ingestion (e.g., chewing gum)
- Protection against oxidation of sensitive functional food additives such as omega-3 fatty acids
- Gastric juice-resistant probiotic bacteria

Agriculture

- Herbicides without flammable solvents
- Herbicides and fertilizers with controlled release with respect to time and place
- Feed additives (vitamins)

Technology

- Dual-component adhesives for thread fixing that react when the screw is turned
- Enzymes, fragrances, etc., that are only released during washing
- Improved heat storage for internal plastering, plaster boards, and cement-based building materials
- Hydrated cement capable of “self repair” of cracks
- Climate-regulating textiles through heat-storing/heat-dispensing microcapsules
- Encapsulated drops of color that, depending on the poling of the electrodes, react white or colored (display technology)

powder is to be produced, the dispersion is filtered or separated and the microcapsules dried using a fluidized bed granulator. In the case of carbonless paper or fragrance cards, the carrier can be directly coated with the capsule dispersion after adding the necessary excipients.

As the coacervate can only exist when there is equilibrium between the electrical charges, it is much more stable the greater the positive and negative charges are, i.e. the more dissociated the colloid and reaction colloid are in the solution. Gelatine acquires an increasingly positive electrical charge the longer the pH of the solution remains below its IEP. As a result, the concentration of the coacervate increases as the pH decreases. However, if the pH falls below a certain limiting value, the yield again decreases.

At the optimal coacervation pH, the positive and negative charges are equal; the resulting coacervate has a neutral charge and thus has minimum solubility.

If the pH subsequently falls below this level, the concentration of protonated amino groups in the gelatine increases. However, the concentration of dissociated COOH groups of the reaction colloid decreases, so that the coacervate returns partially into solution.

Thus, for each particular mixture and depending on the IEP of each polymer, there is a coacervation optimum; in the case of a type A gelatine/gum arabic mixture, this is approximately pH 3.8.

In the case of both acid and alkaline-conditioned gelatines, it can be established that the degree of coacervation increases with increasing Bloom value. At the same Bloom value, the quality of the coacervate increases with increasing viscosity of the gelatine.

In addition, in a gelatine/gum arabic mixture, the yields at low ash levels of the gelatine are considerably higher even if demineralization reduces the viscosity slightly. The important factor is that the concentration of cations should be as low as possible. Negatively charged ions such as sulfate and chloride are better tolerated; the presence of small amounts can in fact benefit the process. However, it should be taken into account that these reactions can be completely different if other gelatine/hydrocolloid combinations are used.

The concentration of the reactive colloid necessary to coacervate a certain amount of gelatine approaches a limiting value asymptotically in the same way as does the pH. Theoretically, in a gelatine/gum arabic mixture, the optimal concentration is 59% gum arabic and hence 41% gelatine. For purely practical reasons, however, as the results are almost identical, a 50–50 mixture of the two polymers is normally used. If carboxymethyl cellulose (CMC) is used instead of gum arabic, as is typically the case today, 1 part of CMC is adequate to coacervate 5 parts of gelatine.

Dilute hydrocolloid solutions are ideal for processing as, according to Ostwald's dilution law, dissociation is at a maximum only in a very dilute solution. As ideal dilutions are not used in microencapsulation for economic reasons, the theoretical yields can never be achieved. In an economic process, the proportion of polymer that can be coacervated is in excess of 80%.

3.2.9.1.2 Coacervation with Modified Gelatines

By selecting a suitable gelatine type, complex coacervation can be carried out without the need for another hydrocolloid. It is therefore possible to achieve coacervation with pigskin gelatine (isoelectric point 9.0) and type B ossein gelatine (isoelectric point 5.0), provided both are demineralized and are at their isoelectric point (IEP). A mixture of pigskin gelatine and succinylated gelatine can also be coacervated. Succinylated gelatine has a very low IEP (4.0) and is produced by treating gelatine with succinic anhydride.

N-phenylcarbamyl gelatine, produced by treating demineralized type B ossein gelatine of high gelation power with phenyl isocyanate, is even able to coacervate without the addition of a reactive colloid. This type of coacervation is probably due to the presence of aromatic structures that reduce solubility. As solubility is at a minimum at the isoelectric point, it is possible to achieve maximum coacer-

vation by continuously reducing the pH. In this so-called simple coacervation, very high yields can be obtained.

Capsules prepared with *N*-phenylcarbamyl gelatine cannot be hardened, as the amino groups are blocked off and can no longer react with the aldehydes. For this reason, this type of gelatine is only used if a high degree of compatibility is required with special fragrances that contain aldehyde groups.

N-phenylcarbamyl gelatine may not be used in pharmaceuticals or food. Succinylated gelatine, however, was approved by the Food and Drug Administration (FDA) for the microencapsulation of aromatic oils in 1968.

3.2.9.2 Microencapsulation by Spray Drying

Another widely used process for microencapsulation is spray drying. In contrast to complex coacervation, this is a relatively simple physical process. An emulsion or dispersion of the product to be encapsulated and a gelatine or gelatine hydrolysate solution are nebulized in a stream of hot air. The relatively large surface area of the small drops allows extremely rapid drying. The oily substances are enclosed within the gelatine matrix formed. The dried product is separated and collected. Substances that are embedded in such a gelatine matrix are, for example, the vitamins A and E, long-chain fatty acids, and carotenoids. After encapsulation they are easy to dose and are protected from environmental influences. They are used, for example, in animal feed and in pharmaceutical applications (see Section 3.2.6).

3.2.9.3 Adhesives and Building Materials

The use of gelatine as a glue is surely the oldest technical application known. Chemically, animal glue is an impure form of gelatine produced using the simplest of techniques – just boiling the raw material. Even today, classical animal glue is sometimes the adhesive of choice in the furniture industry as well as in the manufacture and restoration of musical instruments. Numerous other types of adhesive have been developed from gelatine over time: solid adhesives, non-flammable adhesives, e.g. for use in hot air balloons, foam adhesives, and products for gluing paper. In this area, gelatine's resistance to aggressive solvents is a major advantage. One example of this is in the shoe industry, where gelatine rollers are used to apply adhesives. Similar rollers are also used for applying printing dye based on organic solvents that are incompatible with plastic rollers.

One well-known application of the adhesive properties of gelatine is in the manufacture of matches. The complex chemical mixture forming the match head is made into a foamy slurry with gelatine, and the end of the matchstick is dipped into this. On drying, the characteristic match head is formed (see Fig. 3.105). The particles on the surfaces of sandpaper or grinding disks are frequently applied using gelatine.

In match manufacture, another property of gelatine is utilized – its foaming ability. During the foaming process of the gelatine, pores are formed in match head; these make ignition possible.



Fig. 3.105 One well-known application of the adhesive properties of gelatine is the manufacture of matches.

The pore formation property is also utilized in the building materials industry, where gelatine is used in the manufacture of porous concrete. Gelatine is also suitable as an agent for delaying the setting and hardening of plaster; it is absorbed onto the surface of the crystals, changes their size and shape, and thus inhibits the sulfate from dissolving and then crystallizing. Mortar that contains an additive comprising technical gelatine, plaster, and calcium carbonate sets and dries more quickly than conventional mortar. In this case, gelatine also improves the gloss of the surface on drying. Technical gelatine is also used to control the viscosity of low-temperature cement compounds comprising cement and plaster that are used in oil fields. Gelatine hydrolysate is used in the manufacture of water-resistant concrete and as a component of covering material for concrete flooring.

3.2.9.4 Paper Processing

The second traditional application area for technical gelatine is in the manufacture of paper. In Italy, as early as the 13th century, the raw paper was soaked in a glue solution to improve its handling properties. This “animal gluing” process enabled the absorbency of the paper to be controlled so that the ink used would not run. At the same time, the process improved the gloss and smoothness of the surface as well as its firmness.

Today, technical gelatine is used in the manufacture of corrugated cardboard and for finishing items such as playing cards (see Fig. 3.106). Animal glue is used on a large scale by bookbinders for catalogs and telephone directories as it is fully biodegradable. Gelatine is used as a “natural adhesive” in book restoration (see Fig. 3.107); here it is used to repair fissures in the paper or for re-gluing. It can also be used to fix the color and text of historical documents. Historical musical scores damaged in the floods in Dresden, Germany in 2002 were restored with the help of gelatine.

Gelatine is also a valuable aid when it comes to restoring parchment, as these are related substances. The same applies to the manufacture of leather. In the tanning industry, for example, a complex chemical mixture containing highly concentrated technical gelatine hydrolysates is used in part of the first step of



Fig. 3.106 Playing cards are given their high-quality surface by technical gelatine.



Fig. 3.107 Gelatine is used as a “natural adhesive” in book restoration.

the tanning process. The gelatine hydrolysates tend to be stored in those parts of the hide which have been subjected to heavy movement before (e.g., the axilla); as a result, these parts are relatively thick and sturdy in comparison with the rest of the hide.

3.2.9.5 Analytics

Another classical application of technical gelatine is in standard analytical procedures. In microbiology, airborne germs and viruses can be detected with an air-collecting apparatus that includes a gelatine filter of precisely defined pore size. The filter is not just used to collect germs; the gelatine is used later as a culture medium to incubate the sample.

In ballistics and forensic science, gelatine gel is used as a medium that corresponds closely to the density of muscle tissue (see Fig. 3.108). It can also be reproduced easily. Furthermore, it is completely transparent; the entry, passage through the medium, and deformation of the projectile that takes place en route can be accurately filmed with high-speed cameras. For this purpose, a totally transparent and lightly colored gelatine with a high degree of firmness is the most suitable.

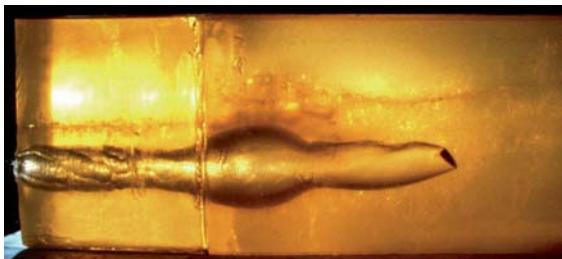


Fig. 3.108 Gelatine gel corresponds closely to the density of muscle tissue. In this way, for example, in forensic medicine, conclusions can be drawn about the behavior of projectiles in animal or human tissues.

After the bullet has been fired into the gelatine block, the latter can be cut into slices, and the visible grooves made by the projectile can be evaluated. The evaluation produces a curve that provides the ballistic analyst with an estimate of the energy that would be dissipated by the bullet in the human body.

In addition, gel formation enables other items such as animal bones or synthetic materials to be embedded in blocks of gelatine. In this way, for example, in forensic medicine, conclusions can be drawn about the behavior of projectiles in animal or human tissues. The same applies to the testing of syringe tips; here, blocks of gelatine can be used to simulate penetration behavior in human tissue.

3.2.9.6 Gelatine Films and Coatings

The surfaces of metals such as aluminum, brass, copper, iron, and steel can be protected from corrosion by coating them with films of gelatine. A good example comes from the area of drilling wells for drinking water (see Fig. 3.109).

When wells are drilled for drinking water, concentrated hydrochloric acid is frequently pumped into the borehole to dissolve any lime that may be embedded in the rock layers deep below ground. In this way, hard rock is rendered porous and permeable to water.

However, the aggressive acid also attacks the bore rod itself. To keep damage to a minimum, anti-corrosion agents must be used. But those based on mineral oil and other chemicals cannot be used for the most part for environmental or other regulatory reasons. Some types of gelatine, however, have proven suitable for this application. The gelatine forms a protective sheath around the bore rod; this reduces the degree of oxidation that can take place on the metal surface. In addition to this excellent protective function for the bore rod, gelatine is also environmentally friendly. As a foodstuff in its own right, it can be used without any restrictions in the area of drinking water.

A similar application involving the successful use of gelatine is geothermal boring. This technique utilizes warm water extracted from great depths for heating buildings. Here too, corrosion protection is necessary but with minimal environmental damage.

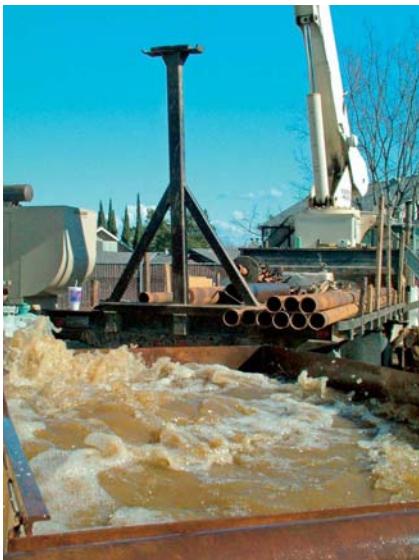


Fig. 3.109 Gelatine coatings can protect the surfaces of metals from corrosion in a very environmentally friendly way.

Gelatine films are also suitable for improving the properties of organic materials. Polyethylene – a substance used commonly as a packaging material – must be surface-treated to reduce permeability to gas if products sensitive to oxygen are to be stored. Coating with a gelatine/formaldehyde film serves this purpose.

Gelatine can also be used in respirator masks. Thin films are applied to the visor panel; the moisture given off by the skin is absorbed, thus preventing the formation of drops through condensation that would otherwise interfere with vision.

As gelatine is not only able to coat human hair (see Section 3.2.8), keratin, and synthetic textile fibers, it is traditionally used in the manufacture and processing of textiles. Collagenous proteins in particular have major advantages in protecting wool from being damaged during the manufacturing process. Positive effects can also be achieved with mixtures of wool and polyester in the manufacture of yarn. Glazes containing gelatine render textiles soft, and gelatine coatings provide yarns with a smooth feel besides making them more resistant to mechanical stress. Manufacturers of impregnating emulsions for textiles also utilize the excellent emulsifying properties of gelatine to stabilize their impregnating solutions during manufacture.

Another innovative application for technical gelatine is in the cultivation of decorative plants and agricultural crops. Used as a buffer layer between the roots of the plant and a plant pot made of renewable materials, it improves the resistance of the pot to moisture and provides the plant with a natural reservoir of water (see Fig. 3.110). In contrast to conventional plastic pots, such a natural fiber pot is



Fig. 3.110 Gelatine used as a buffer layer between the roots of the plant and a plant pot made of renewable materials improves the resistance of the pot to moisture and provides the plant with a natural reservoir of water and – after biodegradation – of nitrogen.

fully biodegradable. The plants can be planted together with the pot, and the gelatine, once degraded, also serves as a nitrogen fertilizer.

This property has already been put to use in agriculture. Gelatine hydrolysates are used as leaf fertilizers as they have an adhesive effect and can also reduce surface tension. The fragments formed on degradation of gelatine hydrolysate and the free amino acids serve the plants as fertilizers over a longer period of time in addition to supporting their metabolism. So-called “agro sponges” have a similar effect; these not only act as water reservoirs but also store specific agrochemicals within the foamed gelatine foam matrix and can be released in a controlled manner.

Technical gelatine hydrolysates are also being successfully used in biotechnology as sources of nutrients. In numerous fermentation processes, e.g., in the manufacture of aromas, they supply the nitrogen required by the microorganisms. In this particular application, technical gelatine hydrolysates are superior to nitrogen sources based on plants, as their composition, and hence nitrogen content, is constant and not subject to significant seasonal variation as is the case of plants. One other positive factor is that technical hydrolysates, in addition to containing collagenous protein, also contain residual salts and fats that serve the microorganisms as additional important nutrients.

Gelatine is thus a true alternative to many of today’s synthetic materials. Completely biodegradable transparent films for foodstuff packaging for example have already been successfully produced from physically hardened gelatine films (German Patents No. 3843844 and 42103440). Numerous modified gelatines have also been developed that can subsequently be polymerized. Methacrylated gelatine for example enables particularly flexible packaging to be prepared for sensitive goods such as foodstuffs and pharmaceuticals (see Fig. 3.111).

The modern foodstuffs industry requires not only transparent film but also large quantities of packaging materials with fat-resistant properties. Generally,



Fig. 3.111 Gelatine is a biodegradable alternative to many of today's synthetic materials. Completely biodegradable transparent films for foodstuff packaging for example have already been successfully produced.

fluorocarbons are used; with these, the fat barrier properties required for the various fat-containing foodstuffs can be precisely controlled.

However, fluorocarbons can seep into foodstuffs; furthermore, they are suspected of being dangerous to health. For this reason they are under evaluation, and the industry is looking for alternatives. Specially modified gelatines have such fat barrier properties, and they could, subject to approval by the food regulatory authorities, completely replace fluorocarbons.

One potential application for gelatine is as a substitute for plastic in the injection molding of articles made of gelatine (German Patent No. 3827061 and International Patent No. 8901501). In this technique, a mixture of gelatine, plasticiz-



Fig. 3.112 Cups, cutlery or plates based on gelatine can be produced using the injection molding technique.

ers, and water is melted under pressure and temperature and injection-molded to the desired form. Biodegradable cups, cutlery, and plates have been produced in this way for the catering industry (see Fig. 3.112).

3.2.9.7 Detergents and Cleansing Agents

The surfactant properties of gelatine are also being successfully used in technical applications. One well-known example is in the detergent solution used for washing dishes, glass, and porcelain. Because of the gelatine hydrolysate that this contains, no residues are left after the dishes have been washed and dried, so that they need not be subsequently polished for perfect gloss (see Fig. 3.113).

A further advantage of this fully biodegradable protein is improved skin compatibility when washing by hand.

A natural detergent based on the combination of the hydrophilic gelatine hydrolysate and a lipophilic fatty acid has been developed for use in detergents (German Patent No. 3929740). This detergent, comprised exclusively of renewable raw materials, is very effective at reducing surface tension, thus enabling the items being washed to be efficiently wetted. At the same time, the “grayness” of the items washed is reduced, and the detergent acts as a color stabilizer, a protective colloid for enzymes, a fiber protector, and much more – all in one single substance. Based on these properties, the detergent can replace at least three of the substances traditionally used in conventional detergents – the co-formers, color stabilizers and “graying” inhibitors – without the washing effectiveness being reduced. Sometimes, less enzyme is required, as, due to the presence of the gelatine hydrolysate with its natural protective colloid effect, the enzymes present are more effective throughout the entire washing cycle. In laboratory experiments, it has been shown that the effectiveness of amylase increases by 20% under these



Fig. 3.113 If a washing-up liquid contains gelatine hydrolysate, no residues are left after the dishes have been washed and dried by themselves so that they need not be subsequently polished for perfect gloss.

conditions. Furthermore, the collagen detergent has no irritating effect on the skin and is completely biodegradable.

3.2.9.8 Electro-plating and Suspension Polymerization

The protective colloid effect of technical gelatine makes it suitable for use in the electro-plating industry. It is used as an additive in galvanizing and electro-plating baths, where it improves the gloss and uniformity of the metallic coatings produced. In the galvanic separation of copper, the addition of technical gelatine enables compact, hard, galvanic precipitates to be obtained and reduces the particle size of the copper precipitated. In a study of approximately 50 surfactant additives used in the electrolytic precipitation of copper alloys, gelatine was assessed as being in the top three with respect to its performance.

In suspension polymerization, gelatine can control particle size distribution while preventing coalescence. This property is used in particular to stabilize particle size in the manufacture of PVC.

3.2.9.9 Environmental Protection

New applications are constantly being found for gelatine in the area of environmental protection. Gelatine solutions of low concentration have proven to be highly effective in flocculating asbestos, lead, copper, calcium, tin, cobalt, nickel, and manganese ions from suspensions. For this reason, gelatine is also used as a selective precipitating agent in the extraction of uranium from ore.

However, it is not only the flocculation property of gelatine that makes it suitable for environmental applications – it is also its ability to form thermo-reversible gels. Gelatine has thus become a proven agent for decontaminating buildings containing asbestos. The contaminated parts of the building are sprayed with a warm solution of gelatine so that, on cooling, a firm but elastic net is formed (see Fig. 3.114). The net is removed and the asbestos mass obtained



Fig. 3.114 Gelatine is a proven agent for decontaminating buildings containing asbestos.



Fig. 3.115 Environmental catastrophes could be avoided by safely binding both spilled oil and any residual oil in the tanker with gelatine.

is mixed with sand and cement. The asbestos fibers are permanently bound in the resulting blocks of mortar, which are then deposited in authorized landfills.

The positive experience gained from this application of gelatine has motivated scientists and engineers to search for other uses in the area of environmental protection.

In 1999, at the University of Duisburg in Germany, scientists developed a process for binding and collecting liquid organic substances such as raw mineral oil using the natural binding properties of gelatine. The process results in a solid mass that can be cut and that remains stable over a longer period, during which the substance can be disposed of in an environmentally friendly way. This method offers a huge potential opportunity for the shipping industry; on the one hand, organic liquids can be rendered solid for safe transport, and, on the other, in the case of an oil spill, for example, a potential catastrophe could be avoided by safely binding both the spilled oil and any residual oil in the tanker with gelatine (see Fig. 3.115). The solid mass could then be safely reconverted into its individual components by melting the gelatine. The emulsion degrades during the process, the water separates, and the oil floats to the surface. It can then be recovered almost quantitatively for its original use.

Many of the applications described in this chapter are certainly niche markets for the gelatine industry because of the volumes involved, or they still require further development. However, they serve to underscore the sheer diversity of uses of gelatine as a multi-functional ingredient. These applications also demonstrate the potential of gelatine for the future, especially in view of the changing trends with respect to the different raw materials processed by the various industries.

References

Annelore Schott, Einsatzmöglichkeiten von Gelatine/Hydrokolloid-Kombinationen in Gummi- und Gelee-Artikeln, information material Gelita AG.

Annelore Schott, Speisegelatine-Herstellung, Eigenschaften und Einsatzmöglichkeiten, reprint by Gelita AG from the journal "Food Technologic Magazine."

- Bannach, W.: Food Gelatine in the Beverage Industries – An Important Help in Juice and Wine Fining, Confructa-Studien III/84.
- Bernstein et al.: J. Am. Acad. Dermatol., 34 (2)/1996.
- Berthold Köhler and Michael Ahlers, Chitosan for Dye Fixation of Highly Lightfast Gelatine Coatings, NIP 20th, 2004.
- Berthold Köhler, Dirk Kisters and Josef Eckl, Gelatine for Matte Inkjet Paper, WO 2005/097513 A1, 2005.
- Berthold Köhler, Gelatine and Dye Fixation, NIP 19th, 2003.
- Berthold Köhler, Light Stability of Gelatine Coatings, ICIS, 2002.
- Beucke, C.: Speisegelatine in der Fleischerei, Die Fleischerei 6/1978.
- Beuker, F.: Gelatine im Sport? Fitness Management International, 16/1998.
- Bogomoletz: The prolongation of life, Sloan & Pearch Inc., New York (1946).
- Brodie: Hair growth benefits from daily gelatine-cystine supplementation, J. Appl. Cosmetol., 2/1984.
- Buchheim, W. et al.: Neue Aspekte zur nutritiven Qualität von Milchproteinen, Deutsche Molkerei Zeitung, Ausgabe 26/1988.
- C. G. B. Cole, Gelatine: Its Properties and its Applications in Dairy Products, www.gelatine.co.za/dairy.htm
- Campbell et al., The preparation and properties of a modified gelatine (oxypolygelatin) as an oncotic substitute for serum albumin, Texas Rep. Biol. Med. 9, 235, 1951.
- Cole, C. G. B.: The Use of Gelatine in Wine Fining, www.Gelatine.co.za/fining.htm.
- D. D. Tourtelotte, Modified fluid gelatine as a new plasma expander, V Congrès International de Transfusion Sanguine, Paris, 1954.
- Daniel, K. T.: Why broth is beautiful, Weston A. Price Foundation, www.westonaprice.org/foodfeatures.
- Dank Gelatine schmeckt auch fettreduzierter Käse cremig – Camembert, Feta und Pizza-Käse im Test, Uptodate Nr. 18, Gelita AG (2005).
- Dr. G. Reich, Pharmazeutische Anwendungsbiete der Gelatine, Institut für Pharma-zeutsche Technologie und Biopharmazie, Universität Heidelberg.
- Dr. Hofmann, K., and Maggrander, K.: Reduzierung des Kochsalzgehaltes in Fleischerzeugnissen durch die Verwendung von Kollagenhydrolysaten, information material Gelita AG.
- Dr. Maren Friedrich, Dissolution Performance of Pharmaceutical Hard Capsule Gelatine Films, PMPS, 2000.
- Dr. Wilfried Babel, Hard and Softcaps Gelatine Alternatives and Substitutions, CRM Meeting, 2005.
- Dr. Wilfried Babel, Herstellung, Füllung und Kontrolle von Gelatkapseln, APV Kurs Nr. 480, 2000.
- Dr. Wilfried Babel, Pharmazeutische Anwendungsbiete von Gelatine, PMPS, 2000.
- Eberhard Dick, Instant Gratification: Gelatine in Desserts, reprint by Gelita AG from the journal "Food Product Design."
- Eberhard Dick, The Role of Gelatine in the Production of Gums, reprint by Gelita AG from the journal "Chocolate & Confectionery International."
- Evaluation of the health aspects of gelatine as a food ingredient, Federation of American Societies for Experimental Biology (1975).
- F. Podczeck, B. E. Jones, Pharmaceutical Capsules, The Pharmaceutical Press, 2004.
- Gelatine Properties, information material Gelita AG.
- Geliderm 3000 – mildes Proteintensid für sanfte Pflege, information material Gelita AG.
- Gelita Story, Verlag Hanseatischer Merkur, 2003.
- Gelita-Proteine – Einsatz in Präparaten der pflegenden Kosmetik, information material Gelita AG.
- Gelita-Sol D in der Sportlerkost, information material Gelita AG.
- Glatzel, H. and Schlierf, G. in: Moderne Diät, information material Gelita AG.
- Gotthoffer, N. R.: Gelatine in Nutrition and Medicine, Grayslake Gelatine Company, Illinois, USA (1945).
- Hard Capsules, Development & Technology, The Pharmaceutical Press, 1987.
- J. Hogan, The intravenous use of colloidal gelatine solutions on shock, J. Amer. Med. Assoc. 64, 721, 1915.

- Johnsen: Protein hydrolysates as moisturizers, cosmetics and toiletries, Ausgabe März 1978.
- Jos Oliive, Fuyuhiko Mori, and Yuzo Toda, Influence of the Molecular Weight Distribution of Gelatine on Interfacial Tension and Photographic O/W Emulsion Stability, ICIS, 2002.
- Jutta Heidt, Hydrocolloid Study (internal study), Gelita AG, 2005.
- Karlheinz Keller, Science and Technology of Photography, VCH, 1993.
- Kofranyi, E. and Jekat, F.: Zur Bestimmung der biologischen Wertigkeit von Nahrungsproteinen, Hoppe-Syler's Z. Physiol. Chem. Vol. 350, p. 1405–1409 (1969).
- Kuhlmann, F.: Basistherapie bei Dünndarmkrankungen, Ärztliche Praxis, Vol. 35, p. 1609 (1975).
- Lebensmittel-Lexikon, Behr's Verlag, 1993.
- Lower: Verwendung von Gelatine, Seife, Öle, Fette, Wache, No. 14.17.18/1983 and No. 7.15/1984.
- Magggrander, K.: Use of Gelatine-Hydrolysates in meat products and ready-to-eat-meals, reprint by Gelita AG from the journal "Die Fleischerei."
- Magggrander, K.: Edible Gelatine in Meat Products – Manufacturing Examples and Processing Tips, Dt. Fachverl. 1991.
- Michael Ahlers et al., Interactions of gelatine with other water-soluble, gel-forming biopolymers, 3rd Freiberg Collagen Symposium, 2004.
- Morganti: Enriched gelatine as skin hydration enhancer, J. Appl. Cosmetol., 5/1987.
- Morganti: Protective effect of collagen upon irritation response of detergents, Int. J. Cosmet. Sci., 5/1983.
- Morganti: Role of insoluble and soluble collagen as skin moisturizer, J. Appl. Cosmetol., 4/1986.
- Morganti: Topical gelatine-glycine and alpha-hydroxy acids for photoaged skin, J. Appl. Cosmetol., 12/1994.
- Peter Hoffmann, Der Einsatz von Gelatine production in Lebensmitteln, Deutsche Milchwirtschaft 8/1984, Seite 269–273.
- Peter Hoffmann, Die Verwendung von Gelatine und Gelatine – Eiweißhydrolysaten in Süßwaren, Süßwaren 112–1985.
- Pfaff, G. and Pfaff, W.: Ernährungsphysiologische Bedeutung und Wirkung von Gelatine – eine Standortbestimmung, Apotheker Journal, Ausgabe 10/1989.
- Pfaff: Ernährungsphysiologische Bedeutung und Wirkung von Gelatine – eine Standortbestimmung, Apotheker Journal, 10/1989.
- Reinhard Schrieber, Der Einsatz von Gelatine in Marshmallows, Gordian, Jahrgang 72, Seite 137–139.
- Reinhard Schrieber, Speisegelatine – praxisgerichtet ausgewählt und verarbeitet, Eucker-und Süßwaren Wirtschaft, Heft 718–1976.
- Ringland, C. and Eschenbruch, R.: Gelatine for juice and wine fining, Food Technology in New Zealand (1983).
- Riso: Protein derivatives in cosmetics, Cosmetics and Perfumery, Vol. 89/1974.
- Scala: Effect of daily Gelatine ingestion on human scalp hair, Nutrition Reports, 13/1976.
- Scharfetter-Kochanek: Adv. Pharmacol., 38/1997.
- Schmidt-Thome et al., Zur Chemie eines neuen Plasmaexpanders, Arzneimittelforsch. 12, 378, 1962.
- Schott, A.: Healthful Foods with Gelatine, The World of Food Ingredients, October 1998.
- Schriever, R.: Speisegelatine für die Fleischwarenerzeugung, Die Fleischerei 4/1975.
- Schriever, R.: Stützen und Aspik-Produkte – Wissenswertes zur Gelatine-Auswahl und Fertigungstechnik, ZFL – Deutsche Zeitschrift für Lebensmitteltechnologie 3/1974.
- Siemensma, A. and Kunst, T.: Sports nutrition, The World of Ingredients, October 1999.
- Steisslinger: Kollagen-Hydrolysate – Herstellung, Eigenschaften und Anwendung in der Kosmetik, Parfümerie und Kosmetik, 9/1991.
- Textheft Fotografie, Fonds der Chemischen Industrie im Verband der Chemischen Industrie, 1999.
- Weissenbach, M. J.: Gelatine-Bierschönung in der Praxis, Brauwelt 18 (1985).
- Weissenbach, M. J.: Gelatine – Klär- und

- Stabilisierungsmittel für Bier, Brauwelt 46 (1983).
- Wucherpfennig, K., Possmann, Ph., Kettern, W., and Scherpe, W.: The effect of gelatine type on fining in white wines. Wein und Rebe, Wissenschaft, Forschung, Praxis 55, 920–937.
www.bmbf.de.
www.chirurgie-online.at.
www.medizininfo.de.

4

The Role of Collagen Hydrolysate in the Prophylaxis of Osteoarthritis and Osteoporosis

Increasing longevity, obesity, poor nutrition, and excess mechanical stress due to work or sports are the major reasons why osteoarthritis and osteoporosis rank as global diseases. This is of course a tremendous challenge for society, as neither condition can currently be cured. In most cases, treatment only relieves the pain and other symptoms caused by the disease. Prevention, therefore, is of the utmost importance. Scientific laboratory experiments and clinical applications have shown that a special form of gelatine – collagen hydrolysate – can contribute favorably to prevention.

4.1 Osteoarthritis

Today, on a worldwide basis, degenerative joint disease is affecting individuals at progressively younger ages and negatively impacting on their quality of life. Estimates confirm that some 15% of the world's population suffer from osteoarthritis brought about either by age-related natural joint wear and tear or by congenital factors. Osteoarthritis, one of many types of joint disease, is characterized by the onset of breakdown of the elastic buffering material of the joints – the cartilage (see Fig. 4.1). This "shock-absorber" material must cope with the large amount of mechanical stress placed upon it daily. Its degeneration leads to pain, loss of mobility, and an enormous decrease in overall quality of life.

The way we live can accelerate the occurrence of osteoarthritis. Physically demanding occupations such as tiling and bricklaying, as well as numerous athletic activities, can cause joint damage. Gross overweight also places unnecessary stress on joints as well as restricting mobility; it also frequently causes diabetes. These are two other factors that give rise to wear and tear of the joints. Osteoarthritis occurs mainly in industrialized countries. In Germany, for instance, half of all 35-year-olds have the first signs of degenerative joint disease, and, in the USA, osteoarthritis and other joint-related conditions affect nearly 70 million people.

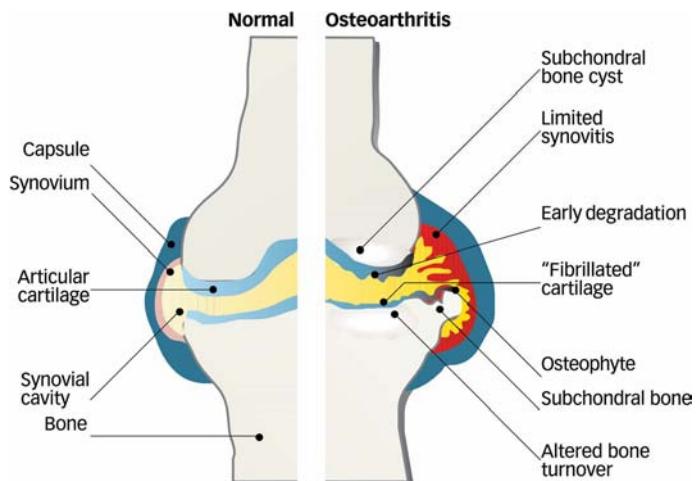


Fig. 4.1 Features of osteoarthritis.

4.1.1 Genesis and Conventional Therapy

The main components of cartilage are the collagen fibers that provide its structural framework and stability and the so-called proteoglycans that surround these fibers, furnishing them with elasticity and support. In healthy cartilage, these substances are constantly being synthesized and broken down. These processes, however, occur in equilibrium. In osteoarthritis, the equilibrium shifts significantly toward breakdown, thus leading to a continuous loss of cartilage mass. The spaces that are created are subsequently filled with less elastic collagen fibers, and these in turn increase the susceptibility of the cartilage to injury. This initiates the process that leads to osteoarthritis, where, in the worst case, the cartilage becomes completely degraded and exposes the underlying bone material.

Today, there is no known cure for osteoarthritis. If joints show signs of degenerative disease, treatment is typically aimed only at relieving pain and inflammation. The last resort is usually surgery, either for smoothing the edges of the joint cartilage or replacing the damaged joint with an artificial one. Thus, conventional therapy treats only the symptoms of osteoarthritis, even though serious side effects may occur. In fact, several drugs have been withdrawn from the market in the past for this very reason, but even proven drugs cause cartilage damage when used over a longer period of time. Non-steroidal anti-inflammatory drugs, for example, tend to inhibit the synthesis of proteoglycans, and the alternative, the drug cortisone, can affect the cartilage-forming cells – the chondrocytes – in such a way that they function to a limited extent only.

4.1.2

Preventive Treatment with Collagen Hydrolysate

The long-term goals of prevention or treatment of osteoarthritis must be to delay the onset of natural, age-related degradation of joint cartilage and – if the cartilage has already been damaged – to protect it from further damage.

This means that the chondrocytes have to be supplied with the necessary building blocks during the renewal phase. Under-supplied cartilage is particularly susceptible to further damage and also cannot regenerate to the same extent. What is required are substances that, when applied on a regular basis, are capable of providing the cartilage with an adequate supply of suitable nutrients. In addition, these nutrients should help the cartilage to regenerate itself to its full extent. Some 800 years ago, Hildegard von Bingen recommended taking “regular and plentiful portions of boiled calf cartilage” (in other words, gelatine) for the condition. Today, researchers and physicians have been able to confirm and explain this statement on a scientific basis. The substance that has proven particularly effective in this application is a special type of gelatine – collagen hydrolysate.

4.1.2.1 Mode of Action

Collagen hydrolysate is characterized by its excellent bioavailability and contains almost three times the amount of proline and glycine present in other proteins. It is precisely these amino acids that are ultimately responsible for collagen's unique 3-D conformation; they also influence the stability of the collagenous structures in cartilage.

Contrary to the long-held opinion that gelatine is fully digested in the intestinal tract, scientists know today that some fragments of the gelatine can pass through the intestinal membrane unaltered. In 1999 a research group headed by Dr. Steffen Oesser, Director of the Collagen Research Institute in Kiel, Germany, showed that collagen hydrolysate peptides were resorbed through the intestinal wall at an average molecular weight of 3300 g mol^{-1} . In addition, it was shown that these collagen fragments were significantly enriched in the joint cartilage.

Dr. Oesser's results were confirmed in an *in-vivo* study on foals, whose cartilage tissue developed more extensively following the addition of gelatine to their feed.

Collagen hydrolysate thus provides the precise and selective supply of the building blocks necessary for the synthesis of the cartilage matrix. Two additional *in-vitro* cellular experiments conducted by Dr. Oesser also showed significant, dose-dependent, stimulation of type II collagen synthesis in chondrocytes brought about by the addition of collagen hydrolysate: collagen hydrolysate stimulated the formation of type II collagen in joint cartilage by a factor of 2.5. Type II collagen is the collagen typically present in cartilage tissue (see Fig. 4.2).

After administration of the hydrolysate, a significant increase in the amount of proteoglycans was also observed. In contrast, there was no increase in protease activity. These observations demonstrate increased new synthesis of the complete cartilage matrix.

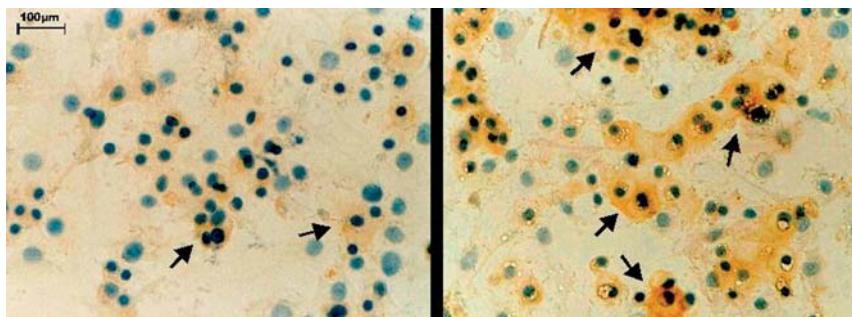


Fig. 4.2 The tight clusters of collagen deposits (brown color) around the chondrocytes (right) indicate the stimulation of collagen biosynthesis by collagen hydrolysate. Left: The chondrocyte culture without addition of collagen hydrolysate.

4.1.2.2 Clinical Studies

The modes of action described can explain the very positive results obtained in the numerous clinical studies conducted with collagen hydrolysate on a variety of groups of volunteers since the late 1970s. The individuals involved in the research studies ranged from elderly people with substantial degenerative joint disease to people with minor osteoarthritic symptoms and high-performance athletes with special joint problems.

In the mid-1980s, Prof. Adam carried out a randomized, double-blind study on 81 patients suffering from osteoarthritis. The results showed that treatment with collagen hydrolysate resulted in a 50% reduction in the pain score for more than half the patients in comparison to the control group (see Fig. 4.3). The results ob-

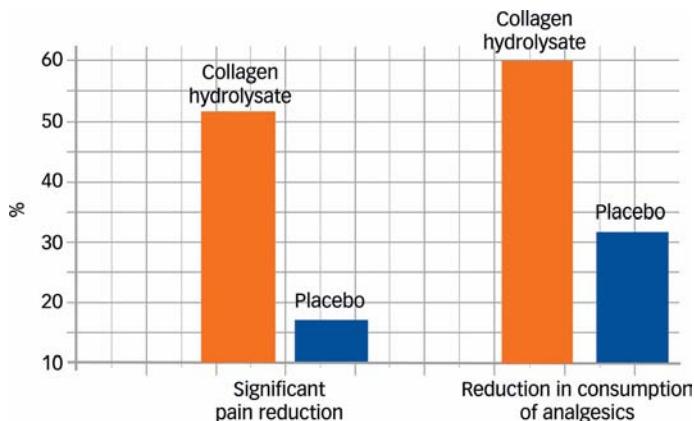


Fig. 4.3 In the mid-1980s, the results of a double-blind study showed that treatment with collagen hydrolysate over a longer period of time reduces pain and the consumption of analgesics in osteoarthritis patients.

tained from this study provided the basis for the granting of a patent for collagen hydrolysate: European Patent No. 0254289 – “Agents for the treatment of osteoarthritis, US Patent No. 4804745.”

Prof. Beuker, Head of the Department of Sports Medicine of the Institute for Sports Sciences at the University of Düsseldorf, Germany, carried out a number of studies to investigate the influence of collagen hydrolysate on various groups of patients, e.g., athletes, elderly persons with joint problems, and patients from a practice for sports medicine. Here too, following a three- or six-month study period involving the administration of collagen hydrolysate, the patients had considerably less pain, and the mobility of their joints had improved.

Dr. Seeligmüller, specialist for orthopedics, sports medicine, and physical therapy in Bonn, Germany, conducted several studies, each involving over 350 patients suffering from degenerative joint disease, by treating them with a mixture of gelatine and L-cystine. After treatment for a minimum period of six months, the patients, on average, experienced less pain and were able to walk longer distances than at the beginning of the study. Several patients even reported being completely symptom-free.

Toward the end of the 1990s, Prof. Moskowitz, Case Western Reserve University in Cleveland, Ohio, one of the leading rheumatologists in the USA, conducted an international osteoarthritis study comprising almost 400 patients suffering from osteoarthritis of the knee. The study was carried out in 20 hospitals in the USA, Great Britain, and Germany. In Germany for example, 112 patients were treated over a period of 24 weeks with a daily dose of 10 g collagen hydrolysate. After this period, the patients in the collagen hydrolysate group had considerably less pain and reported improved mobility (see Fig. 4.4).

In 2004, Dr. Rippe, Shrewsbury, Massachusetts, USA, presented the results of a clinical study involving 250 patients. These patients showed improved joint mobility and joint strength following the administration of a daily dose of 10 g collagen hydrolysate in combination with 300 mg calcium and 60 mg vitamin C.

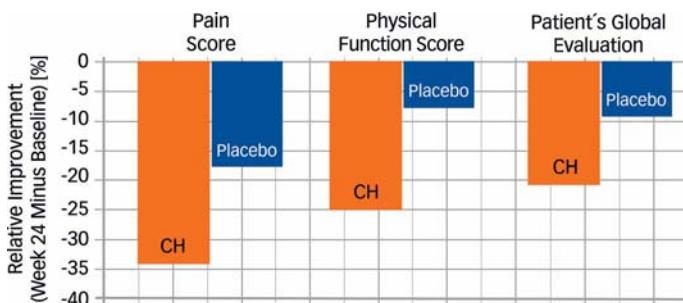


Fig. 4.4 In a further clinical study, collagen hydrolysates significantly reduced pain and improved joint function in German patients with mild- to moderate osteoarthritis.

These clinical studies clearly demonstrate that collagen hydrolysate is an excellent therapeutic substance for osteoarthritis and confirm the pre-clinical studies, which showed that the cartilage cells (chondrocytes) are stimulated by this substance. A daily dose of 10 g collagen hydrolysate over a longer period of time – as a rule at least 3 months – leads to cartilage regeneration and, in turn, to significantly improved joint mobility and less pain. Treatment with collagen hydrolysate proved particularly beneficial in cases of early osteoarthritis of the hip and knee. Excellent success was also achieved in the treatment of cartilage degeneration of the patella and in painful conditions of poly-osteoarthritis of the finger joints. The same applies to pain in the major joints resulting from excessive sports activity, degenerative disease of the vertebral column (e.g., Scheuermann's disease), and damage to cartilage brought about by injury in young people.

4.2 Osteoporosis

Osteoporosis, like osteoarthritis, is a worldwide disease. In the European Union alone, osteoporosis patients account for some 500 000 hospital bed days a year, a number that is expected to double over the next 50 years. Osteoporosis is a condition whereby the bone substance degenerates to such a degree and the bone density decreases so drastically that the bone mass is reduced and its structure becomes porous (see Fig. 4.5). This reduces the capacity of the bones to fulfill their support function and they become inelastic and brittle.

The probability of becoming afflicted with one of the various types of osteoporosis depends on age, gender, lifestyle, and previous history of illness. It is estimated that about 15% of men and 50% of women suffer from the disease, although it normally occurs at a later stage in life. Based on such estimates, some

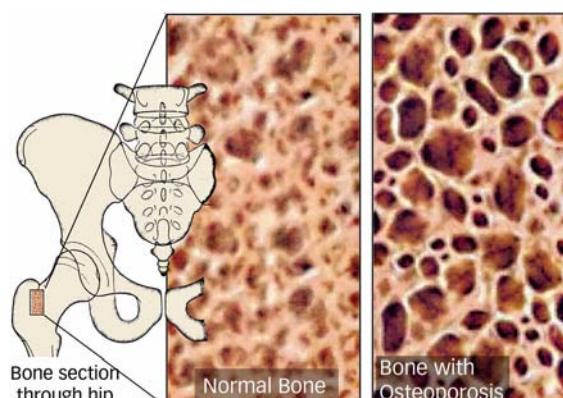


Fig. 4.5 Reduction in bone mass – osteoporosis – is easier to prevent than to treat.

75 million people in Europe, the United States, and Japan suffer from the disease. In Germany, about 10% of the population are affected.

Bones are not composed of inert substances. Like all other tissues in the human body, they consist of a living network of cells that are continuously being renewed, restructured, and broken down. In early years, the renewal process prevails and bone mass increases, a maximum level being attained at around the age of 20–25. However, at the age of about 35, the bones continuously decrease in density and the bone mass is reduced by about 1.5% per year.

This reduction in bone mass – osteoporosis – is easier to prevent than to treat. A well-designed preventive strategy can delay the onset of the disease, hence limiting its seriousness. For many years, prophylaxis and treatment concentrated on ensuring adequate supplies of calcium. This was an obvious solution, as loss of calcium is one of the major reasons for the occurrence of osteoporosis. However, as the primary structural element of bone is collagen, the loss of minerals also means increased loss of collagen. This can be measured by analyzing the urine. By administering collagen hydrolysate, the building blocks required for renewing bone collagen are provided, and the body then uses them for this purpose.

Within the scope of his studies on the effects of gelatine, Prof. Adam studied 120 osteoporosis patients over a period of three years. He treated half with a calcium preparation and half with a collagen hydrolysate preparation. Those in the collagen hydrolysate group were given no other medication. The results were surprising. The concentrations of substances indicating loss of collagen and bone mass were lower in the collagen hydrolysate group than in the control group. This meant that collagen hydrolysate inhibited breakdown more than calcium did. Of particular relevance, however, was the fact that collagen hydrolysate, in contrast to calcium, reduced bone fractures significantly. More investigation has to be done in this respect in order to verify these results scientifically. However, the results achieved to date by osteoarthritis researchers are most encouraging.

4.3

Processing into Food Supplements

In contrast to gelatine, collagen hydrolysate is subjected to further conditioning using enzymatic hydrolysis. As a result of this complex process, specific product properties are achieved that render collagen hydrolysate particularly suitable for use as a food supplement. Among its other properties, collagen hydrolysate is readily soluble in cold water, does not gel in highly concentrated solutions at normal processing temperatures, has a low viscosity, and is easily mixed into other products. It also has little influence on the sensory properties of the finished product. In contrast, other protein preparations such as casein, whey proteins, and soy all produce a bitter taste when the degree of hydrolysis is increased.

From the technological point of view, the only property of collagen hydrolysate that should be carefully monitored is its tendency to foam during dissolution. Also, when developing new products intended to provide health benefits for

joints, the ingestion route has to be considered, as the recommended daily dose of 10 g is relatively high for incorporation into a foodstuff. However, collagen hydrolysate can be produced a number of forms, e.g., powdered products, beverages, or liquid concentrates, all of which are fully accepted by the consumer. Products containing the recommended daily dose of collagen hydrolysate are already being marketed. Another attractive area from the technological and sensory points of view for products offering health benefits for joints is the production of protein bars (see Sections 3.1.4 and 3.2.1.3).

Gelatine and its special form, collagen hydrolysate, are, in contrast to many other “functional ingredients”, foods in their own right. They are recognized as being safe by the US FDA (Food & Drug Administration). The Federal Institute for Drugs and Medical Devices and the Ministry for Consumer Affairs in Germany as well as WHO (World Health Organization) have also confirmed that gelatine and collagen hydrolysate are safe and that there is no risk involved in consuming larger quantities on a regular basis.

4.4

Future Prospects

To date, because of its technological properties, gelatine has played a major role in the industrial manufacture of food. Now it has been shown that a related form of gelatine, collagen hydrolysate, is a suitable “functional ingredient” for the prophylaxis of degenerative joint disease and osteoporosis. This special property will continue to be of importance in the future. In the United States, for example, it is estimated that six out of ten children are either overweight or obese. Consequently, their joints are being subjected to excessive stress at an early age.

The metabolism that takes place in joints and bones, however, is slower than that in other organs. Thus, if success is to be achieved with collagen hydrolysate in the prevention and treatment of osteoarthritis and osteoporosis, the administration of a daily dose of 10 g should be commenced in earlier years. Such a long-term therapy is possible with collagen hydrolysate, as it supplies important nutritional protein and is also well tolerated by the body. Other than rare cases of a feeling of fullness and distension of the stomach, no side effects have been observed for collagen hydrolysate.

In fact, some other positive benefits have been observed during the clinical studies. Reports exist on improved growth of hair and nails as well as a distinct improvement in skin quality. Nails were reported to be less brittle and hair thickness and density were improved. In the skin, oral administration of collagen hydrolysate increases the water binding capacity of the epidermis. This is thought to be brought about by stimulation of collagen synthesis and activation of enzyme systems. The result is a much smoother skin. Thus, collagen hydrolysate is an excellent functional building block for use in the growth sector known as “cosmeceuticals”, i.e. products capable of improving physical appearance.

References

- Adam (1991): Welche Wirkung haben Gelatinepräparate?, Therapiewoche, 41, 2456–2461.
- Adam (1995): Gelatine, möglicher medizinischer Einsatz, Apoth. J., 9, 18–22.
- Beuker et al. (1996): Die Wirkung regelmäßiger Gelatinegaben auf chronisch-degenerative Schäden am Stütz- und Bewegungsapparat, Int. J. Sportsmed., 1, 1–88.
- Moskowitz RW (2000): The role of collagen hydrolysate in bone and joint disease, Semin. Arthritis Rheum., 30, 87–99.
- Oesser et al. (1999): Oral administration of ¹⁴C-labeled gelatine hydrolysate leads to an accumulation of radioactivity in the cartilage of mice (C57/BL), J. Nutr., 129, 1891–1895.
- Oesser et al. (2003): Stimulation of type II collagen biosynthesis and secretion in bovine chondrocytes cultured with degraded collagen, Cell Tiss. Res., 311, 393–399.
- Oesser et al. (2004): Impact of degraded collagen on joint cartilage, Ann. Rheum. Diskuss. 63:1, 375.
- Pfaff (1989): Ernährungsphysiologische Bedeutung und Wirkung von Gelatine – eine Standortbestimmung, Apotheker Journal, Heft 10/89, S. 22.
- Rippe et al. (2004): The effectiveness of collagen hydrolysate supplementation treatment in individuals with symptoms of mild osteoarthritis, EULAR-Kongress 2004.
- Seeligmüller et al. (1989/1993): Therapiewoche 39, 3153 ff. and 43, 1810 ff.
- Timm (1993): Einfluss der Gelatinfütterung auf das Skelett-, Haar-, Knorpel- und Hufwachstum bei Absatzfohlen, Dissertation, Tierärztliche Hochschule Hannover.

5

Future Prospects – Global Megatrends and Opportunities

Gelatine has been a staple for the human race for millennia. It is, and always has been, a valued foodstuff and an indispensable raw material for numerous technological applications, as this book has already shown. Many important products valued by consumers would not exist today without gelatine. Will this still be the case in the future? Will gelatine be just as important for tomorrow's products as it is for today's? Of course, it is not possible to make accurate predictions as to what the future will bring and what role gelatine will play. However, it is possible to use current global trends to establish scenarios and to draw certain conclusions as to how this versatile protein will contribute.

One of the greatest global challenges facing us is the growth of the world's population: according to projections established by the United Nations, it will grow by 2.6 billion by 2050, bringing the total population from 6.5 billion to 9.1 billion (see Fig. 5.1).

5.1

Increasing Population with an Increasing Proportion of Elderly People

Population growth is taking place almost exclusively in developing countries, where the total will increase from today's 5.3 billion to 7.8 billion in 2050. The total population of the 50 poorest countries will increase from 0.8 to 1.7 billion – more than double, and the countries with a younger demographic age, e.g. Uganda, Niger, Congo, and Afghanistan, will see their populations increase by a factor of 3. In contrast, the population of industrialized countries will remain practically constant at today's level of 1.2 billion (see Fig. 5.2).

Another trend that can be gleaned from the United Nations' figures is the significant aging of the population (see Fig. 5.3). Worldwide, the number of people over 60 will increase by a factor of three by 2050 – from currently 672 million to 1.9 billion. In the industrialized countries, the proportion of over-60s will increase from 20% to 32% over the same period. Therefore, the greatest total increase in elderly population will be in developing countries.

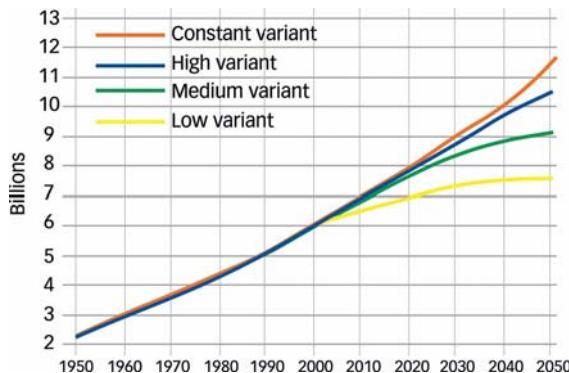


Fig. 5.1 Estimated development of the world population up to 2050 according to UN projections.

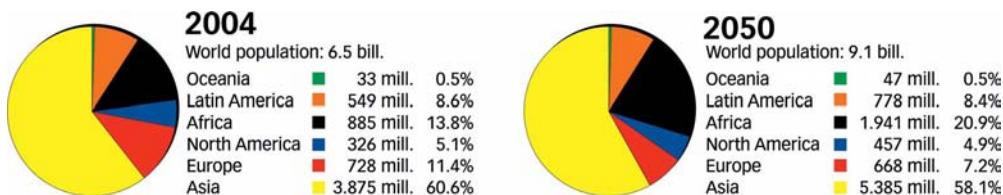


Fig. 5.2 Development of the world population up to 2050 according to region.

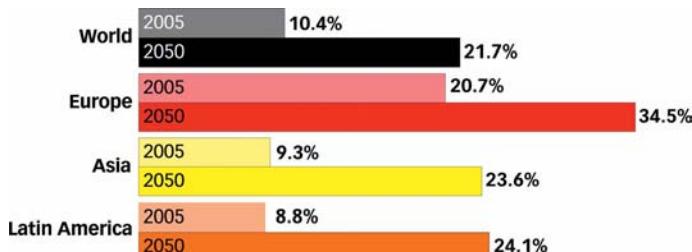


Fig. 5.3 Development of the proportion of over-60s in the world population up to 2050 in the various regions.

5.2

No one Type of Grain can Cover all Nutrient Requirements

On the one hand, this development means that diseases directly associated with age – joint degradation, as one example – will play a growing role. On the other hand, aging will also seriously affect worldwide nutritional requirements. In the developing countries, the primary task will be to provide more basic nutrients, at the same time eradicating deficiencies in amino acids, vitamins, and minerals. In these countries, foodstuffs rich in starch will continue to be the staple diet. No single grain – whether wheat, barley, corn, rice or millet – can meet the complete requirement for all nutrients: the available grain must be supplemented nutritionally and physiologically. As in the case of animals, this can be achieved not only by the use of synthetic vitamins and amino acids, but also by providing other types of food.

For example, food rich in starch contains relatively little lysine. Gelatine, with its high content of lysine, could be instrumental in compensating for this deficiency (see Section 3.2.5), especially as it is easy to transport and process and has a long shelf life. Ethnic and religious aspects can also be addressed by selecting and processing the raw materials in the appropriate manner.

In addition to the value of gelatine as a protein, its technological properties and the pleasing sensory characteristics associated with it are relevant in the area of nutritional supplements. For example, gelatine can indirectly encourage calcium intake. Many people do not drink milk but do consume edible dairy products. The success of fruit yogurts throughout the world – and gelatine is a key ingredient – is confirmation of this (see Section 3.2.2). Another example is oil-soluble vitamins that can be converted into stable, water-soluble food supplements by encapsulation with gelatine hydrolysate (see Section 3.2.9).

5.3

Health is an Invaluable Asset

Like deficiency diseases, many other health problems are created by conditions such as obesity, which is often associated with affluence. However, these health problems affect not only rich countries but also less privileged ones, urban areas particularly. Indeed, the world is being continuously urbanized (see Fig. 5.4). By the year 2007, the majority of people will be living in cities, and two thirds of these will be in developing countries. By 2050, over 6 billion people will be living in cities – today's world population. And this will happen rapidly and dynamically: Mexico City grew in size from 1 million to 8 million people within 30 years; London required 130 years to reach the same size.

If the exploding costs of health care are to be contained in future, health care issues must be addressed in our daily lives, whether in developing or in industrialized countries. This development is primarily driven by a constantly growing population group determined to live as healthily as possible. This group

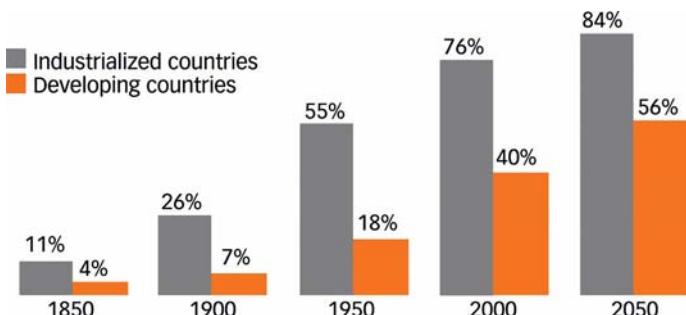


Fig. 5.4 Development of the urban population as a proportion of the total up to 2050.

– “Lifestyle of Health and Sustainability” – is estimated to be a third of the population in the USA. In Europe, it is probably larger. In addition, politicians are becoming more and more active in their attempts to counteract the effects of obesity and diseases such as osteoarthritis that are influenced by affluence. In Holland for example, the largest of the health insurance companies, VGZ, gives a bonus to its members when they purchase low-fat margarine.

5.4

Low-calorie, Low-fat, and Low-carb

In health care, the reduction of calories, fat, and carbohydrates as well as the pursuit of “anti-aging” will become especially important. Anti-aging products are those that actively counteract the aging process. To a certain extent, gelatine falls into this category (see Sections 3.2.5 and 4.0). It is a valuable protein that contains neither cholesterol nor sugar, but it can reduce the caloric value of foods and beverages and stimulate cartilage metabolism, thus helping to prevent osteoarthritis. Therefore, gelatine can provide an interesting and low-cost solution for many issues of this nature. Gelatine can also be valuable in cosmetics, where anti-aging products are becoming much more popular (see Section 3.2.8).

Those who are prepared to look after their own health and well-being tend to be somewhat more egoistic with respect to their needs and wishes in other areas as well. Consumption is thus becoming even more individualized. Today, consumers demand foodstuffs that are tailor-made with respect to when they are consumed and the benefits they offer. Another megatrend is the convenience food market. The consumption of pre-prepared foods in Europe and the USA is estimated to double between 1999 and 2009. The constituents of such convenience products, especially if they are of the low-calorie type, will include hydrocolloids such as gelatine. These play an important role (see Section 3.2.5), as they replace fat by water or air.

These significant consumption trends will at some time in the future also be observed in the emerging nations. Increasing affluence automatically increases

the consumer demands of the population. Perhaps one of the first things to be accomplished will be in the sphere of medication – to replace the somewhat hard-to-swallow tablet with a smoother and more palatable capsule that has a longer shelf life. Also, people are likely to demand a “soft” fruit gum rather than a hard sweet, or a fruit curd or foam rather than a natural one. Here too, gelatine can play a major role, as it combines enjoyable eating with nutrition and technology in an ideal manner.

5.5

The Digital Revolution Continues

The social developments described above will be complemented by new technologies that will also change our world. A good example is the fundamental change from analog to digital photography, a process that is already very advanced.

Digital photography revolutionized the market within a very few years, both qualitatively and quantitatively. General interest in photography has never been as great as it is today. It is estimated that some 130 million cameras were purchased worldwide in 2005, and of these about 100 million were digital cameras. Thus, digital photography, within a few years, had reached a much larger market size than analog photography ever did or ever will. In fact, analog photography is now shrinking continuously. In 2005, according to its own figures, the Eastman Kodak Company generated 54% of its turnover with digital photography; for the first time in its history, digital photography products sold more than analog products. In spite of this, photographic film, and hence photographic gelatine (see Section 3.2.7), will continue to play a role, at least in the medium term. “Single-use cameras” are currently selling at some 450 million units per year worldwide. And there are still many countries with inadequate IT infrastructures where analog photography is still of interest and importance.

Whether analog or digital, however, all these cameras, including mobile phone cameras, which have sold eight times more than digital cameras, only store information. And this creates the demand to have prints on paper to view and to share. Here, in both areas, gelatine provides the basis for the necessary coatings and emulsions (see Section 3.2.7). Thus, growth areas for gelatine are being developed, as many more photographic prints are now being produced than were ever produced when analog photography was the only process available.

5.6

Environmentally Friendly Production Processing Is Gaining Ground

It is expected that environmentally friendly production processes will continue to gain ground. After all, many more people will be living on our planet, and its resources will proportionally become scarcer. It will be the challenge of research and technology to guarantee that the conflict between preserving our resources



Fig. 5.5 To produce food in an environmentally friendly manner, other methods of providing nutrients to plants and protecting them will have to be developed. One small contribution to the overall problem could be to use a gelatine sponge as a depot for the controlled release of nutrients and protective substances.

on the one hand and providing food on the other is solved in an environmentally friendly manner. Agriculture will have to be pursued using much less raw material such as fertilizer, herbicides, and seed. And gene- and biotechnology will surely, for this reason alone, be much more directed toward nutrition and the cultivation of plants. In addition, other methods of providing nutrients to plants and protecting them will have to be developed. If appropriate, this can be achieved with gelatine by using a gelatine sponge (see Fig. 5.5) as a reservoir for the controlled release of nutrients and protective substances. Alternatively, collagen hydrolysate can act as a source of nitrogen for synthetic fertilizers containing minerals (see Section 3.2.9).

And, as man cannot live by bread alone, the production of meat will also increase. Between 1995 and 2020, the demand for meat in developing countries will have increased by over 40%. Therefore the gelatine industry will become all the more important in that gelatine is a high-quality protein, produced from the by-products of meat processing, that can be stored practically indefinitely (see Section 2.2). The constantly increasing world population will demand that all raw materials used in the production of food be completely utilized and not – as is the case today in many countries – disposed of.

5.7

Our Oil Reserves Are Shrinking

Another effect brought about by an increasing world population is the shrinking of our oil reserves. Ultimately there will be a shortage of this valuable raw mate-



Fig. 5.6 Gelatine is not only highly versatile in nutritional and physiological applications, but also extremely multi-faceted technologically. Flexibility will be a key factor in tomorrow's world.

rial. Alternatives will have to be found, and this will continue to be a challenge for our polymer chemists. Numerous ideas for utilizing gelatine have been developed, many of these to a practical stage. Molded items, films, and fibers (see Fig. 5.6) are only a few examples (see Section 3.2.9). None of these has become established on the market to date because of the costs involved. However, a shortage of oil could change this. Gelatine polymers could well become significant products under the right circumstances.

5.8

Gelatine's Flexibility will also be in Demand Tomorrow

The rapid increase in the human population will present complex problems in the future. New technologies and nutritional strategies will have to be developed to solve these. Gelatine can play at least a limited role in keeping these new processes rolling. In the area of environmental protection, it has proven to be an effective agent for decontaminating buildings containing asbestos, for cleaning oil tanks and containers, or for cleaning up oil spills at sea. It is also a component of fully degradable detergents (see Section 3.2.9). It plays an important role in medical applications, where it has been used for centuries as a valuable pharmaceutical excipient. Tomorrow, it will be an integral building block in regenerative medicine (see Section 3.2.6). Gelatine is not only highly versatile in nutritional and physiological applications, it is also extremely multi-faceted technologically (see Section 2.1). And one thing is certain: flexibility will be a key factor in tomorrow's world.

Reference

Rosengrant et al. 2020 Global Food
Outlook, Alternatives and Choices,
International Food Policy, Research
Institute, Washington, 2001.
www.un.org

6 Glossary

AAS (Atomic Absorption Spectrometry)

A highly sensitive method for the quantitative analysis of metals and semi-metals in aqueous solution by vaporizing them and evaluating the resulting spectrum.

Adhesion

The sticky force between a solid interface and another substance, either in solution or particulate.

Acid procedure

A manufacturing process used to produce type A (acid) gelatine. Pigskin is the normal starting material for the process.

ADI (Acceptable Daily Intake)

The amount of a substance (e.g. food additive, vitamin or trace element) in milligrams or micrograms per kg of body weight that, when ingested on a daily basis, is regarded as being medically acceptable. International committees of experts decide on the appropriate levels.

Alkaline (basic) procedure

A manufacturing process used to produce type B (basic) gelatine from pre-conditioned alkaline ossein or bovine hide splits.

Amino acids

The basic building blocks of proteins that are subsequently incorporated into polypeptide chains.

Amino acid sequence

The order of occurrence of amino acids in a protein chain.

Amino acid spectrum

The percentage of individual amino acids in a particular protein.

Amphoteric (Greek amphoteros = both)

Molecules that have both anionic and cationic properties.

Anionic tensides

Surface-active substances with one or more functional anion-active groups.

Aspic

A food application in which pieces of meat, vegetables or other ingredients are set in a gelatine jelly.

 A_w -value

Describes the free water content (water activity) in foodstuffs, a factor that influences chemical and microbiological stability. Favorable A_w -values are less than 0.8; the highest value guaranteeing safety is less than 0.4.

Bentonite

An absorbent type of clay.

Big Bags

Packaging units, normally made of plastic material of 1–2 m³ capacity, for contents of 500 to 1000 kg powder gelatine.

Bloom value

The Bloom value is the measure of the firmness of a gelatine gel. In determining the value, the force required to depress the surface of a 6.67% gel by a plunger with a specific shape and size, by 4 mm is measured 18 hours after the gel has been stored at exactly 10 °C. The Bloom value for a standard commercial gelatine ranges between 50 and 280.

Body (of a capsule)

The smaller part (in diameter) of a hard shell capsule.

Bone chip

Chopped, degreased and dried bone that is subsequently demineralized.

Bovine hide split

Connective tissue from the central layer of the hide that is used as a raw material for the production of gelatine.

BSE (Bovine spongiform encephalopathy)

A fatal, neurodegenerative disease in cattle caused by infectious prions (mis-folded proteins), commonly known as “mad cow disease.”

Cap (of a capsule)

The larger part (in diameter) of a hard shell capsule.

Caplets

Gelatine-coated tablets.

Certification

Confirmation of a standard situation, e.g. Quality Management Systems, according to international standard ISO 9000.

Coagulation

The process of converting the individual components of a solution into a gel accompanied by flocculation.

Coalescence

The fusion of the fine drops of an emulsion to form a separate liquid phase.

Coacervation

The process by which a colloidal oily polymer is converted from a solution into a solid through precipitation.

Cohesion

The sticking together of particles within a substance.

Collagen

The primary protein of the connective tissue in man and animals and the most abundant protein in mammals.

Collagenase

An enzyme that specifically cleaves the peptide bonds in collagen.

Collagen tenside

A chemically modified collagen protein that demonstrates good detergent properties and excellent skin compatibility.

Compounding industry

Specialized companies which prepare mixtures of different hydrocolloids and other additives for use in specific applications.

Conditioning

Chemical pre-treatment of the gelatine raw material by alkali or acid to cleave certain covalent bonds which renders the protein warm water-soluble.

CPMP (Committee for Proprietary Medicinal Products)

Political board of the EU Member States for regulatory affairs concerning medical products on the market.

Cross-linking

Chemical covalent bonding between different parts of a polymer chain or between different polymer chains (in this case, polypeptide chains), which makes the protein partially or totally insoluble.

Degree E

Traditional unit for viscosity measurements, primarily in the glue industry.

Diatomaceous earth

A lightly-colored porous rock composed of the shells of diatoms which is finely ground for filtration material.

Dispersion

A system comprising a continuous liquid phase and one or several finely distributed discontinuous solid or gas phases that are not, or only slightly, soluble in each other. The generic term for an emulsion or suspension.

Draize Test

Application of a test substance to the eye or skin of an animal and the subsequent observation of any adverse effects such as irritation.

Endotoxin

A potentially toxic, natural compound derived from bacteria.

EMEA (European Medicine Evaluation Agency)

A scientific board of experts from the European Union countries that approves new drugs and monitors their safety.

Emulsion

A system comprising very finely distributed, non-miscible liquids. In the case of an oil-in-water emulsion (e.g. milk), the oil phase is distributed in the form of very fine droplets in the solvent phase. A mixture of silver halide crystals in a gelatine solution is often improperly designated as an emulsion as it is in fact a suspension.

EN

A standard published by the European Committee for Standardization. The standardization agencies of the twenty nine national members represent the twenty five member states of the European Union, three countries of the European Free Trade Association (EFTA) and countries who are likely to join the EU or EFTA in the future.

Enzyme

A protein of high molecular weight synthesized in cells and functions as a biocatalyst.

Enzyme stabilizers

Short-chain polypeptides that prolong the effectiveness of enzymes.

Essential amino acids

Amino acids that the body requires because it cannot synthesize them on its own. They must therefore be ingested with foodstuffs as components of proteins.

Excipient

An inactive substance used as a carrier for the active ingredients of a medicinal product or to be used to aid the process by which a product is manufactured.

Extraction

The stepwise dissolution of gelatine from the pre-treated raw material in hot water.

Fining

The clarification of wine, beer or juices by the use of clarification aids.

Food Chemical Codex

The US register of standards for the authorized use and the quality specifications for food additives.

FDA (Food and Drug Administration)

The regulatory organization for the approval and control of foodstuffs and drugs in the USA. The FDA is part of the Department of Health and Human Services.

Gelatine sponges

Blood-stanching gelatine foams used in surgical operations. They are made of dried, chemically cross-linked gelatine foam, have an extremely high absorbent capacity and are highly compatible with the human body.

Gelling power

The ability of a certain amount of gelatine to form a gel of a specific firmness.

Gelometer

Equipment for measuring the firmness of a gel.

Gel strength

In general, the firmness of a gel. It is also expressed as Bloom grams, Bloom value or Bloom in gelatine testing.

Glutin glue

A natural adhesive made by boiling animal tissue containing collagen (skin and bone). It is not specially purified.

HACCP (Hazard Analysis Critical Control Points)

A worldwide-recognized system for the systematic preventive process control during all stages of production and preparation processes mainly in the food, phar-

maceutical and cosmetic industries. Each production step must be checked and tested for the potential presence of microbiological, chemical or physical hazards. The critical points are subject to constant monitoring.

Hard shell capsules

Hard shell gelatine capsules are hollow capsules of various diameters made from pure gelatine with or without color additives. They are composed of two halves and are connected together after they are filled with product.

Hardening

To make a gelatine partially or totally insoluble by cross-linking the molecules by treatment with chemicals, dry heat, radiation and other methods.

Hide split

The center portion of the hide of cattle, obtained by splitting the hide into three layers.

hL

One hectoliter is equivalent to 100 liters. It is a unit of volume used particularly in the beverage industry.

HLB (hydrophilic-lipophilic balance)

A parameter used to classify surfactants according to their degree of hydrophilicity.

HPLC (High-Performance Liquid Chromatography)

A highly sensitive analytical method in column chromatography. The application area for this multi-component analytical technique ranges from the quantitative determination of organic and inorganic ions, neutral organic substances, metal chelates to polymers. It is also used for the measurement of the molecular weight distribution of gelatine.

Hydrolysis

A reaction where chemical compounds are cleaved by water. Hydrolysis takes place by increasing the temperature or by the effect of acids, bases or enzymes.

Hydrocolloids

Substances of high molecular weight that are soluble in water and that can be dispersed or swollen to produce viscous liquids, pseudogels or gels.

Hydrophilic

A hydrophilic molecule or portion of a molecule that is typically polar and charged and capable of hydrogen bonding, enabling it to dissolve readily in water.

Hydrophobic

Hydrophobic molecules tend to be non-polar and are thus attracted to other hydrophobic molecules and non-polar solvents.

Hydroxyproline

A non-essential amino acid found only in collagenous protein and thus used for the determination of gelatine protein.

Hysteresis

A reversible process that does not proceed identically in both directions. The melting and solidification curves of gelatine gels lie e.g. on different temperature levels. However, the starting and end-points of both curves are the same.

ICH (International Committee on Harmonization)

A committee comprising national regulatory authorities and representatives from the pharmaceutical industry. Their goal is to harmonize the regulations as contained in the various national pharmacopoeias.

IEP (Isoelectric point)

The pH at which a molecule exhibits an electrical charge of zero.

Instant gelatine

Cold water-soluble, extremely fine powdered gelatine produced using a special drying process that forms a so-called pseudo-gel.

IP (isoionic point)

The pH of the gelatine molecule itself when no other ions are present in the solution.

ICP (Inductively Coupled Plasma)

Emission spectrometry using a high frequency field for ionization of a gas (for example argon) that can atomize and excite the sample. Used mainly to check for metal ions.

Two types of detectors are typically used:

ICP-OES: Optical Emission Spectrometry

ICP-MS: Mass Spectrometry

ISO 9000

An internationally standardized Quality Management System. Its application in companies is certificated by certain organizations authorized to award such certificates.

Liquid protein

A hydrolyzed gelatine solution with tryptophan, color and flavor added for weight-reducing diets in the United States at the end of the 1970s.

Maceration

A process whereby calcium phosphate is removed from degreased bones by the addition of hydrochloric acid. The demineralized collagen raw material obtained is known as ossein and used in the production of gelatine.

Maillard reaction

A reaction that takes place with amines and amino acids with reduced sugar content, especially with the generation of heat. The Maillard reaction is principally responsible for the brown color that develops when food is heated. During the production of gelatine, it brings about the increasing yellow coloring that appears during the later stages of extraction.

Methacrylated gelatine

A type of gelatine chemically modified with methacrylate groups. It is used for the manufacture of intermediate technical products e.g. for the microencapsulation and packaging industries.

Microencapsulation

The process whereby fine liquid or solid phases are encased within a film-forming polymer (e.g. gelatine). Subsequent to emulsification and coacervation or interface polymerization, they precipitate onto the phase to be encapsulated.

Milk of lime

An oversaturated solution of calcium hydroxide.

Mixed bed

Ion exchange columns, which are filled with a mixture of cation and anion exchange resins.

Mouth feeling

A complex sensory impression created while eating food. This sensory impression is based on hardness, elasticity, chewiness, viscosity and other properties of the foodstuff. It is sensed by the lips, teeth, tongue and the oral cavity.

Nutritional physiology

The science of the influence of nutrition or nutrients on the natural life processes within the organism.

Oscillating rheometer

A special viscometer with mechanical movements used to measure the viscoelastic properties of substances.

Ossein

Demineralized bone material used as a raw material in the production of gelatine.

Osteoarthritis

A complex, chronic joint disease brought about by the degradation of cartilage.

Osteoporosis

A disease brought about by a deficiency of bone tissue and calcium phosphate in the bone, which leads to increased susceptibility to fracture.

PE-coated paper

A paper base for photographic material coated with a very thin film of polyethylene upon which the gelatine emulsion is placed.

PEG

Polyethylene glycol, a polymer of ethylene oxide.

Perlite

An amorphous volcanic glass that has a relatively high water content. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently.

Permeability

The ability of a material to allow e.g. gases or dissolved substances to pass through it.

Pharmacopeia

A book containing directions for the identification of samples, the preparation of compound medicines and the purity of excipients, published by the authority of a government or a medical or Pharmaceutical Society.

Photographic emulsion

A system comprising light-sensitive silver halide microcrystals and the binding agent gelatine. The gelatine enhances the photographic sensitivity. Photographic emulsions are the basis of modern classical photography. To be accurate, the system is in fact a suspension.

Plasma expander

A blood substitute based on modified gelatine or other polymer solutions, which is used to temporarily increase blood volume.

Pre-treatment

Acid or alkaline treatment of the gelatine raw materials before extraction.

Protective colloids

Polymer compounds that, due to the presence of groups in the molecule that are attracted to both water and oil, stabilize disperse colloidal systems.

Protein hydrolysates

Protein hydrolysates are produced subsequent to thermal, chemical or enzymatic degradation, whereby essentially insoluble protein molecules are broken down into soluble proteins, peptides and amino acids.

Purine

A degradation product of uric acid found mainly in meat, which can lead to gout in certain metabolic disorders.

Pyrogen

A fever-inducing substance, which is derived from bacteria that are present during production processes.

Random coil structure

A random coil is a polymer conformation where the monomer subunits are oriented randomly while still being bonded to adjacent units. It is not one specific shape, but a statistical distribution of shapes for all the chains in a population of macromolecules.

Retentate

The part of a filtration that is retained by the membrane. It is the opposite of permeate, the part that is allowed to pass through the membrane.

Scleroproteins

Proteins that have a support function within the organism. They are fibrous in nature and are insoluble in water. Keratin of the hair and nails and the collagen of connective tissue, skin, bone and cartilage as well as the elastins are all scleroproteins.

Soft shell gelatine capsules

Capsules produced from gelatine that contain liquid active ingredient-excipient mixtures in an elastic gelatine shell that can be produced in various thicknesses. They can be closed off with or without a seal.

Succinylated gelatine

Gelatine modified with succinic acid anhydride to provide it with very good swelling properties.

Suspension

A system comprising a continuous liquid phase and one or several finely distributed solid phases.

Syneresis

The exudation of liquid from a gel caused by temperature or aging brought about by internal tension (e.g. the layer of whey on a yogurt).

Tailing

The connecting of molded confectionery pieces by uninterrupted jelly strings to become ropelike.

Tensides

Substances capable of reducing the surface tension of a system. In this way they facilitate the formation of dispersions.

Thermoreversibility

The property of a gel which allows for the conversion from a solid to a liquid state and vice versa as a result of temperature changes.

Tilapia

A warm water fish that inhabits a variety of fresh and, less commonly, brackish water habitats from shallow streams and ponds to rivers, lakes, and estuaries. Very common in aquaculture in the Southern United States and Asia.

Triple helix

Basic structural form of collagen, comprising 3 protein chains. These often have differing amino acid sequences. Collagen type I e.g. has two alpha-1 and one alpha-2 chains, each comprising some 1,000 amino acids.

TSE (Transmissible spongiform encephalopathy)

A group of progressive diseases that affect the brain and nervous system of humans and animals and are transmitted by prions.

Type A gelatine

Gelatine produced using the acid (A) process.

Type B gelatine

Gelatine produced using the basic (B) process.

USDA

United States Department of Agriculture.

USP

United States Pharmacopeia.

Visco-elastic

Behavior of a substance which exhibits both viscous and elastic characteristics.

Viscosity

The degree of internal friction in liquids and gases. The viscosity influences the flow properties of liquids and gases. In the case of gelatine, basic type B has a higher viscosity than type A at the same Bloom level. The higher the temperature the lower the viscosity.

von Bingen, Hildegard

German Abbess and mystic (1098–1179). Was involved with religion, music, biology and medicine.

Zeolite

A mineral (alumino-silicate) of natural or synthetic origin with a micro-porous structure.

Subject Index

a

- adhesion properties 62 f.
- Agfa AG 6 f.
- agglomerated instant gelatine 153 f.
- amphoteric behavior 61 f.
 - isoelectric point 61
- Asahi 33
- aspic products 204 ff.
 - frozen products 210
 - fully sterilized products 209 f.
- assurance process 99 ff.

b

- binding of cooking juice 212 f.
- British Glues and Chemicals 16
- BSE 36

c

- Caesar & Ewald 14
- capsule gelatine 247 ff.
- capsule materials, alternative 251 ff.
 - pastilles 255
 - plasmas substitutes 253 f.
 - vitamin coating 254
- chemically modified gelatines 63 ff.
 - cross-linking 64
 - transglutaminase 65
- coating 266 ff.
- Coignet 12
- collagen 45
- collagen glue 1
- collagen hydrolysate 237 f., 301 ff.
 - as a food supplement (joint and bone health) 307
- combined fining 222
- complex coacervation 283 ff.
- conditioning process 48
- confectionery 163 ff.
 - fruit gummies 163
- connective tissue 275

Cooper, Peter 9

- corned beef 213
 - water binding in fresh meat 213 f.
- cosmeceuticals 308
- cosmetics 272 ff.
 - gelatine hydrolyzate 279
 - haircare 281
 - protective colloid 282
 - protein surfactants 282 f.
 - skin care 278
- Croda 24

d

- D'Arcet recipe 226
- dairy products and pastries 191 ff.
 - stirred and thermally treated fermented milk products 192
- Davis gelatine 16
- Deutsche Gelatine-Fabriken (DGF AG) 7, 14
- DGF Stoess group 23
- dressings 217 ff.
- drip loss 213
- Dynagel 19, 30

e

- Eastman, George 6
- Eastman Gelatine 16
- edible gelatine 99
- elastin 278
- Eli lilly 4
- environmental aspects 96 ff.
- Ewald 24
- Extraco 30
- extraction 75 ff.
 - batch process 75 ff.
 - continuous extraction 78 f.

f

- fining efficiency 224
- fining gelatine 220 ff.

- Fuji 19
 functional ingredient 162
 functional properties of gelatine 51
 future prospects 311 ff.
 – agriculture 316
 – anti-aging 314
 – digital photography 315
 – global trends 311
 – health care 313
 – oil reserves 316 f.
 – worldwide nutritional requirements 313
- g**
 gel formation 51, 52 f.
 gel strength 53 f.
 gelatine and nutrition 226 ff.
 – amino acids 230 ff.
 – biological value 228 ff.
 – low-fat, low-car, low calorie 234
 gelatine capsules 240
 gelatine desserts 163 ff.
 – fruit gummies 163
 gelatine glazing and dipping masses 211
 gelatine hydrolysate 62, 93 ff., 153 ff., 179 ff., 215 f., 226, 235, 238, 281
 – aromas 187
 – chocolate eggs 186
 – cold baked cakes 186
 – convenience food 238
 – gelatine desserts 182 ff.
 – instant beverages 187
 – licorice 187
 – low-carb diet bars 181
 – lozenges 187
 – manufacturing 89 ff.
 – processing 152
 – protein bars 181
 – spicy cereal bars 181
 – sugar-coated candies 186
 gelatine in the pharmacopoeias 239 f.
 gelatine sponges 5
 GELITA AG 14, 38
 Globex process 243
 Goodman Fielder 33
 Göppinger Gelatine-Fabrik Paul Koepff 15
 granulated gelatine 86 ff.
 – standardization and packaging 88 f.
 gummy bears 11
- h**
 hard-shell capsule machine 241
 Heidelberger Gelatine-Fabrik Stoess 14
 hide split 69 ff.
- high-gloss ink-jet paper 268 ff.
 – color stability 268
 – special modifications 268
 hot fining 225
 hydrocolloids
 – confectionery 189
 – dairy 201
 – gelatine in combination with other 201 ff.
 hydrocolloids (functional properties in comparison to gelatine) 119 ff.
 – agar-agar 123 f.
 – alginates 125 f.
 – carrageenans 124 f.
 – gellan gum 133 f.
 – gum arabic 128 f.
 – hydrocolloid blends 135
 – locust bean gum 127 f.
 – modified cellulose 129 ff.
 – pectin 126 f.
 – starch/modified starches 132
 – xanthan gum 133
- hydroxylysine 47
 hydroxyproline 47
- i**
 instant gelatine 91 ff., 150 ff.
 – manufacturing 91 ff.
 – processing 150 ff.
 interaction with
 – sugar 187 f.
 – sugar substitutes 188
- j**
 JELL-O® 9
 Jelly tablets 10
 joint and bone health 238
- k**
 keratin 273
 Kind & Knox 26
 Kind Gelatine 16
 Knox, Charles 9
 Knox Gelatine 13
 Knox sparkling gelatin 26
 Kodak Number 1 camera 6
 Koepff & Söhne 15
 KONICA 19
- l**
 leaf gelatine 89 ff., 146 ff.
 – manufacturing 90 ff.
 – processing 146 ff.
 Leiner 18

liquid protein 11
low-fat butter 198
low-fat meat products 215

m

manufacturing process 66
matt ink-jet paper 271 ff.
– color density 271
mayonnaise 217 ff.
meat and delicatessen products 203 ff.
medical applications 255 ff.
– gelatine-headed probe 255
– gelatine sponges 255
– implantation of heart valves 255
– minimally invasive techniques 257
– regenerative medicine 257
– tissue engineering 259
milk substitute products 203
mogul machine 166 ff.
molecular structure 45 ff.
– primary structure 45
– quaternary structure 46
– secondary structure 46
– tertiary structure 46
molecular weight distribution 48 ff.
– acid-conditioned gelatine (type A) 48
– alkaline-conditioned gelatine (type B) 48

n

native collagen 278
Nitta 19

o

Odin gelatine plant 18
ossein 66 ff.
– maceration 66 ff.
– pressure hydrolysis 69
osteoarthritis 301 ff.
osteoporosis 301 ff.

p

panna cotta 198
Papin, Denis 3
PB Gelatins 13, 27
pharmaceutical applications 239
– hard-shell capsules 241
– soft-shell capsules 243 ff.
pharmaceutical gelatine 99
photographic applications, special tests 115 ff.
– gold number 116 f.
– hardening behavior 116

– photographic properties,
characterization 115 f.
photographic emulsion 259, 263
photographic gelatine 260 ff.
photographic process 260 ff.
photographie 260 ff.
pickled products 214
pigskin 71
powder gelatine 137
– dissolution process 138
– hot-melt process 140
– two-step process 140
pre-fermentation fining 225
preventive treatment with collagen
hydrolyzate 303
– osteoarthritis 301 ff.
– osteoporosis 306 ff.
processing of a gelatine solution 142
– process optimization 144
– setting temperature 143 f.
– setting time 143 f.
– viscosity 142 f.
processing the extracted gelatine 82 ff.
– concentration 85 f.
– drying 86 ff.
– purification 83
– sterilization 86
production of fish and fowl gelatine 79 ff.
– amino acid composition 81
protective colloid function 62

q

quality control 99 ff.
– quality criteria for gelatine 101
– regulatory requirements 100

r

raw material conditioning 72
– acid pretreatment 74
– alkaline pretreatment 73
reduction of baking, frying, and grilling losses 215 ff.

rheology 55 f.

Rotary die process 243

Rousselot 13

Rountree 10

s

Scherer, Robert P. 5

Schrieber/Gareis

slurry 163 ff.

sol-gel transitions 56

– complex viscosity 57

- special chemical/technological tests 110 ff.
 - foam capacity/stability 112
 - gelatine protein 115
 - gelation point 110
 - gelation time 110
 - hydroxyproline 115
 - isoelectric point 113 f.
 - melting point 110
 - molecular-weight distribution 113 f.
 - organic nitrogen compounds 114
 - rheology 111
- stabilization against syneresis 192 ff.
 - fermented milk drinks 194 f.
 - ice cream 194 ff.
 - powdered dairy products 200 f.
 - sandwich spreads and cheeses 198 ff.
 - stabilization of cream 196 ff.
 - whipped desserts 194 ff.
- standard quality tests (final product) 104 ff.
 - bloom value 104 ff.
 - clarity 107
 - color 107
 - conductivity 109
 - inorganic components 108
 - microbiological tests 109
 - odor 108
 - peroxides 108
 - sulfur dioxide 108
 - taste 108
 - viscosity 106 pH 106
 - water content 107
- starch-free molding 168 ff.
 - caramel candy bar fillings 1757 ff.
 - caramel chews 177 ff.
 - cereal bars 179 ff.
 - marchmallows 172 f.
 - meringues 173 ff. soft
 - muesli 179 ff.
 - nougat 177 ff.
- Stoess, Heinrich 6
- sugar-coated tablets 255
- Sundstroem, Lage 11
- surface properties 59
 - emulsions 59
 - foams 59
- t**
- technical applications 283 ff.
 - agro sponges 292
 - animal glue 287
 - ballistics and forensic science 289
 - biodegradable transparent films, cups, curlery, plates 292
 - book restoration 288
 - coatings 290
 - environmental protection 295 f.
 - films 290
 - leaf fertilizers 292
 - match head 287
 - microencapsulation 283
 - natural detergent 294
 - playing cards 288
- technical gelatine 283
- Tessenderlo 23
- texture 52
- thermal degradation 141
- type A gelatine 74 f.
- type B gelatine 73 f.
- v**
- visco-elastic behavior 55
 - cooling and heating curves 55
 - crossover point 55
- viscosity 52
- w**
- Weishardt 12
- y**
- yogurt 191

Related Titles

Ziegler, H. (ed.)

Flavourings

**Production, Composition, Applications,
Regulations**

2007

ISBN-13: 978-3-527-31406-5

ISBN-10: 3-527-31406-7

Bauer, K., Garbe, D., Surburg, H.

Common Fragrance and Flavor Materials

Preparation, Properties and Uses

2001

ISBN-13: 978-3-527-30364-9

ISBN-10: 3-527-30364-2

Wintgens, J. N. (ed.)

Coffee: Growing, Processing, Sustainable Production

**A Guidebook for Growers, Processors,
Traders, and Researchers**

2004

ISBN-13: 978-3-527-30731-9

ISBN-10: 3-527-30731-1

Mollet, H., Grubenmann, A.

Formulation Technology

Emulsions, Suspensions, Solid Forms

2001

ISBN-13: 978-3-527-30201-7

ISBN-10: 3-527-30201-8

Oetjen, G.-W., Haseley, P.

Freeze-Drying

2004

Hardcover

ISBN-13: 978-3-527-30620-6

ISBN-10: 3-527-30620-X