

Recent Progress in Dialdehyde Starch Technology^{*)}

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Introduction

Dialdehyde starch, once a laboratory curiosity, is now a full-fledged industrial chemical that can command a world market. The wealth of information on dialdehyde starch and its uses obtained during the past few years has been disclosed mainly in patents and is not readily available to the average cereal or starch chemist. This review, therefore, brings together the patent literature from 1960 to 1966 and emphasizes the particular areas of dialdehyde starch technology with which the author is familiar. Previous reviews on dialdehyde starch are listed in Table 1.

Table 1
Reviews on dialdehyde starch

1. Dialdehyde Starches. Properties, Preparation, and Technical Perspective. TEGGE, G.: *Stärke* **12** (1960), 321.
2. Dialdehyde Starch. Its Preparation and Its Uses. BEDUNEAU, H.: *Rev. Prod. Chim.* (December 31, 1961), 598.
3. Structure, Reactions, and Technology of Dialdehyde Starch. BORCHERT, P. J.: *Kunststoffe* **51**, 3 (1961), 137.
4. Preparation and Utilization of Dialdehyde Starch. BABOR, K., V. KALÁČ and K. TILARÍK: *Listy Cukrovar.* **80** (1964), 265.
5. Production and Use of Dialdehyde Starch. MEHLTRETTTER, C. L.: *Starch Chemistry and Technology*, Vol. II. Chapter XVII, Academic Press, Inc., New York, in press.

Electrolytic Preparation of Iodic and Periodic Acids

The low-cost production of dialdehyde starch depends upon efficient processes for the manufacture of periodic acid or its water-soluble salts.

A schematic diagram of the first electrolytic cell developed at the Northern Regional Research Laboratory of the U.S. Department of Agriculture for the production of periodic acid from sodium iodate is illustrated in Figure 1. The cell consists of four lead sheet

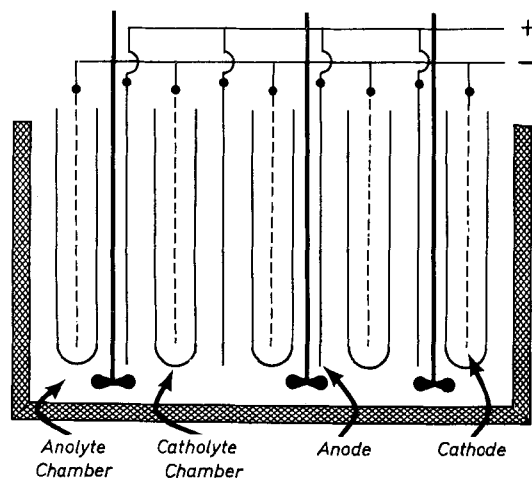


Fig. 1. Schematic diagram of laboratory cell.

anodes (1% silver-lead alloy) and five diaphragms of alundum contained in a 27 cm × 12 cm deep lead-lined wooden box equipped with three air stirrers and a lead cooling coil. The diaphragms were fitted with inlet and outlet glass tubing to permit filling with 5% alkali and flushing with water.

The anolyte liquor contained about 6% sodium iodate, sulfuric acid to pH about 1.5, and about 5% sodium sulfate. During electrolysis sodium ions migrate to the cathode to produce sodium hydroxide and hydrogen. Excess alkali is removed by occasional flushing of the catholyte chambers with deionized or distilled water. Iodic acid is converted to periodic acid by oxygen or peroxide liberated at the catalytic lead dioxide anode.

The electrolytic cell used for larger batch production of periodic acid had an effective volume of about 5.5 gallons of anolyte liquor. The six anodes were prepared from 1/8-in. lead alloy sheet containing 1% silver. There were 14 cathode compartments or diaphragms made of alundum (Norton Company**; RA 84 grade) arranged in 7 pairs so that there was a pair on both sides of each anode. Each diaphragm held a steel rod cathode and appropriate glass tubing for flushing with deionized water. Two air-driven agitators coated with polyvinyl chloride were used. Figure 2 shows the operation of five of these cells in series.

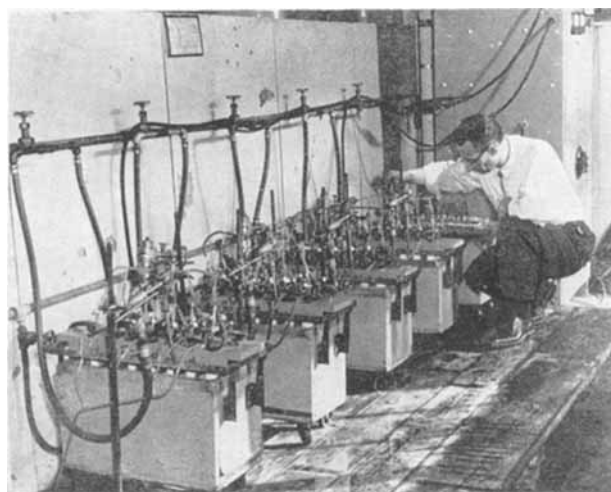


Fig. 2.
Battery of electrolytic cells for periodic acid production.

Later in developing a continuous process for making periodic acid by recycling of iodic acid liquors from dialdehyde starch production, the alkaline catholyte was allowed to drip continuously into the anolyte liquor to maintain sodium ion concentration and good conductivity. In this cell the iodic acid recycled liquor

^{*)} Presented before 1966 Starch Congress, Detmold, Germany, April 27–29, 1966.

^{**) The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.}

was pumped at about 1 gallon per minute into one end of the cell and the overflow from the other and was stored in a 55-gallon polyethylene tank. A flowsheet of the overall dialdehyde starch process is shown in Figure 3 to illustrate the recycle step.

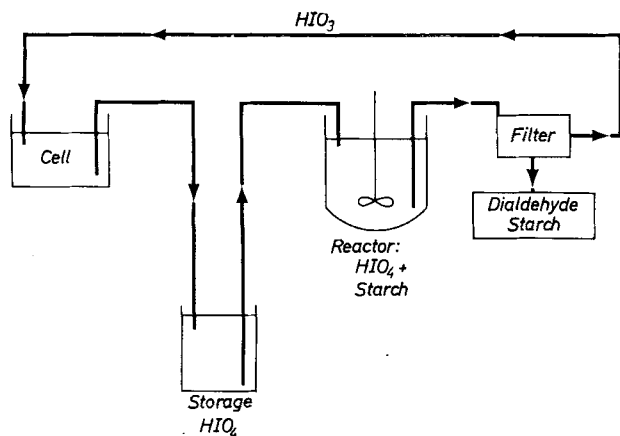


Fig. 3. Flow sheet of dialdehyde starch process.

A compilation of recent publications on the production of periodic acid is given in Table 2. Almost all of these developments are related to improvements in cell design, anode construction, and diaphragm materials.

Reference 1 in Table 2 concerns an annular electrolytic cell designed for continuous conversion of sodium iodate to sodium periodate at current efficiencies of about 80%. Figures 4 and 5 illustrate this type of cell.

MANTELL in 1960-1962, under contract with the Northern Regional Research Laboratory, devised a plate and frame electrolytic cell as a prototype com-

mercial cell for periodic acid production as shown in Figure 6. Novel diaphragms consisting of polyvinyl chloride, polyethylene, and ion exchange membranes were investigated in this cell. The use of ion-exchange membrane cells was further developed by the Ionac

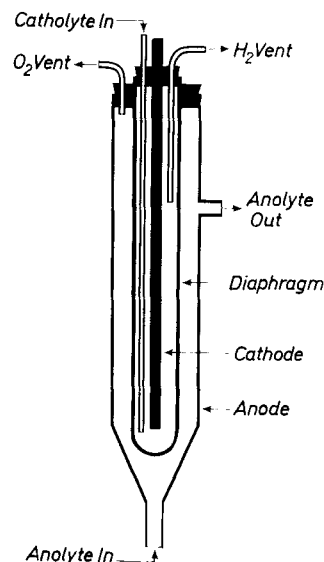


Fig. 4. Annular electrolytic cell diagram.

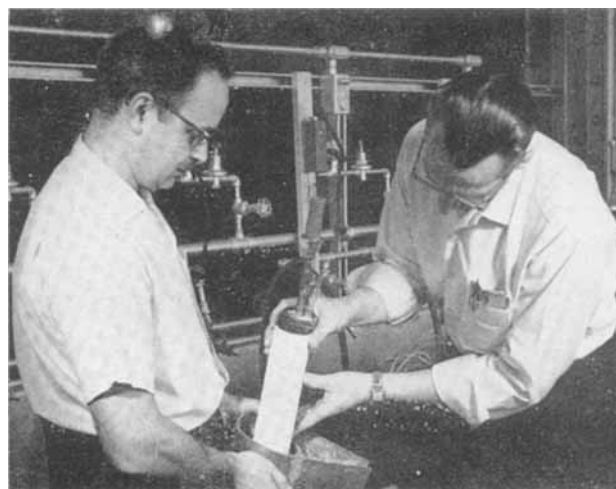


Fig. 5. Experimental annular electrolytic cell.

Chemical Company for the preparation of periodic acid. In 1963, Miles Laboratories obtained Belgium Patent 632 859 that describes the use of synthetic polymer fabrics of suitable porosity in periodic acid electrolytic cells.

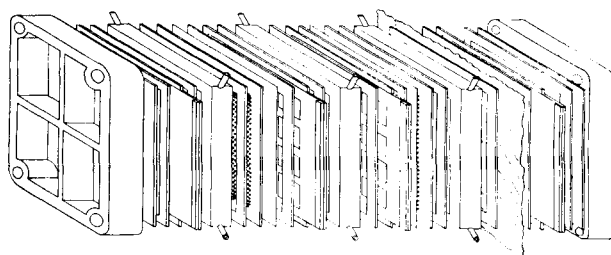


Fig. 6. Cell assembly.

Table 2

Electrolytic preparation of iodates and periodates

1. An Annular Cell for the Oxidation of Iodate. CONWAY, F. H., and E. B. LANCASTER: *Electrochem. Technol.* **2**, 1-2 (1964), 46.
2. Commercial Electrolytic Cell for Periodic Acid Production. MANTELL, Charles L.: *Ind. Eng. Chem.* **1** (1962), 144.
3. Electrolytic Oxidation of Iodate to Periodate. Belgian Patent 632,859 (1963). (Miles Laboratories, Inc.).
4. New Anodes Show Off for Chemical Producers. Anon.: *Chem. Eng.* **72**, (July 19, 1965), 82. U.S. Patent 2945791 (1960), (GIBSON, F. D.).
5. Electrolytic Processes for the Production of Iodic Acid Using a Special Lead Dioxide Anode. AIYA, Y., and S. FUJII: *J. Electrochem. Soc.* **109** (1962), 419. Japanese Patent 5254 (1963). (Sanwa Pure Chemicals Co., Ltd.).
6. Electrolytic Preparation of Periodic Acid and Periodates by the Use of a Lead Anode. Japanese Patent 10751 (1962). (Kurashiki Rayon Co., Ltd.).
7. Electrolysis Preparation for Periodic Acid Without Sulfates. Japanese Patent 5255 (1963).
8. Oxide Anodes. RAZINA, N. F.: *Chem. Abstr.* **60** (1964), 15427 f.
9. Electrolytically Regenerated Periodic Acid for the Oxidation of Starch to Dialdehyde Starch. RAMASWAMY, R., et al.: *Indian J. Technol.* **1**, 3 (1963), 115.
10. Bypassing the Byproduct Route to Iodates. Anon.: *Chem. Week* **86**, 2 (1960), 49.

MANTELL also found that lead alloy anodes containing 1% silver and coated with lead dioxide by electrolysis in dilute sulfuric acid produced less lead dioxide sludge in the cell during periodic acid formation than lead dioxide-coated lead anodes. Recently new anodes consisting of lead dioxide-coated graphite have been developed as replacements for conventional platinum anodes in the production of sodium perchlorate from sodium chlorate and periodates from iodates (Figure 7). Such anodes afford a minimum of sludge during electrolysis.

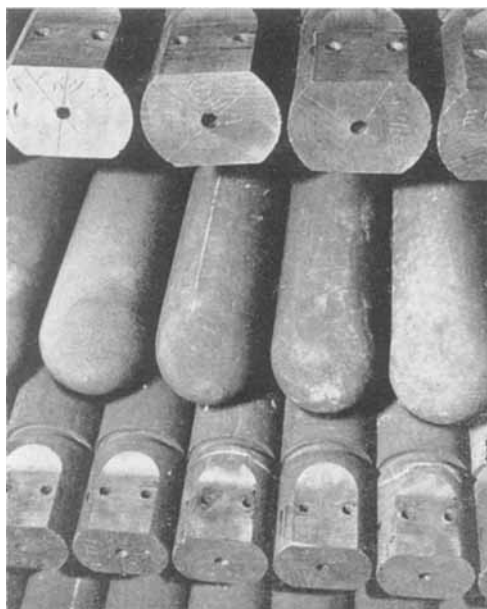


Fig. 7. Commercial lead dioxide-coated graphite anodes (photograph courtesy of Pacific Engineering and Production Company of Nevada, Henderson, Nevada).

AIYA and FUJII described the direct production of periodic acid from iodine in dilute bromine water using a special type of lead dioxide anode. In this cell 75% current efficiency is obtained without the presence of sulfuric acid in the anolyte. This is an advantage if crystalline periodic acid is to be prepared. Japanese Patents 10751 and 5255 both disclose the production of periodic acid from iodic acid in the absence of sulfate ions by using, respectively, a pure lead anode and a lead dioxide anode. Periodic acid solutions useful for the production of dialdehyde starch, however, do not require the absence of sulfate ions.

Reference 8 in Table 2 relates to Russian work with lead dioxide anodes for periodate formation from iodate solutions.

Optimum conditions for the preparation of periodic acid are described by RAMASWAMY et al. (reference 9 in Table 2) using a lead dioxide-coated lead anode, a ceramic diaphragm, aluminum cathode, and sulfuric acid-iodic acid anolyte. The periodic acid solution produced at current efficiency of 75% was used to oxidize tapioca starch to 82% dialdehyde starch at an oxidation efficiency of 99%. Results were fair when sodium iodate was converted to periodic acid in a cell containing an asbestos fiber-covered, nickel-plated iron cathode and lead dioxide anode. Reference 10 in Table 2

concerns producing potassium iodate from potassium iodide by using graphite anodes and nickel cathodes in an undivided cell.

Periodate Oxidation of Starch

Recent literature references to the periodate oxidation of starch are given in Table 3.

Table 3

Periodate oxidation of starch

1. Oxidation of Starch to Dialdehyde Starch. Hungarian Journal. Ref. Abstr. Bull. Inst. Paper Chem. **33**, 7 (1963), 1007.
2. Experience with the In-Cell Process for the Periodate Oxidation of Starch. CONWAY, H. F., E. B. LANCASTER and V. E. SOHNS: Electrochem. Technol. **2**, 1-2 (1964), 43.
3. Two-Stage Process for Dialdehyde Starch Using Electrolytic Regeneration of Periodic Acid. PFEIFER, V. F., et al.: Ind. Eng. Chem. **52** (1960), 201.
4. Process for Periodate Oxidation of Polysaccharides. U.S. Patent 3086969, J. SLAGER (1963). (Miles Laboratories, Inc.).

The Hungarian article describes the in-cell periodate oxidation of various starches which is no longer being used for making dialdehyde starch. A discussion of the technical problems involved in the in-cell process is given by CONWAY, LANCASTER, and SOHNS.

PFEIFER and associates in 1960 prepared periodic acid in an electrolytic cell and used it for the oxidation of starch to dialdehyde starch outside of the cell. Best overall results were obtained at pH 0.7 to 1.5. In 1963, Miles Laboratories was granted U.S. Patent 3086969 that discloses a process for the periodic acid oxidation of starch at pH below 1.0.

Structure of Dialdehyde Starch

Although the dialdehyde starch structure is usually written with free carbonyl or aldehyde groups, evidence at hand indicates the presence of hydrated forms of the dialdehyde units such as the hemialdal structure (I) or the gem-dihydroxy structure (II) as seen in Figure 8. Figure 9 depicts infrared patterns obtained

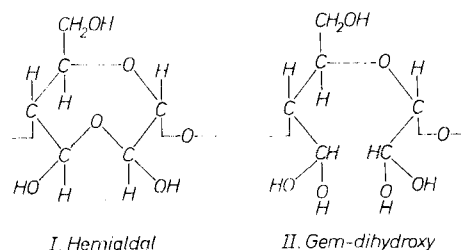


Fig. 8. Structure of dialdehyde starch.

by means of the potassium bromide disk technique, from air-dried dialdehyde starch containing 12% moisture and from the same starch vacuum dried over phosphorus pentoxide at 100°C. The wavelengths 5.76 and 6.10 μ represent the respective absorption bands of carbonyl and water of hydration. It is seen that free carbonyl content increases upon destruction of the hydrate by removal of water.

MILCH and MURRAY (1) have shown (Figure 10) that dialdehyde starch in a 20% aqueous solution prepared by autoclaving at 120°C for 30 minutes at pH 6 may occur in alternate gem-dihydroxy configurations.

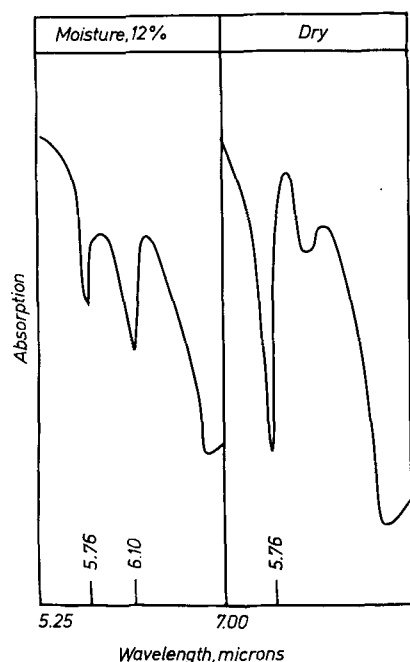


Fig. 9. Dialdehyde starch infrared patterns.

Dialdehyde starch in aqueous dispersion has the strong and broad absorption bands in the 9–11 μ range characteristic of hydrated glyoxal and glycollic aldehyde and entirely lacks the carbonyl stretching vibration at 5.76 μ . In physical studies on periodate-oxidized amylose solutions by ERLANDER et al. (2) other hydrated structures, however, have been suggested.

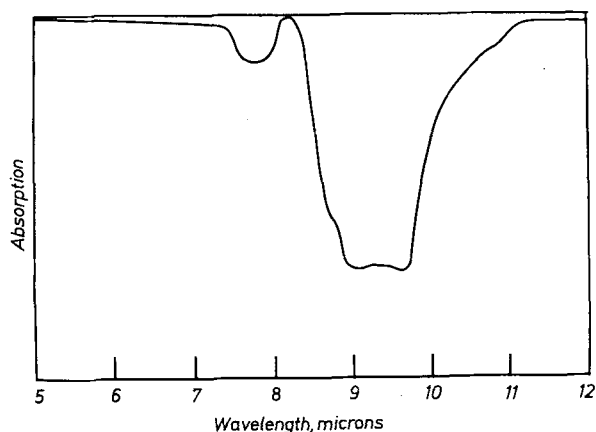


Fig. 10. Infrared spectrum of 20% dialdehyde starch solution.

Reactions of Dialdehyde Starch

The high reactivity of the hydrated carbonyl groups in the dialdehyde starch structure has resulted in numerous products of practical significance in recent years. The crosslinking reactions of this polymeric dialdehyde are of particular value as enumerated in Table 4.

Other reactions of dialdehyde starch and the products resulting therefrom are grouped in Table 5. Of

interest also is a new colorimetric method of analysis for dialdehyde starch (3).

Table 4

Crosslinking reactions of dialdehyde starch in the patent literature

Substrate	Application	Patent
Polysaccharides	Water-resistant films	U.S. 2988455 (1961) American Machine & Foundry Co.
Polyvinyl alcohol	Water-insoluble films	U.S. 3034999 (1962) Miles Laboratories, Inc.
Collagen	Surgical stitching	Fr. 1299855 (1962)
Delimed hides	Tanning	Can. 647684 (1962) Miles Laboratories, Inc.
Gelatin	Hardening	U.S. 3057723 (1962) Eastman Kodak Co.
Gelatin	Hardening	U.S. 3058827 (1962) Eastman Kodak Co.
Gelatin	Hardening	Brit. 907675 (1962) Gevaert Photo-Producten N. V.
Collagen	Tanning	U.S. 3093439 (1963) Johnson and Johnson
Polyvinyl alcohol	Water-resistant films	U.S. 3098049 (1963) Miles Laboratories, Inc.
Phosphoproteins	Water-resistant films	Brit. 941101 (1963) Miles Laboratories, Inc.
Leather	Tanning	U.S. 3114589 (1963) Ledoga S.P.A.
Collagen	Sausage casings	Ger. 1159748 (1963) Naturin-Werk Becker and Co.
Polyvinyl alcohol	Water-resistant films	Jap. 8382 (1964) Okuno Pulp Res. Inst.
Starch amino ethers	Water-resistant films	U.S. 3127393 (1964) Corn Products Co.
Starches	Water-resistant films	U.S. 3145116 (1964) Miles Laboratories, Inc.
Casein and soy protein	Plywood glue	U.S. 3153597 (1964) Northern Regional Research Laboratory
Casein and soy protein	Water-resistant coatings	U.S. 3188223 (1965) Northern Regional Research Laboratory
Casein and clay	Water-resistant paper coatings	Jap. 4519 (1964) Nihon Kasei K. K.
Casein and clay	Water-resistant paper coatings	U.S. 3169073 (1965) Northern Regional Research Laboratory
Casein fibers	Tanning	U.S. 3176002 (1965) Miles S. P. A.

Dialdehyde Starch for the Production of Wet-Strength Paper

The chief industrial application of dialdehyde starch at present is for the production of wet-strength paper toweling and tissue (4). Cationicdialdehyde starches are used for this purpose by wet-end addition to cellulosic pulp. Good retention on the negatively charged pulp is secured through the positive electrical charge on the cationic-dialdehyde starch. Although the mechanism of wet-strength production has not been elucidated, it is believed to be a crosslinking reaction of the hydrated carbonyl functions of dialdehyde starch with the hydroxyl groups of cellulose through hemiacetal formation.

Table 6 refers to the published literature on the use of dialdehyde starch in the preparation of wet-strength paper.

Table 5

Other reactions of dialdehyde starch in the patent literature

Substrate	Product	Patent
Acrylonitrile	Readily dyed copolymer	Jap. 271368 (1960) Kanegabuchi etc.
Dialdehyde starch (hydrolysis)	Erythrose and glyoxal	U.S. 2993387 (1961) Northern Regional Research Laboratory
Dialdehyde starch	Erythritol and glycol	U.S. 3046312 (1962) Northern Regional Research Laboratory
Antibiotics	Water-soluble deriv.	Belg. 620619 (1962) Koninklijke etc.
Melamine	Chemical intermediates	U.S. 3021329 (1962) Miles Laboratories, Inc.
Allyl alcohol	Allylated DAS	U.S. 3063855 (1962) Northern Regional Research Laboratory
Dialdehyde starch (pH 6.5)	DAS of improved prop.	Brit. 927510 (1963) Miles Laboratories, Inc.
Phenol	Phenol deriv.	U.S. 3117105 (1964) Miles Laboratories, Inc.
Acrylamide	Acrylamide deriv.	U.S. 3100203 (1963) Miles Laboratories, Inc.
Polyacrylamide	Polyacrylamide deriv.	U.S. 3117949 (1964) Miles Laboratories, Inc.
Dialdehyde starch (depolymerized)	Trialdehyde	U.S. 3132181 (1964) Northern Regional Research Laboratory
Urea	Polyglucosylol-urea	U.S. 3001979 (1961) Miles Laboratories, Inc.
Urea	Urea deriv.	U.S. 3177250 (1965) Miles Laboratories, Inc.
Guanylurea	Guanylurea deriv.	Jap. 13548 (1963) Sanwa Junyaku K. K.
Guanidine	Guanidine deriv.	Jap. 13800 (1963) Sanwa Junyaku K. K.
Cyanamide	Cyanamide deriv.	Jap. 21250 (1963) Sanwa Junyaku K. K.
Ammonia gas-alcohol	Ammonia deriv.	Jap. 21249 (1963) Asahiy Kaseikogyo K. K.
„Girard's reagent T“	Cationic hydrazone	Jap. 23499 (1963) Miles Laboratories, Inc.
Alcohols (DMSO)	Acetals	Jap. 15550 (1964) Miles S. P. A
Bisulfite	Addition products	U.S. 3098869 (1963) Miles Laboratories, Inc.
Bisulfite	Solution	Jap. 16929 (1964) Ashi Kasei Kogyo K. K.
Bisulfite	Gels	Jap. 16930 (1964) Ashi Kasei Kogyo K. K.
Urea-formaldehyde	Oxymethylated urea deriv.	U.S. 3009889 (1961) Miles Laboratories, Inc.
Urea resin	Derivative	U.S. 3169076 (1965) Miles Laboratories, Inc.
Amino triazine resin	Dispersions	U.S. 3099573 (1963) Miles Laboratories, Inc.
Alkaline	Improved dialdehyde starch	Can. 677622 (1964) Miles Laboratories, Inc.

In reference 16 of Table 6 it is reported that cationic dispersions of dialdehyde starch are generally superior in wet- and dry-strength performance to that of the thermosetting resins examined under the same conditions and at the same level of addition to cellulosic pulp.

Dialdehyde starch is unique as a wet-strength agent in that it produces almost instantaneous wet strength

in paper and allows extremely easy broke recovery. Other advantages are its minimum effect on the water-absorbency properties of paper and its ability to achieve various degrees of permanency of wet strength.

The impetus for the development of dialdehyde starch as an industrial chemical originated in the Northern Regional Research Laboratory of the U.S. Department of Agriculture in Peoria, Illinois, as part of a program to find new uses for cereal grains. The processes were commercialized by Miles Laboratories of

Table 6

Dialdehyde starch in wet strength paper

1. High Wet-Strength Paper by Wet-End Addition of Dialdehyde Starch. Tappi **43** (1960), 639. (Northern Regional Research Laboratory)
2. Dialdehyde Starch Retention by Use of Cationic Starch for High Wet-Strength Paper. Tappi **44** (1961), 430. (Northern Regional Research Laboratory)
3. Preparation of Cationic Dialdehyde Starches for Wet-Strength Paper. Tappi **45** (1962), 750. (Northern Regional Research Laboratory)
4. High Efficiency Wet-Strength Production by Dialdehyde Starch in Closed White Water Systeme. Tappi **45** (1962), 177. (Northern Regional Research Laboratory)
5. Dialdehyde Starch Hydrazones-Cationic Agent for Wet-Strength Paper. Tappi **46** (1963), 400. (Northern Regional Research Laboratory)
6. Cationic Dispersion of Dialdehyde Starch. I. Theory and Preparation. Tappi **47** (1964), 525. II. A Comparative Evaluation in Bleached Softwood Sulfate. Tappi **47** (1964), 583 (Miles Laboratories, Inc.)
7. Wet-Strength Paper Containing Polymeric Dialdehydes. U.S. Patent 3062703 (1962). (Northern Regional Research Laboratory)
8. Process for Making High Wet-Strength Paper Containing Polymeric Dialdehyde. U.S. Patent 3067088 (1962). (Northern Regional Research Laboratory)
9. Cationic Polymeric Dialdehydes and Their Use in Making Wet-Strength Paper. U.S. Patent 3087852 (1963). (Northern Regional Research Laboratory)
10. Wet-Strength Paper Comprising Highly Oxidized Periodate Oxystarch and Process of Preparing the Same. U.S. Patent 3184333 (1965). (Northern Regional Research Laboratory)
11. Method of Sizing Paper with Dialdehyde Polysaccharide-Urea Resin and the Product Thereof. U.S. Patent 3169076 (1965). (Miles Laboratories, Inc.)
12. Aqueous Dispersions of Periodate Oxidized Polysaccharide Amino Triazine Reaction Product and Process of Preparing Same. U.S. Patent 3099573 (1963). (Miles Laboratories, Inc.)
13. Paper Coating Composition. Belg. Patent 640681 (1964). (Miles Laboratories, Inc.)
14. Paper Strengthening Method. Jap. Patent 6570 (1964). (Ashi Kasei Kogyo K. K.)
15. Modifying Cellulosic Fibers. Belg. Patent 612789 (1962). (Miles Laboratories, Inc.)
16. Cationic Dispersions of Dialdehyde Starch. III. Comparative Evaluation in Three Commercial Pulp. Tappi **48** (1965), 583. (Miles Laboratories, Inc.)
17. Reaction Product of a Dialdehyde Polysaccharide with a Metal Salt and Preparing Paper Containing Same. U.S. Patent 3236721 (1966). (Miles Laboratories, Inc.)
18. Water-Dispersible Form of Dialdehyde Polysaccharide and Process Therefrom. U.S. Patent 3236792 (1966). (Miles Laboratories, Inc.)
19. Preparation of Aminoguanidine Derivatives. U.S. Patent 3230213 (1966). (Northern Regional Research Laboratory)

Elkhart, Indiana, and new cationic-dialdehyde starch products were developed by this company. Outside of the United States, the Japanese have done more on the production and applications of dialdehyde starch than others.

Summary

Developments in the field of dialdehyde starch technology in the past 5 years have been reviewed. Particular attention is given to the advances made in (a) the electrochemical preparation of periodic acid for conversion of starch to dialdehyde starch, (b) the reactions of dialdehyde starch, and (c) the application of dialdehyde starch in the production of wet-strength paper.

Zusammenfassung

Es wurden Entwicklungen auf dem Gebiet der Dialdehyd-Stärketechnologie in den vergangenen 5 Jahren besprochen. Besondere Aufmerksamkeit wurde den Fortschritten gewidmet, die auf folgenden Gebieten gemacht wurden: a) die elektrochemische Herstellung von Perjodsäure zur Umwandlung von Stärke in Dialdehydstärke, b) die Reaktionen der Dialdehydstärke und c) die Anwendung der Dialdehydstärke bei der Herstellung von naßfestem Papier.

Résumé

On discute les développements des cinq dernières années dans le domaine de la technologie dialdéhyde-amidon.

don. Plus spécialement on a mis l'accent sur les progrès obtenus dans les domaines suivants:

- a) la préparation électrochimique de l'acide périodique pour la transformation de l'amidon en amidon dialdéhyde,*
- b) les réactions de l'amidon dialdéhyde et*
- c) l'application de l'amidon dialdéhyde à la préparation du papier imperméable à l'eau.*

Literature Cited

- (1) MILCH, R. A., and R. A. MURRAY: J. Am. Leather Chemists' Assoc. LIX (6) (1964), 310.
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- (3) JOSEPH, K. T., and R. R. RAJENDRAN: Bull. Central Leather Res. Inst., Madras, [India] 8 (1962), 606.
- (4) Technical Assoc. of the Pulp and Paper Industry: Wet Strength in Paper and Paperboard, Tappi Monograph Series No. 29 (1965), 50.

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(Arrived: April 22, 1966)

The Isolation of Cereal Starches in the Laboratory

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Introduction

We have recently started an investigation of the properties of cereal starches, in an attempt to extend our earlier studies on barley, oat and wheat starches (1, 2). Experience in this laboratory has shown that for fundamental studies, it is essential to isolate granular starch directly from the plant tissue, avoiding the use of any methods which may cause inadvertent degradation. The extraction and purification of starches from cereals is more difficult than is the case for many other botanical sources, presumably as the cereal grains normally contain much less moisture. Furthermore, the majority of starch is found in the endosperm, where it is embedded in the cytoplasmic matrix, and cracking or milling of the endosperm inevitably inflicts physical damage on a proportion of the granules.

In our earlier work (1, 2), we extracted the grain directly in a Blender in the presence of mercuric chloride to inhibit enzymic activity. The extract was then filtered through muslin, and the granules obtained by sedimentation. Protein impurities, which are considerable in cereal starches, were removed by repeated extraction of a saline suspension with toluene. This purification-procedure is, in fact, generally applicable to starches from a wide range of botanical sources (3), and it reduces the protein-content of the starch to a satisfactorily low level. With cereals, however, the removal of the relatively large amounts of protein extended the extraction operations to a rather unwieldy

degree. Other procedures of starch-isolation have now been considered.

On the industrial scale, the starch granules are loosened in the matrix by a preliminary aqueous swelling, or steeping-process, of the grain. Steeping is carried out usually in the presence of sulphur dioxide, which denatures enzymes and helps to soften the protein-starch matrix (4). Maize is perhaps the most important of the industrial cereal starches. Extensive reports exist in the literature regarding laboratory-scale extraction-methods—for maize (5–7), waxy maize (4, 8–10), and amylo maize (11, 12)—which are based on the SO₂-steeping process.

The recommended steeping conditions are, however, very variable, but more importantly, there is evidence that the starch-product is degraded in the presence of sulphur dioxide (8, 9). Methods have been described in which neutral-steeping has been used (12, 13), but it is essential that the starch is then purified and freed from protein by methods which do not involve chemical treatments, for example by the use of alkali (13, 14).

There are relatively fewer detailed reports of the isolation of other cereal starches, such as barley and wheat starches, although methods involving alkaline treatment (15), sulphur dioxide steeping (16), and neutral-steeping (5, 17, 18, 19) have been described for these materials.

The quantitative effectiveness of the above procedures has been to some extent limited; pure starch in