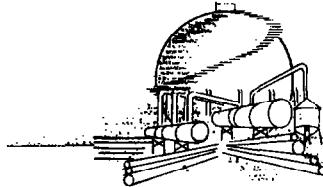


PROCESS ECONOMICS PROGRAM



SRI INTERNATIONAL
Menlo Park, California
94025

Abstract

Process Economics Program Report No. 54A

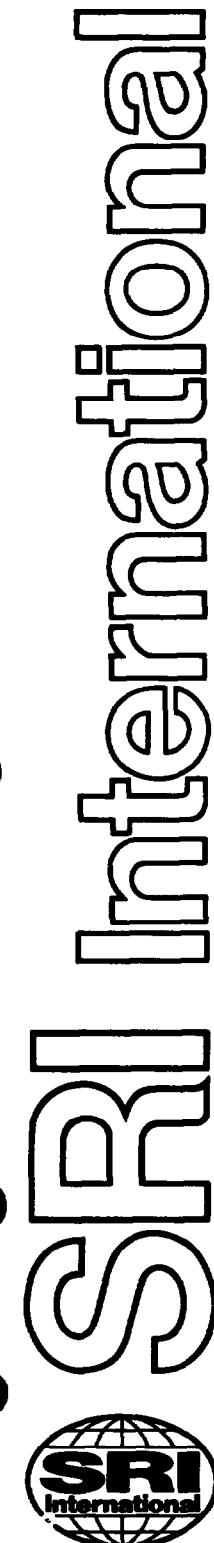
NYLON 66

(February 1980)

Nylon 66 is made by polycondensation of hexamethylene diammonium adipate, commercially known as nylon salt. Nylon salt, made from hexamethylenediamine and adipic acid, is produced as an aqueous solution if it is to be used captively or as a solid if it is to be transferred. The polycondensation starts from an aqueous solution, and produces a nylon melt. The reaction is conducted in three-stages: first in a tank or in a heat-exchanger/column, second in a tubular reactor, and finally in a vessel under a slight vacuum. Nylon melt can be pelletized to form nylon resin, or spinning chips. Nylon resin may be further treated for use in extrusions.

Nylon 66 fiber can be melt-spun from chips, or it can be spun directly from the melt. Processes for making representative grades of carpet staple, carpet yarn, tire cord, textile yarn, and hosiery monofilament are described and evaluated in this report.

PEP'79 YCY



Report No. 54A

NYLON 66

SUPPLEMENT A

by **YEN-CHEN YEN**
Contributions by Feng-Hsin Huang

February 1980

A private report by the
PROCESS ECONOMICS PROGRAM

Menlo Park, California 94025

For detailed marketing data and information, the reader is referred to one of the SRI programs specializing in marketing research. The CHEMICAL ECONOMICS HANDBOOK Program covers most major chemicals and chemical products produced in the United States and the WORLD PETROCHEMICALS Program covers major hydrocarbons and their derivatives on a worldwide basis. In addition, the SRI DIRECTORY OF CHEMICAL PRODUCERS services provide detailed lists of chemical producers by company, product, and plant for the United States and Western Europe.

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1 INTRODUCTION

This report covers the manufacture of nylon 66 from hexamethylene-diamine and adipic acid. The manufacture of these two raw materials is the subject of separate PEP reports (Report No. 31 and Report No. 3).

The present report covers the steps up to production of nylon resin or nylon chips. It also covers fiber production, illustrated by carpet staple, carpet yarn, tire cord, textile yarn, and monofilament. Fabrication of nylon plastics is not included nor is the manufacture of reinforced nylon resin, which is within the scope of PEP Report 51.

2 SUMMARY

General Aspects

Total U.S. production capacity for nylon 66 is 325 million lb/yr resin and about 2,000 million lb/yr fiber. The operating rate is about 85%.

In making nylon 66, hexamethylenediamine and adipic acid are combined to form nylon salt (hexamethylene diammonium adipate). The nylon salt is then polymerized to form a nylon 66 melt, which is formed into chips, or spun directly into fiber. Fiber is also spun from melted chips.

Cost features for making nylon salt are given in Table 2.1. Producing nylon salt as an aqueous solution costs less than producing it as a solid (52¢/lb vs 49.5¢/lb). Major producers make nylon salt captively in an aqueous solution. If nylon salt is to be transferred from one site to another, it has to be in solid form. It can be recovered either from a methanol solution or from an aqueous solution. The latter offers a slight cost advantage.

We have evaluated two processes for polycondensation of nylon salt: one process using a column and a heat exchanger in the first-stage reaction, the other using a tank reactor in the first-stage reaction. The cost features are given in Table 2.2. The economics of these two processes is very similar, with a very slight advantage accruing to the second process. However, SRI believes that the former process should give a product with less cross-linking, and hence is more suitable for making fiber.

Table 2.2 refers to a product in the molten state. This product is processed into chips, or spun directly. The cost features for making nylon chips or resin are summarized in Table 2.3. The costs refer to production starting from HMDA and adipic acid.

Table 2.1

NYLON SALT MANUFACTURE

COST FEATURES

Plant Capacity: 58 Million lb/yr
 at 0.90 Stream Factor
 PEP Cost Index: 320

	In Aqueous Solution	Solid	
		From Methanol Solution	From Aqueous Solution
Battery limits cost (\$ million)	1.5	3.1	2.8
Total fixed capital (\$ million)	2.5	4.7	4.2
Production cost (¢/lb)			
Labor	0.46	0.93	0.91
Materials	46.25	40.52	46.46
Utilities	0.18	0.72	0.49
Depreciation, taxes, insurance	0.52	0.97	0.86
Plant overhead, interest	<u>1.03</u>	<u>1.45</u>	<u>1.42</u>
TOTAL PRODUCTION COST	48.44	50.59	50.14
25%/yr ROI	<u>1.08</u>	<u>2.03</u>	<u>1.81</u>
PRODUCT VALUE	49.5	52.6	52.0
Confidence rating	B	B	B

NOTE: G&A, sales, and research costs not included.

Table 2.2
POLYCONDENSATION OF NYLON SALT TO NYLON 66

COST FEATURES		
Plant Capacity: 50 Million lb/yr at 0.90 Stream Factor PEP Cost Index: 320		
	<u>Based on Du Pont Canada Patents</u>	<u>Tank Reactor in First Stage</u>
Battery limits cost (\$ million)	3.3	3.5
Total fixed capital (\$ million)	5.3	5.3
Production cost (¢/lb)		
Labor	0.80	1.11
Materials	<u>58.03</u>	<u>57.94</u>
Utilities	2.25	1.27
Depreciation, taxes, insurance	1.27	1.28
Plant overhead, interest	<u>1.53</u>	<u>1.76</u>
TOTAL PRODUCTION COST	<u>63.88</u>	<u>63.36</u>
25%/yr ROI	<u>2.65</u>	<u>2.65</u>
PRODUCT VALUE	<u>66.5</u>	<u>66.0</u>
Confidence rating	B	B

NOTE: G&A, sales, and research costs not included.

Table 2.3

NYLON CHIPS AND RESIN FROM HMDA AND ADIPIC ACID

COST FEATURES		
	<u>Nylon Chips</u>	<u>Nylon Resin</u>
Battery limits cost (\$ million)	6.2	12.3
Total fixed capital (\$ million)	13.3	22.4
Production cost (¢/lb)		
Labor	2.76	3.57
Materials	54.49	54.90
Utilities	4.09	4.21
Depreciation, taxes, insurance	3.20	5.39
Plant overhead, interest	3.36	4.11
G&A, sales, research	<u>8.30</u>	<u>10.00</u>
TOTAL PRODUCTION COST	76.20	82.18*
25%/yr ROI	<u>6.65</u>	<u>11.20</u>
PRODUCT VALUE	83	93†
Confidence rating	B	B

* This is a weighted average of 30% extrusion grade, partly natural color and partly colored; 30% colored resin (including injection grade and extrusion grade); and 30% resin compounded with additives; the balance is natural color injection grade. The individual costs of these grades are 78, 80, 85, and 86¢/lb for injection, natural color; injection, colored; extrusion; and compound. The costs do not include the material costs of additives, which may range from negligible to 6¢/lb.

† Weighted average. The individual values are 85, 88, 95, and 99¢/lb for injection, natural color; injection, colored; extrusion; and compound. Material costs of additives should be added.

Table 2.4 lists the costs of production of various fibers, starting from nylon melt or chips.

Technical Aspects of the Processes Evaluated

Nylon Salt

Nylon salt aqueous solution is made by dissolving adipic acid in an aqueous solution of hexamethylenediamine (HMDA) and adjusting the pH to 7.6 to 7.9.

Adding adipic acid and a concentrated HMDA solution to a concentrated nylon salt solution gives solid nylon salt as a precipitate.

Mixing methanol solutions of HMDA and adipic acid also gives solid nylon salt.

Polycondensation by Du Pont Canada Process

Nylon salt solution is evaporated to 50% concentration and then polycondensed in three stages: the first stage in a set of equipment consisting of a column, a heat exchanger, and a separator; the second stage in a tubular reactor, and the third stage in a vessel. The first stage and the second stage are under pressure and the third stage is under vacuum. Between the second and third stages is a separator for release of vapor.

Polycondensation Using a Tank Reactor

The process is the same as above, except that the first-stage reactor is a jacketed tank. Because the heat transfer capacity on this stage is limited, the nylon salt solution leaving the first stage will be a 70% aqueous solution as opposed to the 90% or so solution leaving the first reactor in the Du Pont Canada process. The heat transfer area of the second stage reactor has to be sized for a higher heat load to accommodate the more dilute first stage effluent.

Table 2.4
NYLON 66 FIBER MANUFACTURE

	COST FEATURES				
	<u>Carpet Staple</u>	<u>Carpet Yarn</u>	<u>Tire Cord</u>	<u>Textile Yarn</u>	<u>Hosiery Monofilament</u>
Description	Trilobal, 18 denier, 1% conductive fiber	Hollow square, 1,224 denier yarn, 68 filaments	980 denier yarn, 140 filaments	70 denier yarn, 34 filaments	15 denier, bicomponent
Capacity (million lb/yr)	50	50	50	50	6
Form of nylon 66 feed	Melt	Melt	Melt	Chips	Chips
Battery limits cost (\$ million)	10.7	12.6	15.1	54.4	15.2
Total fixed capital	15.3	18.6	21.8	72.2	20.2
Production cost (¢/lb)					
Labor	3.53	3.41	2.54	9.48	18.55
Materials	67.18	67.04	68.67	88.65	91.88
Utilities	0.67	0.82	0.84	2.69	6.19
Depreciation, taxes, insurance	3.68	4.48	5.22	17.33	40.48
Plant overhead, interest	3.94	3.84	3.14	5.65	10.08
G&A, sales, research	10.00	10.00	10.00	14.00	25.00
TOTAL PRODUCTION COST	89.00	89.59	90.41	137.80	192.18
Credit for waste filament	-1.98	-1.74	-2.34	-3.12	-3.42
NET PRODUCTION COST	87.02	87.85	88.07	134.68	188.76
25%/yr ROI	7.65	9.30	10.90	36.10	84.17
PRODUCT VALUE	95	97	99	171	273
Confidence rating	C+	C+	C+	C+	C

Chip Formation

Nylon melt from the last polycondensation reactor is extruded, formed into chips in the presence of water, dewatered on a screen, and dried in the fluidized state.

Resin for extrusion molding is made by kneading the above resin in a twin-screw extruder under nitrogen, pelletizing, and drying again.

Colored resin is made by blending the above natural-colored resin with pigment together with a little silicone oil.

Resin can be blended with additives (such as a flame retardant) in a compounding extruder (also a twin-screw extruder), extruded, pelletized, and dried.

Carpet Staple

Nylon 66 melt is pumped, filtered, and then spun in several spinning positions, in each of which is a metering pump, a filler, and a spinneret. The filaments from each spinneret form a tow, which is cooled in an air duct, steamed in another duct, and then drawn and textured. The tows are combined and cut into staple, and baled. The shape of the holes in the spinnerets is such that the fiber has a trilobal cross-section.

For making high grade antistatic soil-hiding carpet staple, a small quantity (1%) of conductive fiber is added. This conductive fiber is of a sheath-core structure, the core is carbon black/polyethylene, the sheath is nylon 66 containing 8.5% TiO₂. The former (C/PE) is blended in a mixer, the latter (nylon 66) is made batchwise. The two are then melt-spun in a special-shaped spinneret.

These descriptions of fibers relate to a particular type within the broader category. In the case of carpet staple we are referring to Du Pont's Antron®. One may start either from nylon melt or nylon chips. For a large volume product such as carpet staple or carpet yarn, the starting material often is the melt; for textile yarn and monofilament, it often is chips. Tire cord represents a borderline case.

Carpet Yarn

The spinning of carpet yarn is similar except that each yarn is wound after draw-texturing. The holes of the spinneret are such that each filament has a hollow square cross-section.

Tire Cord

Nylon 66 for making tire cord must be a high tenacity grade, which, compared with the other fibers, has a higher molecular weight and is preferably made by polycondensation in which the last step is conducted at a higher temperature and in which formic acid vapor is added.

The spinning is similar to that for making carpet yarn, but with spinnerets having holes of different size and number, and with different spin-drawing machines because of the different denier and speed.

Textile Yarn

Nylon 66 chips are melt-extruded. From each extruder, the melt passes through a filter, and goes to metering pumps, spinning packs, cooling ducts, steaming ducts, spin-drawing machines, and take-ups. The bobbins from the take-ups are transferred to texturing machines.

Hosiery Monofilament

Nylon 66 chips and nylon 6 chips are heated in the solid state to form a block copolymer, which is then melt-extruded. Also, nylon 66 chips are melted by extrusion. These two melts are fed into the same holes of spinnerets to form filaments of side-by-side structure. After passing through quenching ducts and steaming ducts, the filaments are spun-drawn and taken up on bobbins.

3 INDUSTRY STATUS

Producers and Production Capacity

Producers of nylon 66 resins and fibers in the United States are listed in Table 3.1. The resin production capacities include some reinforced nylon 66 resin, which contains 30% to 40% reinforcing agents. The capacities for fiber vary with the denier.

Among the producers, Du Pont, Monsanto, and Celanese (including its joint venture with ICI, Fiber Industries) make resins and fibers from hexamethylenediamine and adipic acid. Chevron makes resin and fiber from purchased nylon salt, the others make fibers and monofilament from purchased chips, or make resin from purchased fiber waste.

European nylon 66 producers are listed in Table 3.2. The major producers are ICI, Rhône-Poulenc, and Du Pont. The operations of Monsanto in the United Kingdom and Luxemburg closed down in 1979.

A very incomplete listing of nylon 66 producers outside the United States and Europe is given in Table 3.3.

Table 3.4 shows the U.S. production of nylon 66. No data are available on the production in other countries.

Markets

The totals in Table 3.1 also roughly reflect the market shares for these products. Under "industrial continuous filament," tire cord is a major item.

The U.S. market distribution for nylon resin is shown in Table 3.5.

Table 3.1

Company	Plant Location	Capacity (million lb/yr)							
		Resin	Textile	Continuous Filament	Industrial	Textile	Carpet	Staple and Tow	Monofilament
E. I. du Pont de Nemours & Company									
Plastics Products & Resins Dept.	Parkersburg, WV	165							24
Textile Fibers Dept.	Camden, SC Chattanooga, TN Martinsville, VA Richmond, VA Seaford, DE Waynesboro, VA		x x x x x x	x x x x x x		x x x x x x	x x x x x x	6	
Subtotal		165	240	344	270	28	210	6	24
Monsanto Company									
Monsanto Plastics & Resin Co.	Pensacola, FL	70							
Monsanto Textile Co.	Dekat, FL Greenwood, SC Pensacola, FL		x x x	x x x	115	x x x	x x x	4	
Subtotal		70	94	90	115	16	390	4	4
Chevron Chemical Co. of Puerto Rico	Guayama, PR	3	50	21					
Fiber Industries, Inc.	Greenville, SC Shelby, NC			20			x x		
				20			55		
Wellman, Inc.									
Wellman Industries, Inc., Man-made Fiber Div.	Johnsonville, SC	8						40	
Celanese Corporation									
Celanese Plastics Co.	Bishop, TX	40							
Adell Plastics, Inc.	Baltimore, MD	20							
Allied Chemical Corp.									
Fibers Division	West Conshohocken, PA	15						<1	
Keyser-Roth Corp.									
Yarn Processing Division	Creedmoor, NC	10							
Polymers, Inc.	Middlebury, VT							5	
Dayco Corp.									
Star Textile & Research Inc.									
Texapol Corp.	Bethlehem, PA	4							
Ametek, Inc.									
Special Filaments Div.	Odenton, MD							2	
Berkley & Company	Spirit Lake, IA							1	
Johnson Filaments, Inc.	Williston, VT							<1	
Monofilaments, Inc.	Waynesboro, VA							<1	
Newton Filaments, Inc.	Homer, NY							<1	
Pletaril Company	Birdsboro, PA							<1	
Shakespeare Company								2	
Monofilament Div.	Columbia, SC							3	
E. B. & A. C. Whiting Company	Burlington, VT							<0.8	
Total		325*	394	475	385	44	695	10	40 (app.)
				1,254			749		
							~2,000		

*Part of the production is reinforced nylon resin.

Table 3.1 (Concluded)
NYLON 66 PRODUCERS IN THE UNITED STATES

Company	Plant Location	Raw Material	Trademark	Remarks
E. I. du Pont de Nemours & Company				
Plastics Products & Resins Dept.	Parkersburg, WV		Zytel®	
Textile Fibers Dept.	Camden, SC Chattanooga, TN Martinsville, VA Richmond, VA Seaford, DE Waynesboro, VA	From HMDA and adipic acid	Du Pont® Atron® Centrec® Cordura® Hyten®	Resin capacity including nylon 612 and copolymers.
Monsanto Company				
Monsanto Plastics & Resin Co.	Pensacola, FL		Vydyne®	Resin capacity including nylon 69.
Monsanto Textile Co.	Decatur, FL Greenwood, SC Pensacola, FL	From HMDA and adipic acid	Blue G® Celon® Cumulof® Ultrona®	
Chevron Chemical Co. of Puerto Rico	Guayama, PR	From purchased nylon salt	Vecana®	
Fiber Industries, Inc.	Greenville, SC Shelby, NC	From HMDA and adipic acid	Celanese® Cedilla®	
Wellman, Inc.				
Wellman Industries, Inc., Man-made Fiber Div.	Johnsonville, SC	From purchased chips and waste fiber	Wellon® Wellstrand®	Resin capacity including nylon 6.
Celanese Corporation				
Celanese Plastics Co.	Bishop, TX	From HMDA and adipic acid	Celanese Nylon®	
Adell Plastics, Inc.	Baltimore, MD	From purchased waste fiber		Capacity including nylon 6.
Allied Chemical Corp.				
Fibers Division	West Conshohocken, PA	From purchased chips and waste fiber	Nypel®	Resin capacity including some nylon 6.
Kayser-Roth Corp.				
Yarn Processing Division	Creedmoor, NC	From purchased chips		
Polymers, Inc.	Middlebury, VT	From purchased chips		Capacity including nylon 6 and 612.
Dayco Corp.				
Star Textile & Research Inc.				
Texapol Corp.	Bethlehem, PA	From purchased waste fiber		Capacity including nylon 6.
Ametek, Inc.				
Special Filaments Div.	Odenton, MD			
Berkley & Company	Spirit Lake, IA			
Johnson Filaments, Inc.	Williston, VT			
Monofilaments, Inc.	Waynesboro, VA			
Newton Filaments, Inc.	Homer, NY			
Plateril Company	Birdsboro, PA			
Shakespeare Company				
Monofilament Div.	Columbia, SC			
E. B. & A. C. Whiting Company	Burlington, VT			
		From purchased waste fiber		Capacity including nylon 6, 12, 612, 11, and copolymers.

Table 3.2
NYLON 66 PRODUCERS IN EUROPE

Country	Company	Plant Location	Capacity (million lb/yr)		Product	Trademark	Remarks
			Resin	Fiber			
Belgium	Fabelta SA	Zwijnaarde, Oost-Vlaanderen	8.8	22.1	Yarn	Fabelnyl®	
Finland	Lappfiber Oy	Tornio, Lappi		2.2	Yarn		
France	Rhône-Poulenc Industries SA	Chalampe, Haut-Rhin	55.1				Resin capacity includ- ing nylon 6/10.
	Textile Division	Albi, Tarn Besançon, Doubs Givet, Ardennes Lyon-Vaise, Rhône St-Laurent-Blangy, Pas-de-Calais Vaulx-en-Velin, Rhône		211.6	Yarn and staple	Nylfrance®	*
Germany, West	Akzo Chemie GmbH	Obernburg-Am-Main, Bayern	6.6				
	BASF Aktiengesellschaft	Ludwigshafen	55.1				
	Benckiser-Knapsack GmbH	Ladenburg, Baden-Württemberg		40.1			
	Du Pont de Nemours (Deutschland) GmbH	D-Kreis Unna, Nordrhein-Westfalen Vettrop-Uber-Hamm, Nordrhein-Westfalen	n.a.				Resin capacity includ- ing nylon 6/12.
	Enka AG	Obernburg-Am-Main, Bayern	6.6	125.7	Yarn and staple	Enka Nylon® Enka Perlon®	
	Hoechst AG	Not specified		n.a.			
	ICI (Europa) Fibers GmbH	Üstringen, Baden-Württemberg		132.3	Yarn and staple	Bri-Nylon®	
	Norddeutsche Faserwerke GmbH	Neumünster, Schleswig-Holstein		n.a.	Yarn and staple	Siks Perlon®	Also producing nylon 6 (formerly Gelsenberg Faserwerke).
	Rhodia AG	Freiburg/Br.		20		Rhodiaceta Original Nylon 66	Formerly Deutsche Rhodiaceta.
		Rottweil a. N./Württ		20	Yarn and staple		
	TextilWerke Deggendorf GmbH	Deggendorf, Bayern		6.6	Yarn		
Greece	Etna SA	Athens		3.6	Yarn		
	"Vomvix"-P. Svolopoulou & Chr. Coutroubis SA	Athens		8.8	Yarn		Also producing nylon 6.
Ireland	Wellman International Ltd.	Mullagh, Cavan		11	Staple	Wellon®	Also producing nylon 6.
Italy	Montefibre SpA	Pallanza, Piemonte		63.9	Yarn	Helion®	
	Ticfil	Caronno Pertusella, Lombardia		2.2	Yarn		
Netherlands	ICI Holland BV	Rozenburg		13.2			
Spain	BASF Espanola, SA	Tarragona		6.6			Including nylon 6.
	SAFA	Blanes, Gerona San Julian De Ramio, Gerona		44.1	Yarn and staple	SAFA®	Including nylon 6.
	Smiatec	Torrelavega, Santander		n.a.	Yarn and staple		Including nylon 6.
Sweden	Sonesson Plast AB	Malmö		n.a.	Monofilament		
Switzerland	Viscosuisse Ag	Emmenbruecke, Luzern Widnau, St. Gallen		55.1	Yarn	Nylsuisse® Flixor®	
United Kingdom	Imperial Chemical Industries Ltd (ICI)	Billingham, Cleveland	39.7	n.a.	Yarn		
	Fibres Division	Doncaster, Yorkshire Gloucester, Gloucestershire Pontypool, Gwent, Wales		284.4	Yarn, staple, and tow	Bri-Nylon® Counterstat® Tendrille® Timbrille®	
	Nymofil Ltd.	Poulton-le-Fylde, Lancashire		n.a.	Monofilament		Also producing nylon 6.
	Peri-Lusta Ltd.	Leek, Staffordshire		n.a.	Monofilament		Also producing nylon 6.
USSR		Chernigov, Ukraine Klin Kursk				Anid® (tire yarn)	Also producing nylon 6.
Total			202.7	1,200			

Table 3.3
NYLON 66 PRODUCERS OUTSIDE THE UNITED STATES AND EUROPE

Country	Company	Plant Location	Capacity (million lb/yr)		Product	Trademark	Remarks
			Resin	Fiber			
North America							
Canada	Du Pont Canada Ltd.	Kingston, Ontario	70		Yarn, staple, and tow	Antron® Cantreco® Du Pont®	
	Millhaven Fibers, Ltd.	Millhaven, Ontario		5			
South America							
Argentina	Ducilo Saic	Gerazagueli Mercedes		20	Yarn	Nylon Ducilo®	Capacity is total of nylon 66 and 6.
Brazil	Celanese Do Brasil-Fibras Quimicas Ltda	São Bernardo do Campo, São Paulo	n.a.	Yarn	Celtrel® Celtrel BCF®	Using chips from the United States.	
	Rhodia SA	Santo André	n.a.	Yarn and staple	Dropnyl® Rhodianyl®		
Peru	Manufacturas Del Sur SA	Arequipa	n.a.				Also making nylon 6 fiber.
Uruguay	Hilados Sinteticos SA (HISISA)	Estación Manya, Montevideo	n.a.	Yarn	Hisilon®		
Asia							
Israel	Nilil	Migdal Ha-Emek	n.a.	Yarn			
	Rogosin Industries of Israel	Ashdod		2			
Japan	Asahi Chemical Industry Co. Ltd.	Moriyama Nobeoka, Miyazaki	15.4	56.3	Yarn, mono- filament, and spun- bonded	Asahi Kasei Nylon® Leona®	
	Toray Industries, Inc.	Nagoya Aichi Aichi	11	8	Yarn	Tapilon® Promilan®	
Turkey	UBE Industries, Ltd. Sentetik Iplik Fabrikalari, A.S. (SIFAS)	Ube, Yamaguchi Bursa	2.7	n.a.	Yarn		
Oceania							
Australia	Fibremakers Ltd.	Baywater, Victoria	30		Yarn and monofilament	Bri-Nylon®	
		Penrith, N.S.W.			Tire cord		
New Zealand	Fibremakers (N.Z.) Ltd.	Wiri, Auckland	n.a.		Yarn and staple	Bri-Nylon®	
Africa							
South Africa	South African Nylon Spinners (Pty) Ltd.	Belleville, Cape Providence		11	Yarn	Bri-Nylon®	

Table 3.4

NYLON 66 PRODUCTION IN THE UNITED STATES
(Million lb/yr)

	Resin		Fiber	
	Amount	Percent of Total Nylons	Amount	Percent of Total Nylons
1972	104 ^b	66	1,349 ^a	68
1973	136 ^b	66	1,527 ^a	70
1974	135 ^b	66	1,521 ^a	72
1975	89 ^b	66	1,208 ^a	65
1976	163 ^b	66	1,375 ^a	66
1977	168 ^b	66	1,558 ^b	67
1978	182 ^a	67	1,708 ^b	67
1979 (Jan.-June)			934 ^b	69

Sources: a) CEH
 b) PEP

Table 3.5

MARKET DISTRIBUTION FOR ALL NYLON RESINS IN THE UNITED STATES*
(Percent)

Injection molded goods

Automotive components	31.6
Electric and electronic components	11.2
Machinery components	8.5
Hardware and furniture components	6.9
Parts of consumer articles and appliances	9.9
Other	<u>1.5</u>
Subtotal	69.6

Extrusion molded goods

Film, strapping, and extrusion coating	10.4
Nontextile monofilaments (>0.1 mm)	6.5
Wire and cable	5.4
Tubing	3.1
Other	<u>2.7</u>

Subtotal	28.1
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Other applications

* The above analysis by CEH of SRI is for all nylon resins, but roughly applies to nylon 66.

Prices

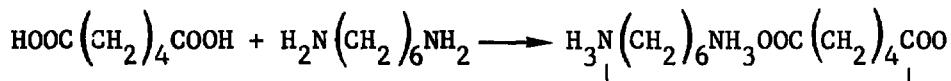
The prices of some nylon 66 products in November 1979 were as follows:

	<u>Price per lb</u>
Carpet staple	
Antron®	\$1.06
Other grades	88¢-98¢
Carpet yarn	
1,225 denier yarn, for public buildings	\$1.49
1,500 denier yarn, for residences	\$1.28
Tire cord	\$1.29
Monofilament, 15 denier	\$2.47
Textile yarn, 70 denier	\$1.36
Resins--natural color, injection (0.05 to 0.14¢/lb additional for other grades)	\$1.34
Resins (from waste filament)	\$1.10

4 NYLON SALT

Review of Processes

Nylon salt or AH salt is hexamethylene diammonium adipate. It is the precursor of nylon 66:



Patents on nylon salt preparation received at SRI after the issue of PEP Report 54 are listed in Table 4.1.

There are essentially two kinds of processes for preparing nylon salt: processes using alcohol as solvent, and processes using water as a solvent. The process evaluated in PEP Report 54 uses methanol as a solvent for HMDA and for adipic acid; nylon salt, being only slightly soluble in methanol, would precipitate when the solutions are mixed. Reference 71592 relates to an improvement on such an operation. References 71581 and 71637 cite propyl alcohol as the solvent.

References 71518, 71578, and 391583 describe processes for producing nylon salt solution by neutralization of HMDA and adipic acid in water. Unlike the processes using alcohol, which give nylon salt as a solid, these processes give an aqueous solution of nylon salt. Since the present commercial process for making nylon 66 starts with an aqueous solution of nylon salt, the production of nylon salt in solution form is generally preferable, if the nylon salt is used captively (as is most often the case). However, nylon salt aqueous solution is not stable in air, and surge storage should be limited to less than a day. To increase the surge capacity, reference 71548 suggests storing the half acid salt, and neutralizing it shortly before it is used for making nylon 66.

Solid nylon salt can be obtained from aqueous solution by concentration and cooling (71881). But a better way to make solid nylon salt

Table 4.1

NYLON SALT PREPARATIONPATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71581	Mitsui Toatsu	10/31/66
	HMDA in 99% isopropanol is added to a solution of adipic acid in 99% isopropanol at reflux temperature, and filter at 70°C.	
71637	USSR	11/24/66
	HMDA and adipic acid are heated in 75%-80% isopropanol to 65-70°C.	
71881	USSR	6/20/69
	A nylon salt solution is concentrated to 85% at 70-80°C, and cooled to 20°C for crystallization.	
71592	Asahi Chemical	4/7/70
	Adipic acid slurry in methanol and HMDA in methanol solution are used; temperature and concentration are controlled to cause the formation of nylon salt in rhombic crystals, which are less liable to shatter and form dust.	
71518	Ube	3/23/71
	Solution of HMDA and adipic acid is circulated between one tank and a second larger tank; pH in the second tank is adjusted to 7.9 ± 1; part of the contents of the second tank is withdrawn as nylon salt solution.	
391583	Asahi Chemical	5/8/71
	Nylon salt is precipitated by dissolving adipic acid in a nylon salt solution and then adding HMDA.	
71567	Hoechst	11/25/72
	HMDA and adipic acid are added in small portions to a kneader, and mixed for 1 hour. The rotation is reversed and the batch is mixed 1 more hour.	
71568	ICI	1/25/73
	Adipic acid aqueous solution is added to a nylon salt solution, and then HMDA aqueous solution is added; the solid precipitate is nylon salt; the filtrate is recycled after it is treated with active carbon.	
71578	Toray	11/14/74
	Neutralization and active carbon treatment are conducted at 30-50°C.	
71548	ICI	6/30/75
	Acid half-salt of adipic acid and HMDA is stored, and fully neutralized shortly before use.	

from aqueous solution is to use the processes described in references 391583 and 71568; adipic acid is added to the nylon salt solution, and then HMDA is added, causing nylon salt to precipitate.

A unique process is described in reference 71567 of Table 4.1. HMDA and adipic acid are reacted in bulk to form nylon salt. Product quality may be difficult to control in this process.

A Process for Making Aqueous Nylon Salt Solution

Process Description

The design bases and assumptions are given in Table 4.2. The flow sheet is shown in Figure 4.1. The compositions of streams marked on Figure 4.1 are listed in Table 4.3. A major equipment list and a utilities summary are given in Tables 4.4 and 4.5 respectively.

Molten HMDA is pumped from T-101 to dissolver V-101, where it is dissolved in deionized water, to form a 23% solution. This solution is conveyed to jacketed agitated reactor R-101. Adipic acid is added. At the same time, a large stream of nylon salt solution is circulated between R-101 and R-102. In R-102, which is also a jacketed agitated reactor but larger than R-101, pH is adjusted to 7.6-7.9 by adding 70% HMDA aqueous solution. (A small HMDA tank, not shown in Figure 4.1, is provided for this purpose.) A stream corresponding to the input of HMDA and adipic acid is withdrawn from R-102 to T-103. This is nylon salt solution in 40% concentration.

In this process, HMDA and adipic acid of high quality are assumed to be used. The water is deionized. As a result, the nylon salt solution needs no active carbon purification.

Cost Estimates

Capital investment and production cost are estimated in Tables 4.6 and 4.7 respectively.

Table 4.2
MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION

DESIGN BASES AND ASSUMPTIONS

Reference	71518
Raw materials	
HMDA	
Color, APHA	10 max
Iron (ppm)	1 max
1,2-Diaminocyclohexane	60 mol per million 60 max
Purity (wt%, dry basis)	99.9 min
Adipic acid purity	99.8%-99.9%
Color, APHA (20% in methanol)	6-10 max
Ash (ppm)	5-8 max
Iron (ppm)	1 max
Volatile acid, as acetic acid (ppm)	25 max
Reaction	
96-104°F (35-40°C)	
Final pH	7.9 ± 1 (at 40 ± 1°C)

Figure 4.1

MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION

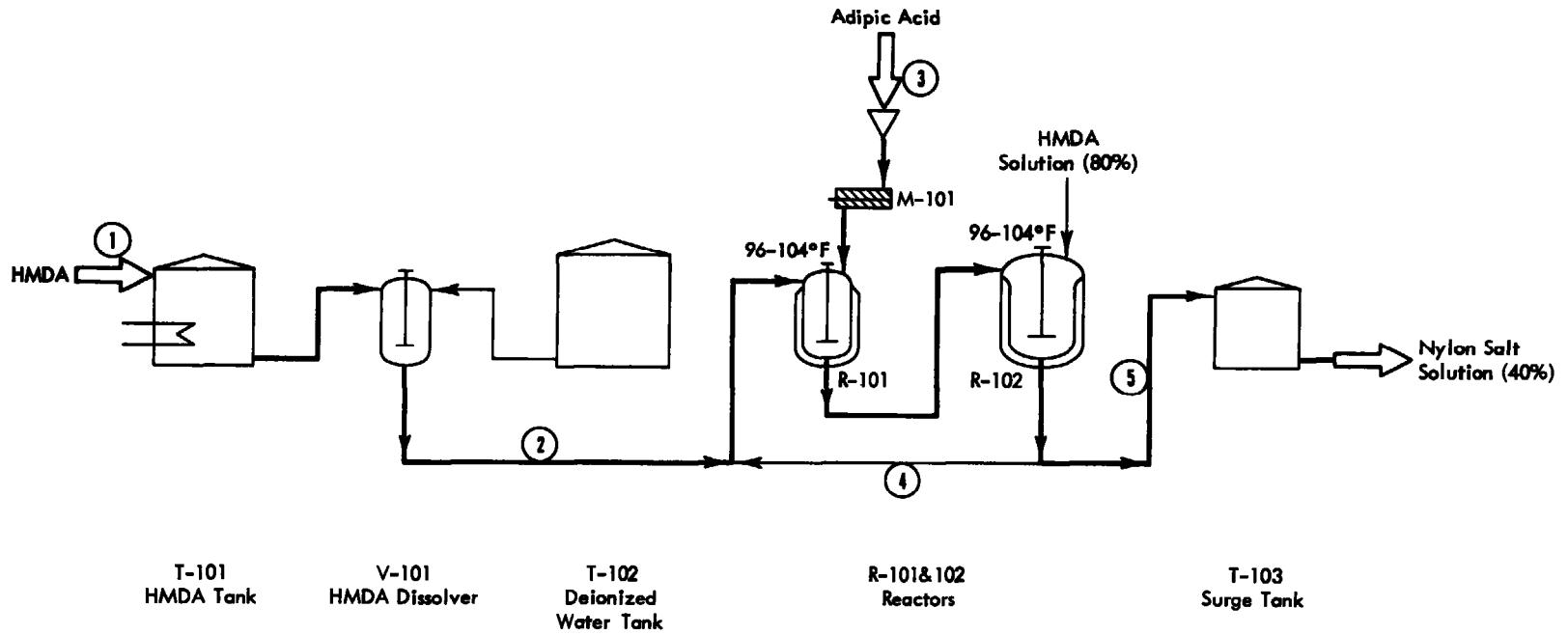


Table 4.3

MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION

STREAM FLOWS

Plant Capacity: 58 Million lb/yr
 (26,000 Metric Tons/yr) Nylon Salt
 at 0.90 Stream Factor

	Mol Wt	Stream Flows (1b/hr)				
	(1)	(2)	(3)*	(4)	(5)	
Hexamethylenediamine	116	3,278	3,278	--	--	20
Impurities	120	2	2	4	--	6
Adipic acid	146	--	--	4,164	--	--
Water	18	--	11,421	--	171,307	11,109
Nylon salt	262	--	--	--	<u>110,350</u>	<u>7,357</u>
Totals, 1b/hr		3,280	14,701	4,168	281,657	18,492
kg/hr		1,488	6,668	1,891	127,757	8,388
Totals, 1b-mols/hr		28	663	29	9,938	645
kg-mols/hr		13	301	13	4,508	293

* Solid stream.

Table 4.4
MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION

MAJOR EQUIPMENT				
<u>Equipment Number</u>	<u>Name</u>	<u>Size (gal)</u>	<u>Material of Construction</u>	<u>Remarks</u>
<u>Reactors</u>				
R-101	Reactor	1,100	304 ss clad	
R-102	Reactor	5,500	304 ss clad	
<u>Tanks</u>				
T-151A,B	HMDA storage tanks	22,000 ea	304 ss	Not shown on flow sheet.
T-101	HMDA tank	8,000	304 ss	
T-102	Deionized water tank	15,000	304 ss	
T-103	Surge tank	20,000	304 ss	
<u>Vessels</u>				
V-101	HMDA dissolver	860	304 ss clad	
<u>Miscellaneous Equipment</u>				
M-101	Feeder		304 ss	
<u>Pumps</u>				
100 Section: 10, including 5 operating, 5 spares; 34 operating bhp				

Table 4.5

MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION

UTILITIES SUMMARY

Plant Capacity: 58 Million lb/yr
(26,000 Metric Tons/yr) Nylon Salt
at 0.90 Stream Factor

	Battery Limits
	Total
Average consumption	
Electricity (kw)	85
Process water (gpm)	30
Steam at 50 psig (lb/hr)	800
Inert gas, low pressure (scfh)	8,000
Peak demands	
Steam at 50 psig (lb/hr)	2,500
Inert gas, low pressure (scfh)	16,000

Table 4.6

MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTION**CAPITAL INVESTMENT**

**Plant Capacity: 58 Million lb/yr
(26,000 Metric Tons/yr) Nylon Salt
at 0.90 Stream Factor
PEP Cost Index: 320**

	<u>Cost</u>	<u>Capacity Exponent</u>	
		<u>Up</u>	<u>Down</u>
Battery limits equipment, f.o.b.			
Reactors	\$ 112,000	0.66	0.66
Vessels and tanks	238,200	0.39	0.38
Miscellaneous equipment	6,400	0.60	0.60
Pumps	<u>46,800</u>	0.39	0.31
Total	\$ 403,400	0.47	0.45
BATTERY LIMITS INVESTMENT	\$1,495,000	0.47	0.44
Off-sites			
Process water treatment	\$ 8,000	0.70	0.70
Steam generation	59,200	0.82	0.82
Inert gas	145,800	0.95	0.54
Tankage	191,700	0.35	0.35
Utilities and tankage investment	\$ 486,000	0.67	0.48
General service facilities	396,000		
Waste treatment	<u>99,000</u>		
OFF-SITES INVESTMENT	\$ 981,000	0.67	0.48
TOTAL FIXED CAPITAL	\$2,476,000	0.52	0.45
Start-up costs	\$1,484,000		
Working capital	<u>\$3,832,000</u>		
TOTAL CAPITAL INVESTMENT	\$7,792,000		

Table 4.7

MANUFACTURE OF NYLON SALT IN AQUEOUS SOLUTIONPRODUCTION COSTS

Plant Capacity: 58 Million lb/yr
 (26,000 Metric Tons/yr) Nylon Salt
 at 0.90 Stream Factor
 PEP Cost Index: 320

	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Adipic acid	38.3¢/lb	0.55837 lb	21.39
HMDA	55.5¢/lb	0.44589 lb	<u>24.75</u>
Gross raw material cost			46.14
Utilities			
Steam	\$5.00/1,000 lb	0.109 lb	0.05
Process water	\$1.10/1,000 gal	0.245 gal	0.03
Electricity	2.65¢/kwh	0.012 kwh	0.03
Inert gas, low pressure	60¢/1,000 scf	1.09 scf	<u>0.07</u>
Total utilities			0.18
Labor			
Operating, 1.5 men/shift	\$14.20/hr	0.0002 man-hr	0.32
 <u>Million lb/yr</u>			
	<u>29</u>	<u>58*</u>	<u>116</u>
Investment (\$ million)			
Battery limits	1.1	1.5	2.1
Off-sites	<u>0.7</u>	<u>1.0</u>	<u>1.5</u>
Total fixed capital	1.8	2.5	3.6
Scaling exponents	0.45	0.52	
Production costs (¢/lb)			
Raw materials	46.14	46.14	46.14
Utilities	0.18	0.18	0.18
Maintenance materials, 3%/yr of BL cost	0.11	0.08	0.05
Operating supplies, 10% operating labor	<u>0.07</u>	<u>0.03</u>	<u>0.02</u>
Variable costs	46.50	46.43	46.39
Operating labor	0.64	0.32	0.16
Maintenance labor, 3%/yr of BL cost	0.11	0.08	0.05
Control laboratory, 20% operating labor	<u>0.13</u>	<u>0.06</u>	<u>0.03</u>
Total direct costs	47.38	46.89	46.63
Plant overhead, 80% of total labor	0.71	0.37	0.20
Taxes and insurance, 2%/yr of fixed capital	0.12	0.09	0.06
Depreciation, 10%/yr of fixed capital	0.62	0.43	0.31
Interest on working capital, 10%/yr	<u>0.68</u>	<u>0.66</u>	<u>0.65</u>
Plant gate cost	49.51	48.44	47.85
G&A, sales, research, % of fixed capital	<u>negl</u>	<u>negl</u>	<u>negl</u>
NET PRODUCTION COST	49.51	48.44	47.85
25%/yr return on fixed capital, before taxes	<u>1.55</u>	<u>1.08</u>	<u>0.78</u>
PRODUCT VALUE	51.06	49.52	48.63

*Base case.

A Process for Making Solid Nylon Salt from a Methanol Solution

Solutions of HMDA and adipic acid in methanol are mixed in an agitated jacketed reactor. Nylon salt forms and precipitates. It is separated by a centrifuge, washed twice with methanol, and then dried. The mother liquor and washing solution are combined, distilled for recovery of methanol, with the bottom product being evaporated in a scraped surface evaporator.

The process is essentially the same as that described in Section 6 of PEP Report 54, except that the nylon salt is dried instead of being dissolved in water. The list of main equipment and the utilities summary are given in Tables 4.8 and 4.9. The flow sheet is not given because of its similarity to the corresponding flow sheet in PEP Report 54.

The capital investment and production cost are estimated and given in Tables 4.10 and 4.11 respectively. As expected, the costs are higher than those in Tables 4.6 and 4.7, which are for production of nylon salt in aqueous solution.

This process gives a solid nylon salt which can be transferred from one site to another. Furthermore, impurities in HMDA and adipic acid are partly removed by methanol; this would allow the use of less pure HMDA and adipic acid.

Table 4.8
SOLID NYLON SALT FROM METHANOL SOLUTION

MAJOR EQUIPMENT																																																																																																																																																																																																																																									
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Table 4.9
SOLID NYLON SALT FROM A METHANOL SOLUTION

UTILITIES SUMMARY

Plant Capacity: 58 Million lb/yr
(26,000 Metric Tons/yr) Nylon Salt
at 0.90 Stream Factor

	<u>Battery Limits</u>
	<u>Total</u>
Average consumptions	
Cooling water (gpm)	382
Electricity (kw)	102
Steam at 50 psig (lb/hr)	9,400
Inert gas, low pressure (scfh)	3,300
Peak demands	
Cooling water (gpm)	465
Electricity (kw)	131
Steam at 50 psig (lb/hr)	11,840
Inert gas, low pressure (scfh)	10,000

Table 4.10
SOLID NYLON SALT FROM A METHANOL SOLUTION

CAPITAL INVESTMENT				
	<u>Cost</u>	<u>Capacity Exponent</u>		
		<u>Up</u>	<u>Down</u>	
Battery limits equipment, f.o.b.				
Reactors	\$ 76,800	0.66	0.66	
Columns	9,100	0.46	0.43	
Vessels and tanks	290,400	0.37	0.36	
Exchangers	87,300	0.49	0.63	
Special equipment	241,900	0.61	0.60	
Miscellaneous equipment	112,000	0.66	0.66	
Pumps	<u>73,300</u>	0.16	0.12	
Total	\$ 890,800	0.50	0.49	
BATTERY LIMITS INVESTMENT	\$ 3,122,000	0.48	0.45	
Off-sites				
Cooling tower	\$ 209,100	0.28	0.28	
Steam generation	211,400	0.82	0.82	
Inert gas	113,500	0.52	0.54	
Utilities and tankage investment	\$ 641,000	0.57	0.53	
General service facilities	753,000			
Waste treatment	<u>188,000</u>			
OFF-SITES INVESTMENT	\$ 1,582,000	0.57	0.53	
TOTAL FIXED CAPITAL	\$ 4,704,000	0.50	0.46	
Start-up costs	\$ 1,745,000			
Working capital	<u>\$ 4,051,000</u>			
TOTAL CAPITAL INVESTMENT	\$10,500,000			

Table 4.11
SOLID NYLON SALT FROM A METHANOL SOLUTION

PRODUCTION COSTS			
	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Adipic acid	38.3¢/lb	0.56147 lb	21.50
HMDA	55.5¢/lb	0.44555 lb	24.73
Methanol	8.2¢/lb	0.0086 lb	<u>0.07</u>
Gross raw material cost			46.30
Utilities			
Cooling water	4.5¢/1,000 gal	3.12 gal	0.01
Steam	\$5.00/1,000 lb	1.28 lb	0.64
Electricity	2.65¢/kwh	0.014 kwh	0.04
Inert gas, low pressure	60¢/1,000 scf	0.449 scf	<u>0.03</u>
Total utilities			0.72
Labor			
Operating, 3 men/shift	\$14.20/hr	0.0005 man-hr	0.64
<u>Million lb/yr</u>			
	<u>29</u>	<u>58*</u>	<u>116</u>
Investment (\$ million)			
Battery limits	2.3	3.1	4.4
Off-sites	<u>1.1</u>	<u>1.6</u>	<u>2.2</u>
Total fixed capital	3.4	4.7	6.6
Scaling exponents	0.46	0.50	
Production costs (¢/lb)			
Raw materials	46.30	46.30	46.30
Utilities	0.72	0.72	0.72
Maintenance materials, 3%/yr of BL cost	0.23	0.16	0.11
Operating supplies, 10% operating labor	<u>0.13</u>	<u>0.06</u>	<u>0.03</u>
Variable costs	47.38	47.24	47.16
Operating labor	1.29	0.64	0.32
Maintenance labor, 3%/yr of BL cost	0.23	0.16	0.11
Control laboratory, 20% operating labor	<u>0.26</u>	<u>0.13</u>	<u>0.06</u>
Total direct costs	49.16	48.17	47.65
Plant overhead, 80% of total labor	1.42	0.75	0.40
Taxes and insurance, 2%/yr of fixed capital	0.23	0.16	0.11
Depreciation, 10%/yr of fixed capital	1.18	0.81	0.57
Interest on working capital, 10%/yr	<u>0.74</u>	<u>0.70</u>	<u>0.68</u>
Plant gate cost	52.73	50.59	49.41
G&A, sales, research, % of fixed capital	<u>negl</u>	<u>negl</u>	<u>negl</u>
NET PRODUCTION COST	52.73	50.59	49.41
25%/yr return on fixed capital, before taxes	<u>2.93</u>	<u>2.03</u>	<u>1.42</u>
PRODUCT VALUE	55.66	52.62	50.83

*Base case.

A Process for Making Solid Nylon Salt from an Aqueous Solution

An ICI patent (71568) and an Asahi Chemical patent (391583) teach the production of solid nylon salt from aqueous solution, by first adding solid adipic acid and then adding concentrated HMDA solution to a saturated nylon salt solution. The nylon salt precipitates and is separated by filtration. The filtrate is recycled for adding adipic acid. The precipitated nylon salt is washed with methanol, and vacuum dried.

This process is very similar to the one using methanol, except that methanol is used only for washing, not for dissolving; hence, there is less methanol circulation, a smaller methanol tank and the methanol recovery column could be smaller. The capital investment and production cost are roughly estimated to be as shown in Table 4.12. Note that, compared with the process using methanol, the investment is lower by 10%, and the product value is lower by 0.5¢/lb. In the present process, however, it is expected that the methanol, being in lesser quantity, would provide less of a purification function in this process than it does in the methanol process.

Table 4.12

SOLID NYLON SALT FROM AN AQUEOUS SOLUTION

PRODUCTION COST SUMMARY

Plant Capacity: 58 Million lb/yr
 (26,000 Metric Tons/yr) Nylon Salt
 at 0.90 Stream Factor
 PEP Cost Index: 320

	Million lb/yr		
	<u>29</u>	<u>58*</u>	<u>116</u>
Investment (\$ million)			
Battery limits	2.0	2.8	4.0
Off-sites	<u>1.0</u>	<u>1.4</u>	<u>2.0</u>
Total fixed capital	3.0	4.2	6.0
Scaling exponents	0.47	0.51	
Production costs (¢/lb)			
Raw materials	46.26	46.26	46.26
Utilities	0.49	0.49	0.49
Maintenance materials, 3%/yr of BL cost	0.21	0.14	0.10
Operating supplies, 10% operating labor	<u>0.13</u>	<u>0.06</u>	<u>0.03</u>
Variable costs	47.09	46.95	46.88
Operating labor	1.29	0.64	0.32
Maintenance labor, 3%/yr of BL cost	0.21	0.14	0.10
Control laboratory, 20% operating labor	<u>0.26</u>	<u>0.13</u>	<u>0.06</u>
Total direct costs	48.85	47.86	47.36
Plant overhead, 80% of total labor	1.40	0.73	0.39
Taxes and insurance, 2%/yr of fixed capital	0.21	0.14	0.10
Depreciation, 10%/yr of fixed capital	1.05	0.72	0.51
Interest on working capital, 10%/yr	<u>0.73</u>	<u>0.69</u>	<u>0.67</u>
Plant gate cost	52.24	50.14	49.03
G&A, sales, research, % of fixed capital	<u>negl</u>	<u>negl</u>	<u>negl</u>
NET PRODUCTION COST	52.24	50.14	49.03
25%/yr return on fixed capital, before taxes	<u>2.59</u>	<u>1.81</u>	<u>1.29</u>
PRODUCT VALUE	54.83	51.95	50.32

*Base case.

A Process for Making Solid Nylon Salt from Dimethyl Adipate and HMDA

A BASF patent (71572) teaches a process for making solid nylon salt from dimethyl adipate and HMDA, by heating these two substances in a nylon salt solution at 95-100°C, with recovery of methyl alcohol by condensing the evolving vapor. As the reaction products cool, nylon salt is precipitated, and the filtrate is recycled for the next batch. A brief evaluation shows that, as compared with the process using adipic acid, this process would require a larger reactor because of its longer reaction time (4 hr versus 30 min), and higher utilities consumptions because of the higher reaction temperature (75 to 100°C versus 60°C) and the vaporization of methanol. This process would not be economically viable unless dimethyl adipate is substantially cheaper than adipic acid, on an equal molar basis. Dimethyl adipate is made from butadiene, carbon monoxide, and methanol in the presence of mono- or di-methoxy-cyclohexane. The latter acts as a de-hydration agent and turns into cyclohexanone (462160, 307549). A rough evaluation shows that the product value of adipic ester made by this process is much higher than that of adipic acid made by the conventional cyclohexane process, on an equal molar basis. Hence the process for making nylon salt from adipic ester cannot be economically viable.

5 POLYCONDENSATION OF NYLON SALT IN AQUEOUS SOLUTION

Review of Processes

Nylon producers often prepare nylon salt (hexamethylene diammonium adipate) captively as a dilute aqueous solution. For polycondensation, this solution has first to be concentrated to a 50%-70% solution. If the starting material for the polycondensation is solid nylon salt, it is dissolved in hot water to form a solution of the above concentration.

For preparation of nylon 66, the aqueous nylon salt solution is heated. Water is evaporated, and molecules of hexamethylene diammonium adipate condense with each other to form the polyamide (nylon 66), with release of water. The temperature of the reaction is 450 to 550°F; at the final stage it is always at the high end of the range, which is above the melting point of nylon 66. Hence, the product is a molten mass.

Batch processing is still used in small plants or for the production of special grades. The batch process has the disadvantage that the quality may not be uniform, not only from batch to batch, but even in the same batch, because the portion last discharged has had a longer residence time than the portion first discharged. This disadvantage is more serious the larger the capacity. The reactor size assumed in the evaluation of the batch process in PEP Report 54 (8 ft diameter by 11 ft high) is too large; a reactor one-half that size, or about 2,000 gallons, is about the largest that can be used.

Table 5.1 lists the patents on batch polycondensation received at SRI after the issue of PEP Reports 54 and 94. (PEP Report 94 on polyamides other than nylon 66 and nylon 6 contains some relevant patents, in Sections 4 and 9.) The dual agitators advocated in reference 71595 and the inclined reactor described in reference 71560 are notable improvements. However, there is little incentive to adopt new features, because all major producers are using the continuous process for the production of their

Table 5.1

POLYCONDENSATION FOR NYLON 66 PRODUCTION, BATCH PROCESS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71574	Soc. de la Viscose Suisse	8/20/57
	Polycondensation of nylon salt in water solution without using high pressure, by adding excess HMDA. SRI's comment: the product quality would not be good.	
71595	Toyo Spinning	9/21/69
	The reactor is provided with two, coaxial agitators; in the initial stage, the upper agitator rotates at a lower speed than the lower agitator; when the polymerization progresses and the level of the contents in the reactor falls, the speed of the upper agitator is increased and that of the lower one is decreased. Foaming and gel formation are reduced.	
71575	USSR	11/13/69
	Polycondensation of nylon salt is conducted in the presence of 1%-3% C ₈ + aliphatic diamine.	
71560	Karl Fischer	8/30/73
	An inclined reactor with a stirrer is used; a part of the agitator dips into the reaction mass and then emerges from it during each revolution; the reaction is accelerated.	

main grades, retaining the batch process for small volume special grades, which are made in existing batch autoclaves.

The continuous process is carried out in the following manner: The reaction takes place in several stages in different equipment. The first stage of the reaction takes place under a pressure greater than 250 psig (18 atm), to prevent the loss of HMDA. This stage of the reaction can be in a tank or vessel, in tubes, or in any equipment which can be conveniently constructed to withstand the pressure. The water vapor is either removed from the reactor through a throttle valve, or removed in a subsequent separator. The last stage of polycondensation takes place under atmospheric pressure or subatmospheric pressure in order to further facilitate the removal of water. Throughout the reaction, temperature at an appropriate level, varying from 392°F (200°C) to 572°F (300°C), more often between 518°F (270°C) and 554°F (290°C), is maintained at each stage. At the point where the pressure changes from 250 psig or higher to atmospheric, provision must be made to avoid freeze-congealing due to sudden evaporation of water, for example, by using tubes of successively smaller diameters, with outside heating. The whole design should be such that the reaction mass is subject to minimum exposure to heat in order to avoid degradation and to avoid dead spots and splashes on walls which may cause gel formation. In the final stage of polycondensation, the flow should be at a uniform rate and have little or no backmixing, in order to get as uniform a product as possible.

With a very few exceptions, the numerous processes in the patents on continuous polycondensation to make nylon 66 are based on the principle described in the preceding paragraph.

Table 5.2 lists the patents about continuous polycondensation for producing nylon 66 received at SRI and after the issue of PEP Reports 54 and 94. Among them, two patents assigned to Du Pont Canada (71530 and 71558) describing a novel process are especially noteworthy. In this process, a heat exchanger and a separator, with a circulating stream between them, are used as a first-stage reactor. HMDA evolved is recovered by a tray column and a partial condenser. This reactor is highly

Table 5.2

POLYCONDENSATION FOR NYLON 66 PRODUCTION, CONTINUOUS PROCESS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71525	Nylon Spinners	10/26/62
	The shape of the connection of the tubular flasher-reactor with the separator facilitates the separation of steam and reduces splashing of the molten mass.	
462068	Toyobo	3/4/67
	In falling-film polycondensation the film is treated with inert gas.	
71594	Toray	2/21/69
	Three reactors in series serve to make nylon 66 from a 70% solution; the order of the flow to the reactors is changing in rotation. Gel formation is prevented.	
71517	Fiber Industries	9/23/69
	The reaction product flows from the tubular reactor to a vessel; the level of the molten product is controlled by a radioactive detector.	
71600	Asahi Chemical	11/4/69
	The level of molten nylon 66 and the nitrogen pressure in the degassing vessel is controlled automatically; therefore, a constant residence time is maintained, and the quality is uniform.	
71598	Hitachi	10/9/70
	A continuous process consisting of taper shaped evaporator and vacuum agitator reactor, with part of polymer recycled to the evaporator.	
462152	USSR	4/6/71
	A continuous polycondensation system with vertical tubes between a melter and a reactor, and a central steam pipe.	
462031	ICI	5/3/71
	The mixture of liquid and gas from continuous polycondensation reactor passes sideways into a separation vessel via a chute which directs the liquid polymer smoothly to a pool of molten polymer.	
406639	ICI	9/7/72
	Reactor made of titanium instead of stainless steel has the advantages: (1) product has higher viscosity, (2) less loss of HMDA during reaction.	
71530	Du Pont Canada	3/5/73
	First-stage polycondensation (from a 50% nylon salt solution to a prepolymer, containing 10% water, 91% reacted, relative viscosity 425) takes place in a shell-tube type exchanger, with circulating reaction mass; the reactor is connected to a separator which is surmounted by a column; the feed solution flows down the column; vapor from the separator flows up the column and then is partially condensed at the top to recover HMDA.	

Table 5.2 (Concluded)

POLYCONDENSATION FOR NYLON 66 PRODUCTION, CONTINUOUS PROCESS**PATENT SUMMARY**

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71558	Du Pont Canada	2/27/74
	This is related to 71530. The prepolymer from the first-stage polycondensation goes to a tubular reactor for a second-stage polycondensation, and then to a separator and finisher. The level of the polymer in the finisher is kept at a constant level by controlling the pressure in the tubular reactor, activated by a stream of superheated steam, which is from the partial condenser of the column mentioned in 71530.	
71542	BASF	4/8/74
	A continuous process consisting of a heat exchanger, a completely full column at 280°C and 80 atm for 45 minutes' residence time (where 80% polymerization is attained); a throttle; an arc at 180-210°C and 10-20 atm, a tubular evaporator at 250-300°C and 8-15 atm; a separator at 165-270°C with 30 minutes' residence time; another heat exchanger to raise to 270-290°C; and a twin-extruder with residence time of 25-40 minutes.	
71557	Du Pont	5/6/74
	Static mixers put in the tubular reactor; loss of HMDA is reduced.	
71603	UBE	4/4/75
	A 65%-80% nylon salt solution is heated at 240-280°C for 2-4 hours, and then sprayed into a chamber blanketed with nitrogen at 1 atm; solid polymer obtained is heated at 270-280°C to increase mol wt.	
71641	Toyo Spinning	4/8/75
	A horizontal continuous polycondensation reactor consists of a jacketed vessel with two horizontal rotating axes equipped with circular discs, which have radial wings attached.	
462142	Asahi Chemical	10/30/76
	Continuous polycondensation controlled by vacuum.	
71778	UBE	1/14/77
	Nylon salt solution is evaporated at 240-280°C and 13-20 atm for 2-4 hours, and then pumped to a vacuum chamber at 360 mm Hg and 270-280°C for 0.5-3 hours.	
71628	BASF	1/22/77
	The final stage of polycondensation is achieved in a nylon 66-steam foam at 260-280°C for 20-60 minutes.	
462045	Wiltzer, K., et al.	10/5/77
	Continuous polycondensation with heat transfer from nylon melt to monomer-containing reaction mixture. (Example on nylon 6, but principle should be applicable to nylon 66.)	

Note: Also refer to 387538 and 387216 in PEP Report 94.

efficient with respect to heat transfer; in the relatively short residence time of less than 1 hour, a 50% nylon salt solution can be converted to a prepolymer, with 95% of the nylon salt being reacted and with the prepolymer containing only 10% free water. This is of much higher degree of polycondensation than is attained by a tank-type reactor in 3 hours. Because of the higher degree of polycondensation of the product from this first-stage reactor, the load in the next stage is reduced; so is the residence time. Hence it is expected that the product made by this kind of equipment should have less cross-linking (for the same relative viscosity) and should be less liable to gel; it would be eminently suitable for making fibers.

Two patents in Table 5.2, reference 71598 (Hitachi) and reference 71603 (Ube), are novel and depart from the general description given above. The Hitachi patent describes the use of an evaporator followed by an agitated reactor; SRI does not believe this procedure can give a product with sufficiently high molecular weight and uniform quality for commercial use. The Ube patent describes spray drying of the polymer; SRI suspects this process would entail frequent cleaning of equipment.

Table 5.3 lists patents on various problems related to polycondensation, both batch and continuous. Most of them are about the cleaning of equipment. One patent (71624) relates to a device for avoiding plugging of the vent. Another patent (71535) relates to the recovery of HMDA in the condensate of the vapor from polycondensation. The two Du Pont Canada patents (71530 and 71558) mentioned earlier also include features for HMDA recovery.

Additives are often introduced during the polycondensation. These will be described in Section 6 (resins and chips), because such additives are mostly intended to impart certain desirable properties to resins and chips. In this section, we are concerned with only the polycondensation. Only two kinds of additive are relevant to the polycondensation per se. One is a viscosity stabilizer that limits the degree of polymerization even on prolonged reaction. This is either a slight excess of HMDA or adipic acid, or better still, a small amount of monofunctional amine or

Table 5.3

POLYCONDENSATION FOR NYLON 66 PRODUCTION,
OTHER FEATURES IN MANUFACTURE

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71596	Toyo Spinning	12/28/70
	The equipment is steam flushed after shutting down, to prevent polymer degradation.	
71577	Unitika	8/30/72
	The equipment is cleaned with α -piperidone.	
71605	Unitika	11/11/72
	The equipment is cleaned with diethylene glycol-NaOH solution.	
71535	Du Pont	1/10/74
	HMDA in the condensate is recovered by contacting it with anion exchange resin, and subsequently leaching the resin with adipic acid solution.	
71544	Du Pont	2/24/76
	Gelled polyamides are contacted with a hydroxy-containing organic compound to permit its flushing.	
71624	Du Pont	3/26/76
	Plugging of the vent steam line containing entrained polymer is avoided by water injection.	
71580	Honda, T.	7/29/76
	Gelled polyamides are dissolved by halogenated nitrosylsulfuric acid at 40-80°C.	

acid. The one mostly used is acetic acid. Triphenyl carboxy alkyl phosphonium halide and diphenyl ethyl carboxy alkyl phosphonium halide are also mentioned (71887). Another kind of additive relevant to polycondensation per se is a reaction accelerator. Alkali phenylphosphinate, polyphosphoric acid, or Sr- or Zn-hypophosphite increases the rate of polycondensation (71260, 71104). Triethyltitanate increases the rate in the last stage of polycondensation (71606).

On the following pages, two processes are evaluated: one is adopted from the two Du Pont Canada patents mentioned before; the other is based on earlier patents and probably represents conventional practice.

A Polycondensation Process for Making Nylon 66 in a Du Pont Canada Reactor

Process Description

The design bases and assumptions of the evaluated process are given in Table 5.4. The flow sheet is shown in Figure 5.1 (foldout at end of report). The compositions of streams marked on Figure 5.1 are shown in Table 5.5. The major equipment list and utilities summary are given in Tables 5.6 and 5.7 respectively.

The present evaluated process is assumed to start from a captively produced aqueous nylon salt solution. Figure 5.1 can therefore be considered as a continuation of Figure 4.1 (also at end of report). The nylon salt solution as prepared has a concentration of about 40%. It is evaporated in evaporator S-101 to a 50% solution. After passing through line filter S-102 A or B (cleaned alternately) and being cooled to 120 to 140°F in E-102, the solution is stored in a surge tank. It is pumped to 265 psia, and then enters E-201 to be heated by high temperature water vapor (from C-201) to 400°F (210°C). It then enters one of the trays of column C-201. It flows down the column, mixes with the water reflux in the column, and leaves the last tray of the column and enters the bottom of R-201. A solution of HMDA in the acetic acid is added at this point by a metering pump. If needed, titanium dioxide is also added here as a water slurry. R-201 is heated by Dowtherm® on the shell

Table 5.4

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

DESIGN BASES AND ASSUMPTIONS

References	71558, 71530 (Du Pont Canada patents) 70791, 71624, 71557, 71549 (Du Pont patents)
First Stage of Polycondensation	446°F (230°C), 265 psia, 50 minutes (in separator); product, 10% water, 95% reacted; water vapor removed during the reaction.
Second Stage of Polycondensation	446°F (230°C) to 536°F (280°C), 265 psia to 45 psia, 20 minutes; product, 1.7% water, 98.5% reacted; water vapor remains with the melt, to be separated in a subsequent separator.
Third Stage of Polycondensation	520°F (270°C), 300 mm Hg, 45 minutes; product, relative viscosity 4.0, water vapor removed by a vacuum system.

side; the nylon salt solution is in the tubes. The top of R-201 is connected to separator V-201, where water vapor is released, and the sump liquid is pumped back to the bottom of R-201. The water vapor passes upward through the column, and is partially condensed in E-201, which supplies the reflux of the column.

Separator V-201 is divided by a weir into a circulation region and a plug-flow region. The stream overflows from the former to the latter, and then is pumped by a gear pump to flasher-reactor R-202. On entering R-202, the stream contains 10% water, and 95% of the nylon salt has been converted to polyamide; the relative viscosity is 3.8.

Flasher-reactor R-202 consists of tubes with the following dimensions:

<u>Length (ft)</u>	<u>Diameter (in.)</u>
350	1-3/4
300	2-3/4
125	4-1/2
25	5-1/2

The whole set is immersed in a heat transfer medium. At several points inside the tubes, static mixers are put in to break up any slug-type flow and to reduce HMDA loss. If necessary, additives such as stabilizers are introduced at an intermediate point through metering pumps.

In R-202, reaction proceeds to a degree that at the exit point, 98.5% of the nylon salt has been converted to polyamide with relative viscosity of about 10. The water content in the liquid (now a molten phase) is only 1.7%; the balance of the water is in vapor form. This mixture discharges from R-202 to separator S-201. S-201 is maintained at atmospheric pressure. The molten mass enters tangentially, and falls downward, helped by a spiral conveyor; the water vapor disengages from the molten mass and leaves S-201. Below the separator is finishing reactor R-203. Between S-201 and R-203 is a screen with holes. The molten polyamide passes through the screen and forms a pool in R-203. R-203 is maintained at 300 mm Hg by a steam jet, and at 520°F by heat-transfer-liquid heating. The residence time in R-203 is 40 minutes. At the bottom of R-203 is a gear pump, withdrawing a molten nylon 66 having a relative viscosity of 40. This is transferred to spinning, or to a die for pelletizing. (The operations of pelletizing and spinning will be described in Sections 6 and 7 respectively.)

There are three important control devices. A level indicator in R-201 actuates the speed control of the gear pump feeding stream 7. In finishing reactor R-203, another level indicator actuates the speed control of the gear pump feeding material from V-201 to the flasher-reactor R-202. By these controls, the levels in S-201 and R-203 are controlled at a preset level. Furthermore, a stream of superheated steam (a side stream of the water vapor leaving E-201 that is superheated by a heat transfer medium in E-202 to 520-530°F) enters R-202 at the beginning of the 3 in. section of R-202. This steam stream is controlled by a valve which is actuated by the pressures at the end of the 2 in. pipes section and the 3 in. pipes section. The above device controls the pressure of the two-phase flow region in the 3 in. and 4 in. section of R-202, and minimizes the cyclic fluctuations of levels in R-201 and R-203. By means

of the above control device, the residence time in the reactors can be maintained constant, even if the withdrawal rate of nylon melt from R-203 varies, as is often the case when the molten nylon is used directly for spinning. (Some of the spinning positions may have to be shut down because of yarn breakage, for example.)

The water vapor leaving the top of E-201 may contain a trace of nylon salt or oligomer. On passing through the throttle valve, such nylon salt or oligomer may congeal and cause plugging. To prevent this, water is added at a point shortly after the throttling.

The condensate from V-101, V-202, and V-203, as well as that from the barometric condenser of vacuum jet M-201, is water containing a little HMDA, other amines, ammonia, nitriles, imines, or oxygenated compounds from these compounds. It should be biodegraded before it is discharged.

Even with good design and proper operation, the reactors may foul up with gelled product after several weeks of operation. Also, when the operation is shut down for maintenance, the residual product in the equipment tends to gel. To remove the gel, the equipment is first flushed with steam, then flushed with a chemical such as α -pyrrolidone, α -piperidene, glycol plus sodium hydroxide, a polyhaloalcohol, or a carboxylic acid (71544, 71577, 71605), followed by further steam flushing, and finally, cutting or burning if necessary.

Table 5.5

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

STREAM FLOWS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor

	Mol Wt	Stream Flows (lb/hr)				
		(1)	(2)	(3)	(4)	(5)
Hexamethylenediamine	116	20	10	10	28	--
Impurities	120	6	3	3	--	--
Nylon 66	226	--	--	--	--	--
Water	18	11,109	7,211	3,898	--	12,000
Nylon salt	262	7,357	7,357	--	--	7,361
Acetic acid	60	--	--	--	11	--
Totals, lb/hr		18,492	14,581	3,911	39	19,361
kg/hr		8,388	6,614	1,774	18	8,782
Totals, lb-mols/hr		645	429	217	0.42	695
kg-mols/hr		293	195	98	0.19	315

	Mol Wt	Stream Flows (lb/hr)				
		(6)	(7)	(8)	(9)	(10)
Hexamethylenediamine	116	--	--	10	8	--
Impurities	120	--	--	3	2	--
Nylon 66	226	42,174	6,024	--	--	6,342
Water	18	4,998	714	7,188	760	12
Nylon salt	262	2,688	384	--	--	--
Acetic acid	60	--	--	--	--	--
Totals, lb/hr		49,860	7,122	7,201	770	6,354
kg/hr		22,616	3,230	3,266	349	2,882
Totals, lb-mols/hr		475	68	399	42	29
kg-mols/hr		215	31	181	19	13

Table 5.6

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

MAJOR EQUIPMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor

<u>Equipment Number</u>	<u>Name</u>	<u>Size</u>	<u>Material of Construction</u>		<u>Remarks</u>		
<u>Reactors</u>							
R-201	Reactor	3,000 sq ft	Shell: Carbon steel				
R-202	Reactor	800 ft lg, 1.75 to 5.5 in. dia	Tubes: 304 ss				
R-203	Finisher	4 ft dia x 10 ft high	Shell: Carbon steel Tubes: 304 ss				
<u>Exchangers</u>							
E-101	Condenser	3,000	14.00	Carbon steel	Carbon steel		
E-102	Cooler	600	1.40	Carbon steel	304 ss		
E-201	Partial condenser	300	4.50	Carbon steel	304 ss		
E-202	Steam superheater	10	0.01	Carbon steel	304 ss		
E-203	Condenser	1,400	9.40	Carbon steel	Carbon steel		
E-204	Condenser	820	0.90	Carbon steel	Carbon steel		
<u>Furnaces</u>							
H-201	Dowtherm® unit	12.6	Carbon steel		Not shown in figure.		
<u>Tanks</u>							
T-101	Surge tank	1,500	304 ss				
T-201	Acetic acid tank	2,000	316 ss				
T-202, 3,4	Additive tanks	2,000 ea	304 ss				
<u>Vessels</u>							
V-101	Receiver	500	304 ss				
V-201	Separator	1,000	304 ss				
V-202	Receiver	500	304 ss				
V-203	Receiver	50	304 ss				
<u>Columns</u>							
G-201	Column on reactor	16	2.5	304 ss	304 ss		
<u>Special Equipment</u>							
S-101	Evaporator	1,100 sq ft	304 ss				
S-102A,B	Filters		304 ss				
S-201	Separator		304 ss		2 ft dia 8 ft high.		
<u>Miscellaneous Equipment</u>							
M-201	Vacuum jet		Carbon steel				
M-202	Cleaning facilities				Not shown in figure.		
<u>Pumps</u>							
100 Section: 4, including 2 operating, 2 spares; 12 operating bhp							
200 Section: 16, including 8 operating, 8 spares; 4 operating bhp							

Table 5.7

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

UTILITIES SUMMARY

Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Nylon 66 Melt
at 0.90 Stream Factor

	Battery Limits <u>Total</u>	100 <u>Section</u>	200 <u>Section</u>
Average consumptions			
Cooling water (gpm)	2,380	1,050	1,330
Electricity (kw)	21	11	10
Steam at 100 psig (lb/hr)	13,300	13,000	300
Inert gas, high pressure (scfh)	300		300
Fuel oil (million Btu/hr)	21		21
Peak demands			
Cooling water (gpm)	2,954	1,268	1,686
Steam at 100 psig (lb/hr)	16,100	15,600	500
Inert gas, high pressure (scfh)	600		600

Process Discussion

According to reference 366790 (a British Nylon patent), a single elongated tubular reactor can produce polyamide up to 250 kg/hr, starting from a 48% nylon salt solution. The factor limiting the scale-up is slug formation, which is due to the water vapor formed in the tubes. In the present design, the water vapor in R-202 is about 30% greater than the water associated with the production of 250 kg/hr polyamide from a 48% nylon salt solution. With the insertion of a static mixer in the tubes, we believe a single unit can handle the production. However, this is nearly the maximum size, and if the plant capacity is doubled, two units of R-202 have to be used; separator S-201 and finishing reactor R-203 must also be provided in duplicate, because it is not advisable to have branch connections between R-202 and S-201.

The dimensions of R-201 are calculated from the residence time (based on reference 71530, assuming 50% of the space in the 4-1/2 in. and 5-1/2 in. pipes is filled with water vapor) and the necessary heat transfer area. There are formulas in references 71723 and 366790 for calculation of tube size. But the latter relates to a reactor forming polyamide from nylon salt solution and therefore gives too large a size, and the former is for flashing only and gives too short a tube.

The condensate from V-101, V-202, and V-203 can be treated by an ion exchange resin for recovery of HMDA. However, in doing so, some impurities will also be recycled. Furthermore, the amount of HMDA in the condensate has been minimized by several design features (limiting the evaporation in S-101 so that the final solution composition is 50%, rather than 60%-70%; refluxing in C-201 and E-201; and using a motionless mixer in R-202). Hence, the condensate is treated as wastewater.

Cost Estimates

The capital investment and production cost estimates are given in Tables 5.8 and 5.9 respectively. In the estimate for production cost, additives are excluded. The usage of these additives depends on the

type of product, and hence would be considered in cost estimates of resin or fiber (Sections 6 and 7).

According to an ICI patent (406639), use of titanium reactors instead of stainless steel ones can reduce the vaporization of HMDA, and the product is more viscous. However, the investment would be increased substantially. A rough estimate shows that the capital investment would increase by about 1.1 million U.S. dollars if the reactors and related equipment (separators and column) are made of titanium instead of stainless steel, resulting in an increase of 0.26¢/lb for the production cost, and an increase of 0.80¢/lb for the project value.

In Table 5.9 nylon salt is priced at 49.5¢/lb. This is the product value of nylon salt in aqueous solution, at 58 million lb/yr, corresponding to 50 million lb/yr nylon 66 (Table 4.7). Since nylon salt is often made captively by nylon 66 producers, especially if it is to be in solution form, it would be more equitable to use the product value of nylon salt at a production capacity corresponding to the production capacity of nylon 66 rather than to use a constant value. Following this principle, the raw material cost, production cost, and product value of nylon 66 at 25 million lb/yr and 100 million lb/yr in Table 5.15 should be adjusted as follows:

<u>Plant Capacity (million lb/yr)</u>	<u>Adjustment (¢/lb product)</u>
25	+1.79
100	-1.03

As shown in Tables 4.7, 4.11, and 4.12, the nylon salt produced in solid form would have a product value higher than that produced in aqueous solution by 2.5¢ to 3¢/lb. In reality, if solid salt is used, very probably it is transferred from another plant or even procured from another company. We have no information about the market price of nylon salt, but it is not likely to be lower than 55¢/lb. The use of nylon salt at this price would cause the production cost of nylon 66 given in Table 5.15 to increase by at least 9¢/lb.

Table 5.8

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

CAPITAL INVESTMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor
 PEP Cost Index: 320

	Total			Nylon Salt			Polycondensation		
	Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent	
		Up	Down		Up	Down		Up	Down
Battery limits equipment, f.o.b.									
Reactors	\$ 238,400			\$			\$ 238,400	0.86	0.64
Columns	17,500						17,500	0.76	0.62
Vessels and tanks	164,700			31,200	0.81	0.36	133,500	0.89	0.38
Exchangers	150,900			68,500	0.60	0.52	82,400	0.48	0.43
Furnaces	137,000						137,000	0.79	0.79
Special equipment	112,000			92,800	0.70	0.69	19,200	0.95	0.60
Miscellaneous equipment	35,200						35,200	0.60	0.60
Pumps	<u>203,000</u>			<u>52,700</u>	0.48	0.39	<u>150,300</u>	0.19	0.16
Total	\$ 1,058,700	0.69	0.50	\$ 245,200	0.64	0.53	\$ 813,500	0.70	0.49
BATTERY LIMITS INVESTMENT	\$ 3,323,000	0.61	0.45	\$ 837,000	0.57	0.50	\$ 2,486,000	0.62	0.44
Off-sites									
Cooling tower	\$ 396,100			\$ 169,900	0.60	0.40	\$ 226,200	0.57	0.43
Steam generation	264,400			255,900	0.82	0.82	8,500	0.82	0.82
Inert gas	44,400						44,400	0.23	0.22
Utilities and tankage investment	\$ 846,000	0.66	0.54	\$ 511,000	0.74	0.64	\$ 335,000	0.53	0.40
General service facilities	834,000								
Waste treatment	<u>272,000</u>								
OFF-SITES INVESTMENT	\$ 1,952,000	0.66	0.54						
TOTAL FIXED CAPITAL	\$ 5,275,000	0.63	0.48						
Start-up costs	\$ 1,768,000								
Working capital	<u>\$ 4,439,000</u>								
TOTAL CAPITAL INVESTMENT	\$11,482,000								

Table 5.9

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

PRODUCTION COSTS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor
 PEP Cost Index: 320

	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Nylon salt	49.5¢/lb	1.1641 lb	57.62
HMDA	55.5¢/lb	0.00219 lb	0.12
Acetic acid	20.7¢/lb	0.00174 lb	0.04
Gross raw material cost			57.78
Utilities			
Cooling water	4.5¢/1,000 gal	22.5 gal	0.10
Steam	\$5.00/1,000 lb	2.1 lb	1.05
Electricity	2.65¢/kwh	0.003 kwh	0.01
Fuel oil	\$3.30/million Btu	3,311 Btu	1.09
Inert gas, high pressure	80¢/1,000 scf	0.047 scf	negl
Total utilities			2.25
Labor			
Operating, 2 men/shift	\$14.20/hr	0.0004 man-hr	0.50
Costs by Section (thousand \$/yr)			
	<u>100 Section</u>	<u>200 Section</u>	
Labor			
Operating	62	187	
Maintenance	25	75	
Control laboratory	<u>12</u>	<u>37</u>	
Total labor	99	299	
Materials			
Nylon salt	28,812		
HMDA		61	
Acetic acid		18	
Maintenance	25	75	
Operating	<u>6</u>	<u>19</u>	
Total materials	28,843	173	
Utilities			
Cooling water	22	28	
Steam	512	12	
Electricity	2	2	
Fuel oil		546	
Inert gas, high pressure		<u>2</u>	
Total utilities	536	590	

Table 5.9 (Concluded)

NYLON 66 BY POLYCONDENSATION IN A DU PONT CANADA REACTOR

PRODUCTION COSTS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor
 PEP Cost Index: 320

	Million lb/yr		
	25	50*	100
Investment (\$ million)			
Battery limits	2.4	3.3	5.1
Off-sites	<u>1.4</u>	<u>2.0</u>	<u>3.1</u>
Total fixed capital	3.8	5.3	8.2
Scaling exponents		0.48	0.63
Production costs (¢/lb)			
Raw materials	57.78	57.78	57.78
Utilities	2.25	2.25	2.25
Maintenance materials, 3%/yr of BL cost	0.29	0.20	0.15
Operating supplies, 10% operating labor	<u>0.10</u>	<u>0.05</u>	<u>0.02</u>
Variable costs	60.42	60.28	60.20
Operating labor	1.00	0.50	0.25
Maintenance labor, 3%/yr of BL cost	0.29	0.20	0.15
Control laboratory, 20% operating labor	<u>0.20</u>	<u>0.10</u>	<u>0.05</u>
Total direct costs	61.91	61.08	60.65
Plant overhead, 80% of total labor	1.19	0.64	0.36
Taxes and insurance, 2%/yr of fixed capital	0.30	0.21	0.16
Depreciation, 10%/yr of fixed capital	1.52	1.06	0.82
Interest on working capital, 10%/yr	<u>0.92</u>	<u>0.89</u>	<u>0.87</u>
Plant gate cost	65.84	63.88	62.86
G&A, sales, research, % of fixed capital	<u>negl</u>	<u>negl</u>	<u>negl</u>
NET PRODUCTION COST	65.84	63.88	62.86
25%/yr return on fixed capital, before taxes	<u>3.80</u>	<u>2.65</u>	<u>2.05</u>
PRODUCT VALUE	69.64	66.53	64.91

*Base case.

A Polycondensation Process for Making Nylon 66 Using Tank Reactor in First Stage of Polycondensation

Process Description

The nylon salt solution at 40% concentration is evaporated in S-101 to a 70% solution. See flow sheet in Figure 5.2 (foldout at end of report). This concentrated solution, after passing through a line filter, is pumped to evaporative reactor R-201. The evaporative reactor is a tank with jacket and partitions; the partitions are hollow and are connected with the jacket (as shown in the cross-sectional view). The jacket is filled with Dowtherm® or other heat transfer fluid. The reaction product from the evaporative reactor enters a flasher-reactor.

The design bases and assumptions are given in Table 5.10. The compositions of streams marked in Figure 5.2 are shown in Table 5.11. The major equipment list and the utilities summary are given in Tables 5.12 and 5.13 respectively.

From the flasher-reactor, the stream flows to separator S-201, where vapor is separated from the melt. The melt flows to finishing reactor R-203.

The condensates from the evaporation and reaction in V-101 and V-201 are collected in tank T-301. This is water containing a little HMDA. After passing through a line filter, this water stream is contacted with an ion exchange resin in V-301. HMDA is adsorbed and the outflowing water is discharged for biodegradation treatment. After adsorption, the resin is treated with an adipic acid solution and then with deionized water, and is used for adsorption of HMDA again. Two adsorbers (V-301 and V-302) are provided, for alternative adsorption and regeneration. The aqueous solution recovered during regeneration is neutralized by HMDA and added to the nylon salt solution feed to evaporator S-101.

The condensate from V-202 is not treated for HMDA recovery because it has too high an impurity content. It is biodegraded and discharged.

Table 5.10

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

DESIGN BASES AND ASSUMPTIONS

References	70336, 70681, 100356, 70791 (reactors) 71535 (HMDA recovery) 71674, 71557 (other features)
First stage of polycondensation	450°F (232°C) 265 psia, 3 hr; product 50% reacted, 16% water. Water vapor removed during evaporation.
Second stage of polycondensation	450°-545°F (232°-285°C), 265 to 65 psia, 40 minutes; product 98.5% reacted, 1.7% water. Water vapor remains with the melt, to be separated in a subsequent separator.
Third stage of polycondensation	520°F (376°C), 300 mm Hg, 45 minutes; product, relative viscosity 40-45; water vapor removed by a vacuum system.

Table 5.11
NYLON 66 BY POLYCONDENSATION,
FIRST STAGE IN A TANK REACTOR

	Mol Wt	Stream Flows (lb/hr)						
		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Hexamethylenediamine	116	20	--	20	48	--	30	10
Impurities	120	6	4	6	--	--	4	10
Nylon 66	226	--	--	--	--	3,174	--	--
Water	18	11,109	415	7,955	--	1,486	2,174	1,980
Nylon salt	262	7,242	7,357	--	--	3,680	--	--
Acetic acid	60	--	--	--	11	--	--	--
Adipic acid	146	--	--	--	--	--	--	--
Totals, lb/hr		18,377	7,776	7,981	59	8,340	2,208	2,000
kg/hr		8,336	3,527	3,620	27	3,783	1,002	907
Totals, lb-mols/hr		645	51	442	0.60	111	121	110
kg-mols/hr		293	23	201	0.27	50	55	50

	Mol Wt	Stream Flows (lb/hr)					
		(8)	(9)	(10)*	(11)	(12)	(13)†
Hexamethylenediamine	116	--	3	--	6	--	--
Impurities	120	--	3	--	--	--	--
Nylon 66	226	6,342	--	--	--	--	--
Water	18	12	15,935	--	--	1,000	5,800
Nylon salt	262	--	--	--	--	119	--
Acetic acid	60	--	--	--	--	--	--
Adipic acid	146	--	--	66	--	--	--
Totals, lb/hr		6,354	15,941	66	6	1,119	5,800
kg/hr		2,882	7,231	30	3	508	2,631
Totals, lb-mols/hr		29	885	0.45	0.05	56	322
kg-mols/hr		13	402	0.21	0.02	25	146

* Solid feed.

† Sum of two streams.

Table 5.12
NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

MAJOR EQUIPMENT					
Plant Capacity: 50 Million lb/yr (23,000 Metric Tons/yr) Nylon 66 Melt at 0.90 Stream Factor					
<u>Equipment Number</u> <u>Name</u> <u>Size</u> <u>Material of Construction</u> <u>Remarks</u>					
<u>Reactors</u>					
R-202A,B	Flasher-reactors	Each 800 ft, 1.75 to 5.5 in. dia	Shell: carbon steel Tubes: 304 ss		
R-201	Evaporative reactor	4,000 gal	304 ss clad		
R-203	Finisher	4 ft dia, 10 ft high	304 ss		With inner partition and jacket.
<u>Exchangers</u>					
E-101	Condenser	1,200	9.10	Carbon steel	Carbon steel
E-201	Condenser	350	0.23	Carbon steel	Carbon steel
E-202	Condenser	400	0.30	Carbon Steel	Carbon steel
<u>Furnaces</u>					
H-201	Dowtherm® unit	6.7		Carbon steel	Not shown in figure.
<u>Tanks</u>					
T-201	Acetic acid tank	2,000	316 ss		
T-202,3,4	Additive tanks	2,000 ea	304 ss		
T-301	Condensate tank	3,000	304 ss		
T-302	Adipic acid tank	1,000	304 ss		
T-303	Dilute nylon salt tank	3,000	304 ss		
<u>Vessels</u>					
V-101	Receiver	500	304 ss clad		
V-201	Receiver	100	304 ss clad		
V-202	Receiver	70	304 ss clad		
V-301,2	Resin vessels	200 ea	304 ss		
<u>Special Equipment</u>					
S-101	Evaporator	2,100 sq ft	304 ss		
S-102A,B	Filters		316 ss		
S-201	Separator	2 ft dia, 8 ft high	304 ss		
S-301	Filter		316 ss		
<u>Miscellaneous Equipment</u>					
M-101	Feeder		304 ss		Not shown in figure.
M-201	Ejector		Carbon steel		
M-202	Cleaning facilities				Not shown in figure.
M-301	Feeder		304 ss		Not shown in figure.
<u>Pumps</u>					
100 Section: 6, including 3 operating, 3 spares; 28 operating bhp					
200 Section: 14, including 7 operating, 7 spares; 2 operating bhp					
300 Section: 10, including 5 operating, 5 spares; 4 operating bhp					

Table 5.13

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

UTILITIES SUMMARY

Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Nylon 66 Melt
at 0.90 Stream Factor

	Battery Limits <u>Total</u>	100 <u>Section</u>	200 <u>Section</u>	300 <u>Section</u>
Average consumptions				
Cooling water (gpm)	2,030	1,500	530	
Electricity (kw)	65	24	36	5
Process water (gpm)	12		1	11
Steam at 100 psig (lb/hr)	7,000	7,000		
Inert gas, high pressure (scfh)	1,200		1,200	
Fuel oil (million Btu/hr)	12		12	
Peak demands				
Process water (gpm)	15		2	13
Inert gas, high pressure (scfh)	1,800		1,800	

Process Discussion

The fundamental difference between this process and the process evaluated before is the use of tank reactor R-201. The heat transfer in this kind of equipment is very slow, hence the residence time is increased to 3 hours and partitions are used in addition to the jacket. The feed to R-201 is a 70% solution, not a 50% solution as in the previous process; the nylon salt conversion is 50% (as compared with 95% in the previous process) and the product stream contains 16% water (as compared with 10% in the previous process).

Because of the composition of the stream entering R-202, the load in R-202 is about double that in the previous process. The quantity of evaporation exceeds the amount that a single tubular reactor can efficiently handle. Hence, R-202 has to be in duplicate.

The HMDA content in the vapor from R-201 would be higher than in the corresponding stream in the previous process, because there is no column for refluxing. There also would be some HMDA loss during the evaporation in S-101. These streams are treated for recovery of HMDA. In recovery of HMDA, other impurities such as 1,2-diaminocyclohexane (in the HMDA), and hexylamine and pentylamine from decomposition of nylon salt (71694), are also recovered and tend to accumulate in the system until they finally leave through S-201. Hence the condensate from S-201, which is collected in V-203, is not treated for HMDA recovery; instead it is discharged as wastewater.

The total residence time is 1.8 times that in the previously described process based on Du Pont Canada patents. Hence, it is expected that the product made by this process would be slightly darker and that the molecular structure would contain some branching.

Cost Estimates

The capital investment and production cost are estimated in Table 5.14 and 5.15 respectively.

The remarks about the effect of the unit price of nylon salt given under the other process (the Du Pont Canada process) apply equally here.

From a comparison of Tables 5.9 and 5.15, it is seen that there is little economic difference between these two processes: the process using the tank evaporator offers some savings in utilities, but these savings are counteracted by other cost items. However, the process using Du Pont Canada's patented reactor should give a product with better color and less branching in the structure, because of the shorter residence time in the reactors. For fiber use at least, this is advantageous.

Table 5.14

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

CAPITAL INVESTMENT													
	Total			Nylon Salt			Polycondensation			HMDA Recovery			
	Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent		
		Up	Down		Up	Down		Up	Down		Up	Down	
Battery limits equipment, f.o.b.													
Reactors	\$ 300,800			\$ 9,100	0.48	0.48	\$ 300,800	0.95	0.83	\$ 115,400	0.37	0.36	
Vessels and tanks	227,300			21,000	0.53	0.46	102,800	0.92	0.31	3,200	0.60	0.60	
Exchangers	49,300						28,300	0.43	0.36				
Furnaces	83,200						83,200	0.79	0.79				
Special equipment	192,000			166,400	0.68	0.68	19,200	0.95	0.60	6,400	0.90	0.90	
Miscellaneous equipment	44,800			6,400	0.60	0.60	35,200	0.61	0.61	3,200	0.60	0.60	
Pumps	<u>128,300</u>			<u>25,300</u>	0.34	0.27	<u>78,800</u>	0.20	0.17	<u>24,200</u>	0.15	0.11	
Total	\$ 1,025,700	0.71	0.56	\$ 228,200	0.62	0.60	\$ 648,300	0.81	0.60	\$ 149,200	0.37	0.34	
BATTERY LIMITS INVESTMENT	\$ 3,474,000	0.63	0.50	\$ 871,000	0.56	0.54	\$ 2,159,000	0.72	0.53	\$ 444,000	0.30	0.27	
Off-sites													
Cooling tower	\$ 348,000			\$ 249,700	0.51	0.38	\$ 98,300	0.51	0.38	\$ 400	1.36	0.04	
Process water treatment	4,800										4,400	0.62	0.78
Steam generation	153,700			153,700	0.82	0.82				59,500	0.43	0.29	
Inert gas	39,500												
Utilities and tankage investment	\$ 679,000	0.59	0.48	\$ 484,000	0.64	0.53	\$ 190,000	0.48	0.34	\$ 5,000	0.62	0.78	
General service facilities	831,000												
Waste treatment	<u>346,000</u>												
OFF-SITES INVESTMENT	\$ 1,856,000	0.59	0.48										
TOTAL FIXED CAPITAL	\$ 5,330,000	0.64	0.50										
Start-up costs	\$ 1,864,000												
Working capital	<u>\$ 4,384,000</u>												
TOTAL CAPITAL INVESTMENT	\$11,578,000												

Table 5.15

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

PRODUCTION COSTS			
Plant Capacity: 50 Million lb/yr (23,000 Metric Tons/yr) Nylon 66 Melt at 0.90 Stream Factor PEP Cost Index: 320			
	Unit Cost	Consumption/lb	¢/lb
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Nylon salt	49.5¢/lb	1.146 lb	56.73
HMDA	55.5¢/lb	0.00882 lb	0.49
Adipic acid	38.3¢/lb	0.01041 lb	0.40
Acetic acid	20.7¢/lb	0.00174 lb	0.04
Gross raw material cost			57.66
Utilities			
Cooling water	4.5¢/1,000 gal	18.5 gal	0.08
Steam	\$5.00/1,000 lb	1.1 lb	0.55
Process water	\$1.10/1,000 gal	0.114 gal	0.01
Electricity	2.65¢/kwh	0.01 kwh	0.03
Fuel oil	\$3.30/million Btu	1,761 Btu	0.58
Inert gas, high pressure	80¢/1,000 scf	0.189 scf	0.02
Total utilities			1.27
Labor			
Operating, 3 men/shift	\$14.20/hr	0.0005 man-hr	0.75
Costs by Section (thousand \$/yr) <u>100 Section</u> <u>200 Section</u> <u>300 Section</u>			
Labor			
Operating	62	187	124
Maintenance	26	65	13
Control laboratory	<u>12</u>	<u>37</u>	<u>25</u>
Total labor	100	289	162
Materials			
Nylon salt	28,364		
HMDA	245		
Adipic acid	199		
Acetic acid		18	
Maintenance	26	65	13
Operating	<u>6</u>	<u>19</u>	<u>12</u>
Total materials	28,840	102	25
Utilities			
Cooling water	30	11	
Steam	276		
Process water		1	6
Electricity	5	7	1
Fuel oil		291	
Inert gas, high pressure		<u>8</u>	
Total utilities	311	318	7

Table 5.15 (Concluded)

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR**PRODUCTION COSTS**

**Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Nylon 66 Melt
 at 0.90 Stream Factor
 PEP Cost Index: 320**

	<u>Million lb/yr</u>		
	<u>25</u>	<u>50*</u>	<u>100</u>
Investment (\$ million)			
Battery limits	2.5	3.5	5.4
Off-sites	<u>1.3</u>	<u>1.8</u>	<u>2.9</u>
Total fixed capital	3.8	5.3	8.3
Scaling exponents	0.50	0.64	
Production costs (¢/lb)			
Raw materials	57.66	57.66	57.66
Utilities	1.27	1.27	1.27
Maintenance materials, 3%/yr of BL cost	0.30	0.21	0.16
Operating supplies, 10% operating labor	<u>0.15</u>	<u>0.07</u>	<u>0.04</u>
Variable costs	59.38	59.21	59.13
Operating labor	1.49	0.75	0.37
Maintenance labor, 3%/yr of BL cost	0.30	0.21	0.16
Control laboratory, 20% operating labor	<u>0.30</u>	<u>0.15</u>	<u>0.07</u>
Total direct costs	61.47	60.32	59.73
Plant overhead, 80% of total labor	1.67	0.88	0.49
Taxes and insurance, 2%/yr of fixed capital	0.30	0.21	0.17
Depreciation, 10%/yr of fixed capital	1.51	1.07	0.83
Interest on working capital, 10%/yr	<u>0.92</u>	<u>0.88</u>	<u>0.85</u>
Plant gate cost	65.87	63.36	62.07
G&A, sales, research, % of fixed capital	<u>negl</u>	<u>negl</u>	<u>negl</u>
NET PRODUCTION COST	65.87	63.36	62.07
25%/yr return on fixed capital, before taxes	<u>3.80</u>	<u>2.65</u>	<u>2.07</u>
PRODUCT VALUE	69.67	66.01	64.14

*Base case.

Production of Different Grades

The processes as described above and based on reaction conditions in Tables 5.4 and 5.10 give a product with a relative viscosity of 40 to 45, which is suitable for making textile and carpet fibers. For making molding resins used in injection molding, the relative viscosity should be 50 to 55. This can be achieved by either increasing the residence time or increasing the vacuum in R-203.

If the end product is tire cord or extrusion moldings, the nylon 66 should have a relative viscosity in the range of 80 to 110. To achieve such a high degree of polymerization by extending the reaction time in R-203 would be impractical. In this case, one of the following three methods can be used:

- The temperature of R-203 is increased to 280°C. There is danger of gel formation in this approach. A remedy is to add formic acid vapor over the surface of the melt in R-203 (71528).
- The melt from R-203 is reacted further in a twin-screw extruder under nitrogen at 290 to 300°C for 1 to 10 minutes (70716), or, the solid resin or chips can be extruded in such a reactor.
- The solid resin or chips are heated under nitrogen at 250°C for 3 to 5 hours (70608). The time can be shortened if the resin or chips contain phosphoric acid (388734).

Batch Polymerization

The two processes evaluated above are continuous. A batch polymerization process can also be used. At the prescribed capacity of 50 million lb/yr, it would be necessary to use eight reactors of about 1,800 gal capacity each. An estimate shows that the investment would be higher, and more labor would be required. If the production capacity is one-fourth of the above, i.e., about 12.5 million lb/yr, the use of two batch reactors instead of the three successive reactors used in the continuous process would decrease the capital investment.

The Recycling of Wastewater

Reference 462215, a Du Pont Deutschland patent, advocates the use of the wastewater formed in the polycondensation for preparing nylon salt. If this procedure is used, the whole section 300 of Figure 5.2 can be omitted; the process water used in nylon salt would be reduced to the amount for makeup. A calculation shows that in using this way of recycling of wastewater, there would be a lowering of product value by the following amounts:

1.8¢/lb for a 25 million lb/yr operation

1.0¢/lb for a 50 million lb/yr operation

0.6¢/lb for a 100 million lb/yr operation

However, the above is based on an assumption that, aside from the savings due to the recycling, everything will remain the same. In reality, in order that the recycling would not cause accumulation of impurities in the system leading to undesirable consequences such as gelling of polycondensation equipment, the HMDA should have a very high purity, which would make it more expensive. If the unit price of HMDA is increased by 2%-6% because of its high purity (this range corresponds to the operation capacity), any cost advantage due to recycling would be wiped out.

6 NYLON RESINS AND CHIPS

The nylon 66 melt obtained by polycondensation, as described in Section 5, is not a product. It is not even an intermediate, in the sense that it is never stored for any significant length of time. It is either immediately extruded to form molding resins or spinning chips, or directly transferred by a gear pump for spinning. When a batch process is used for polycondensation, direct spinning is out of the question, and resins or chips are always made. The spinning will be discussed in Section 7. This section deals with the formation of resin or chips.

Review of Processes

Substances are added to nylon 66 to convey certain desirable properties to the final molded products or fibers, viz.:

- Stable against heat, oxygen, light, or weather (for fiber and molding resin).
- Antistatic (for fiber).
- Flame retardant (for both fiber and molding resin, but more often for fiber).
- Easier or faster to mold (for molding resin).
- Easier to dye (for fiber).
- Soil hiding (for carpet fiber).
- Improved mechanical properties (for molding resin).

A quite comprehensive collection of patents on additives were presented in PEP Report 54. Patents received by SRI after the issue of Report 54 are summarized here in Tables 6.1 through 6.4. Table 6.1 lists patents related to additives introduced during polycondensation, mainly for resin. Table 6.2 lists patents related to stabilizers added during polycondensation, mainly for fiber. Table 6.3 lists patents related to other kinds of additives to fiber, also introduced during polycondensation. Table 6.4 lists patents related to additives to solid resins that are extruded again to form pellets for molding. In Table 6.4, the

Table 6.1
ADDITIVES TO NYLON 66 DURING POLYCONDENSATION, MAINLY FOR RESIN
PATENT SUMMARY

Reference No.	Assignee	Priority Date	Additive	Purpose
71923	Inventa	3/27/58	Cupric chloride plus organic quaternary ammonium iodide	Stabilization against heat
389688	Toray	12/14/66	Caprolactam, 0.1%-1.5%	Stabilization against heat better than plain nylon 66
71563	Celanese	6/12/67	Iodoform; may be in combination with a copper compound	Stabilization against heat and atmospheric oxidation
388390	Snaia Viscosa	3/6/69	Allyl chloride 0.02%-0.2% plus p copper 30-150 ppm as copper salt	Stabilization against discoloration
71551	Ciba-Geigy	5/19/69	Bis-(hindered phenol)-alkylene diphosphonate and phosphonacetate	Stabilization against oxidation degradation (less color development and weight loss)
71622	Teijin	6/25/69	Triphenylphosphine oxide, 5%-20%; antimony oxide, 1%-5%	Flame-retardation
388175	Celanese	3/17/70	1,4-Diaminocyclohexane adipate, 0%-1%	Lower residual volatile matter at same relative viscosity
389561	Ciba-Geigy	12/7/70	1,3-bis[3(3,5-di-tertbutylhydroxyphenyl)propionamido]ethane plus sodium hypophosphite	Stabilization against heat (less color development and weight loss)
71552	ICI	1/18/71	Calcium fluoride (plus alkylene diamine and zinc stearate added to resin)	Fast cycling
71550	Ciba-Geigy	4/12/71	Triethyl-bis(3,5-di-tertiary butyl-4-hydroxybenzyl)-phosphonacetate	Stabilization against thermal and oxidative degradation (less color development and weight loss)
71974	Foster Grant	6/12/75	Low mol wt polybutadiene and a dimerized fatty acid	High impact
71618	BASF	10/14/75	Ester of an aliphatic alcohol with 4-10 C atoms	Film made from nylon is of uniform transparency and thickness
462056	BASF	5/20/76	Phenyl hydrazine, 0.01%-5%	Stabilization against heat, oxygen, and radiation
71671	Snaia Viscosa	1/22/76	Alkylene dicarbonate, 0.4%-0.9%	Increasing relative viscosity--for making extrusion grade resin
71773	BASF	1/26/77	Red phosphorus plus an aluminum salt of nitrilo-triacetic acid	Flame proofing
71921	Ciba-Geigy	5/9/77	Halogenated dicarboxylic acid derivative of symmetrical triazines	Flame proofing
462143	Mitsubishi Gas Chem.	10/8/77	Hydrazine	Stabilization
462248	BASF	11/30/77	Brominated styrene oligomer	Flame-retardant

Note: See also 71952 in Table 6.4.

Table 6.2
STABILIZERS FOR NYLON 66 MAINLY FOR FIBERS, ADDED DURING POLYCONDENSATION

PATENT SUMMARY				
Reference No.	Assignee	Priority Date	Additive	Purpose
392560	Inventa	6/29/60	Cu-acetate plus benzyltrimethylammonium iodide	Stabilization against heat
71583	Yamaura, S.	6/28/66	p-MeC ₆ H ₄ SO ₃ Na or PhSO ₃ NH ₂	Stabilization against thermal deterioration, especially in molten state (less gelling or less increase of amino-end groups, hence less breaking in spinning)
71582	Unitika	8/16/66	Mg salt of mono- or diester of phosphorous acid	Same as 71583
71584	Unitika	8/29/66	Mg-diphenyl phosphate or Mg-diethyl phosphate	Same as 71583
392600	Unitika	4/28/67	Phenylguanidine-sulfite adduct plus a Mn salt	Stabilization against light and heat; improved whiteness and dyeability toward acid dyes
71786	ICI	8/19/67	(8(4-hydroxy-3,5-tert-butylphenyl) propionic acid plus diethyl phosphate	Stabilization against heat or light
71586	Unitika	11/30/67	Ba salts of mono- or diesters of orthophosphoric acid or phosphorous acid	Stabilization against thermal deterioration, especially in molten state
71587	Unitika	11/30/67	Cupric or cuprous salts of mono- or diesters of orthophosphoric acid	Same as 71586
71992	ICI	4/13/70	TiO ₂ coated with Mn-phosphate plus NaH ₂ PO ₄ plus a phenol	Stabilization against heat and light
420400	Ciba-Geigy	12/7/70	1,2-bis[3,5-di-t-butyl-4-hydroxy-phenyl] propionamido] ethane	Stabilization against oxidative and thermal degradation
420399	Ciba-Geigy	12/7/70	Above phenyl plus Mn-acetate plus phenylphosphonic acid	Stabilization against light and heat
462036	Bayer	12/23/70	Tetraphenyl copper phthalocyanine plus colloidally dispersed red iron oxide	Nonweathered green color
71553	Monsanto	7/3/72	400-600 ppm Cu in dissolved form plus 0.4%-2.2% inorganic halide	Stabilization against radiation and weathering (as synthetic turf)
462153	Hurt, V., et al.	9/26/73	CuCl ₂ plus 2-mercaptobenzimidazole	Stabilization against heat and light
71961	ICI	11/30/73	Sterically hindered phenol plus reducing P compound and a S compound as thiadipropionate	Stabilization against heat, oxygen, and light
71615	Allied Chemical	1/30/74	2-Mercaptobenzimidazole copper salt plus 8-hydroxyquinoline Mg salt	Stabilization against heat
71619	Soc. Viscose Suisse	5/24/74	1,6-Bis(3,5-di-tert-butyl-4-hydroxy-phenoxy) hexane or similar compounds	Stabilization against thermal and oxidative deterioration (reduce loss of strength on heating in air)
71531	ICI	7/5/74	Triphenylsilane or triethylaminoborane, plus tris (methyl-hydroxybutylphenyl)-butane	Stabilization against heat during the treating of fiber or fabrics
71533	Du Pont	7/31/74	Copper nitrate plus potassium iodide plus potassium phenylphosphinate	Stabilization against heat and oxidation. Less copper loss by using nitrate instead of acetate.
71536	Du Pont	7/31/74	Copper salt plus KBr/KI plus potassium phenylphosphinate, with KBr:KI ratio >0.33	Stabilization against heat and oxidation. Less copper loss by using KBr/KI at prescribed ratio.
462007	Du Pont	11/10/75	Copper salt plus KI plus hexamethylene diammonium phenylphosphonate	Stabilization against heat and light; acid dyeability
71767	Allied Chemical	1/10/77	Cupric dichlorobispyridine or cupric dichloro-bisquinoline	Stabilization against thermal-oxidative degradation

Note: See also Table 6.1; 71999 of Table 6.3; and 71550, 71551, 71563, 71923, 389561, 389688.

Table 6.3
ADDITIVES TO NYLON 66 FOR FIBERS, INTRODUCED DURING POLYCONDENSATION
(OTHER THAN STABILIZERS)

PATENT SUMMARY				
Reference No.	Assignee	Priority Date	Additive	Purpose
71887	British Nylon Spinners	6/9/64	Triphenyl carboxyalkyl phosphonium halide	Increased dyeability; also stabilizes the viscosity
71792	Monsanto	9/10/64	N-(2-aminoethyl) piperazine, 0.38%; caprolactam, 3%	Improved dyeability
462167	Hoechst	9/26/64	N-alkyl phosphoric acid amide, 0.2%-0.4%	Antistatic
71999	ICI	6/23/65	Phosphonic acid salt of an organic diamine	Improved dyeability and thermal stability
71842	Toyo Spinning	10/21/65	A polyamide made from bis(2-aminoethyl) ester and adipic acid, up to 40%	Moisture retentive
462174	Du Pont	4/3/67	Polyalkylene ether, 2%	Antistatic
71785	Toyo Rayon	5/27/67	Polyethylene oxide, 3%	Antistatic
71864	Soc. Rhodiaceta	6/27/67	K-hydroquinosulfonate or Na-pyrocatecholsulfonate, 0.5%	Increased dyeability with basic dyes
71866	ICI	2/13/68	HMDA plus Cu-phenylphosphinate plus KI plus MOAc	High tenacity; suitable for tire cord
71789	ICI	4/18/68	Titanium dioxide or other pigment in water containing 1% diethanolamine (based on TiO ₂)	Even distribution of pigment
462023	Toray and Sanyo	4/25/68	Phosphoric ester of an addition product of a carbonamide compound and an alkylene oxide	Antistatic
388222	ICI	5/14/68	Phosphonamide, 25 ppm (as P)	Antistatic
71981	Monsanto	7/9/68	Trimethylolpropane monoalkylether	Improved acid dyeability
388270	ICI	10/28/68	Dimethylisophthalate or similar ester, 0.9%-1.3%	Increases the relative viscosity without increasing the cross-linking; yarn tenacity increased
462199	Kanegafuchi	4/24/69	Polyethylene glycol diisocyanate	Antistatic
462066	Teijin	5/13/69	Biphenylsulfonic acid derivatives	Good affinity to basic dyes
71589	Teijin	6/2/69	Cetylpalminate, 0.2%, added to a molten nylon which has amine end group <25%	Better tenacity after drawing
462072	Asahi Chemical	6/27/69	Polyethylene glycol derivative plus copper salt	Antistatic and heat stable
71606	ICI	7/17/69	Tetraethyltitannate	Improved dyeability
388556	Teijin	8/14/69	Chlorinated triphenyl, 2%-15%, plus alkylamine-alkylene oxide (10%-30% on chlorinated triphenyl)	Flame-resistant
71983	Soc. Rhodiaceta	8/22/69	Allyl alcohol plus PO plus EO, then polymerized	Antistatic
71840	Hoechst	8/20/69	Cycloaliphatic or aromatic polyamine	Improved dyeability
392576	Monsanto	5/11/70	Tertiary alkylpolyoxymethylene amine, 4%-6%	Antistatic
71734	Du Pont	7/15/70	p-Aminobenzoic acid dimer, 4%	Higher tenacity
462078	Toray	8/15/70	Sericite powder	Lower dynamic friction
462082	Toray	10/18/70	Phosphorous ester	Prevent thermodegradation at spinnerets and therefore less fiber breakage
462098	Asahi Chemical	12/22/70	Oligometric triazine derivative	Improved dyeability
71989	Fiber Industries	1/7/72	Sulfoaryloxycarboxylic acid or salt	Basic dyeability
462087	Asahi Chemical	3/24/72	p-Phenylen bis(p-sulfobenzoate) di Na-salt	Improved dyeability to basic dyes
71779	Allied Chemical	3/29/72	A reaction product of polyetherpolyol from ethylenediamine and dimethylterephthalate	Antistatic (carpet yarn)
462029	Snia Viscosa	3/31/72	Polyethylene glycol with average mol wt of 20,000 and a narrow mol wt distribution	Durable antistatic property
462091	Asahi Chemical	4/11/72	2-Diethylaminol ethanol and propylenediamine	Improved dyeability to acid dyes and direct dyes
71740	Snia Viscosa	4/15/72	Polyoxyethylenated omega-aminodecanoic acid or polyoxyethylenated sulfanilic acid	Antistatic
388015	Allied Chemical	5/30/72	Tetrol from ethylenediamine plus hindered phenol	Antistatic
71993	Allied Chemical	7/12/72	Tetrol from ethylenediamine plus diepoxyde	Antistatic
71672	Allied Chemical	10/11/72	Tetrol from ethylenediamine, extended by diisocyanate	Antistatic
71973	Bayer	12/2/72	A polycondensate of dimethyladipate, octadecane-1, 12-diol, and N-methylidiaminopropane with addition of hypophosphorous acid	Antistatic

Table 6.3 (Concluded)

ADDITIVES TO NYLON 66 FOR FIBERS, INTRODUCED DURING POLYCONDENSATION
(OTHER THAN STABILIZERS)

PATENT SUMMARY				
Reference No.	Assignee	Priority Date	Additive	Purpose
462090	Asahi Chemical	4/11/72	Triethanolamine	Improved dyeability to acid dyes and direct dyes
462044	Inventa	5/2/73	Small amounts of Pb, Zn, or La compounds	Permit identification of particular polyamide batch
71985	Phillips Petroleum	6/14/73	Alkali metal salt of aminobenzenesulfonic acid	Improved acid and basic dyeability
462039	Sandoz	8/10/73	$R-N-\overset{\text{H}}{\underset{\text{CH}_2\text{CH}_2\text{O}}{\text{CH}_2\text{CH}_2\text{CH}_2\text{N}}} \text{H}$ $\text{H} \quad \text{H}$ $\text{CH}_2\text{CH}_2\text{O} \quad \text{CH}_2\text{CH}_2\text{O}$	Antistatic
71994	Allied Chemical	10/18/73	PO-EO-ethylene diamine copolymer plus hindered phenol	Antistatic
71647	Allied Chemical	10/23/73	Tetrol from ethylenediamine, extended by diisocyanate, plus hindered phenol	Antistatic
71670	Asahi Chemical	12/26/73	$\text{HO}(\text{CH}_2)_n\text{OOCCH}_2\text{H}_3 (\text{SO}_3\text{MCO}(\text{CH}_2)_n\text{OH}$, the substitution on benzene ring is 1,3,5 position	Improved dyeability by basic dyes
462124	Sumitomo Chemical	2/4/74	Aromatic phosphite plus pyridine	?
71988	Allied Chemical	2/15/74	PO-EO-triethylene diamine copolymer plus hindered phenol	Antistatic
462127	Sumitomo Chemical	4/26/74	Phosphorus compound RR'POAr and a tertiary amine	?
71940	Allied Chemical	5/10/74	A polyether based on EO, PO, and diamine, and methylene-bis-cyclohexylidene diisocyanate	Antistatic
462203	Allied Chemical	8/5/74	Tetrol from an diamine and polyoxyalkylene oxide	Antistatic
71995	Allied Chemical	8/5/74	Poly-PO-EO on a diamine plus diepoxide plus hindered phenol	Antistatic
71659	Fiber Industries	9/12/74	Sulfoaryloxy carboxylic acid or salt	Improved dyeability by acid dyes
71998	Du Pont	9/26/74	$\text{N},\text{N}'\text{-di(3-aminopropyl) piperazine}$ plus adipic acid	Deep acid dyeability
71547	Bayer	4/30/75	Polyetherurethane, made from ethylene oxide, glycol carbonate, and N-methylstearylamine	Antistatic
71968	Monsanto	7/22/75	Salt of bis(β -carboxyethyl) methylphosphine oxide and HMDA	Antistatic, moisture transport, moisture regain and flame resistant
71753	Phillips Fibers	3/2/76	A reaction product of a block copolymer of propylene oxide, ethylene oxide, and ethylene diamine and a dicarboxylic acid ester	Antistatic
71741	Du Pont	9/17/76	Titanium dioxide dispersed in tetrasodium pyrophosphate	Used as sheath of conductive filament
71766	Allied Chemical	3/30/76	Li salt of sulfonated polystyrene-methyl acrylate	Improved dyeability, with light-fastness and ozone resistance
71761	Allied Chemical	1/26/77	Li, Mg, or Ca salt of a sulfonated polystyrene	Same as 71766
71763	ICI	5/25/77	A derivative of boric acid and polyoxyalkylene	Soil hiding (carpet yarn)

Note: See also reference 462243 in Table 6.4.

Table 6.4
ADDITIVES TO NYLON 66 RESIN TO FORM MOLDING COMPOUNDS
PATENT SUMMARY

Reference No.	Assignee	Priority Date	Additive	Purpose
462020	American Enka	11/4/57	Tumbled first with wax and then with pigment	Coloring
392559	Hoechst	7/28/62	BuO ₂ CCON(C ₁₈ H ₃₇) ₂	Antistatic
392568	Sanyo Chemical	12/23/63	A polymer made from polypropylene and stearyl-amine-HCl and lauryl tetrapropylene glycol phosphate	Antistatic
71527	Du Pont	9/1/65	Halide of Zn, Cd, Pb, or rare earth, 3%-15%, plus 1%-5% copper oxide	Flame resistant
392580	Toyo Rayon	12/14/65	Trichloroethylene	Increase melt viscosity
71948	ICI	5/26/66	Cyclohexylphosphoric acid	Increase mol wt
462046	BASF	11/9/66	Hydrazodicarboxylic acid ester of an acyl derivative of hydrazine	Improved processibility in injection molding
366974	Du Pont	8/7/70	Lead borate plus chlorinated terphenyl	Flame retardant
71593	Toray	11/24/70	Hexabromobenzene plus K ₂ Cr ₂ O ₇	Flame retardant
462083	Toray	11/30/70	Polyamide cross-linked with acrylic acid, and blended with brominated hydrocarbon	Flame retardant
462097	Toray	5/9/72	CaCl ₂ plus water	Impact-resistant
462100	Asahi Chemical	6/2/72	Polyethylene glycol and aluminum stearate	Injection moldability improved
462101	Asahi Chemical	6/2/72	Mineral oil and calcium stearate	Injection moldability improved
71960	Firestone Tire and Rubber	1/22/73	Hexabromobenzene plus Sb ₂ O ₃	Flame retardant
71532	BASF	2/24/73	Acid esters of 2,6-di-t-butylphenol butanol	Stabilization against heat and oxidation
71959	Allied Chemical	3/5/73	Red phosphorus (dry blended with resin, and aged at 170°C)	Flame retardant
71951	ICI	5/14/73	Resin already containing cyclohexylphosphoric acid is coated with Zn-stearate	Nucleation (shorten the injection cycle)
71737	Monsanto	9/5/73	1,2-Dimethyl-1,2-diethylbiphosphine disulfide	Flame-resistant
71621	Dynamit Nobel	11/14/73	Tris-halophenoxy-1,3,5-triazine	Flame-resistant
462026	Du Pont	1/23/74	Zn- or Mg-ferrite and organic halide	Flame-resistant
71950	Muanyagipari Kutato Intezet	3/19/74	CrCl ₃ solution	Increase melt viscosity
71538	BASF	6/14/74	2,6-Dibutyl-p-cresol plus n-dodecylmercaptan	Stabilizes against heat
462117	Toray	10/2/74	Cyanuric acid, cyanurate or isocyanurate	Flame-resistant
462053	Hoechst	10/7/74	Alkali salt of a phosphonic, diphasphonic, or triphosphinic acid plus an amine	Flame retardant
462235	Toray	11/7/74	Melamine and trimethyl cyanurate	Flame retardant
71617	Monsanto	12/20/74	Ferric chloride plus Dechlorane® 25 (a chlorinated alicyclic compound) plus Betanox® (an antioxidant, a condensation product of phenyl β-naphthylamine and acetone) plus a plasticizer (such as DOP)	Flame retardant, and not brittle
71952	Rhone-Poulenc	2/14/75	Copper stearate plus KI plus 2,2-dimethyl-1,3-propanediol	Heat stabilizer
71616	Monsanto	3/3/75	C ₁₂ to C ₂₀ aliphatic alcohol plus an aluminum salt of C ₁₂ to C ₂₀ fatty acid	Flame retardant and good mold release characteristics
462052	Hoechst	3/14/75	Similar to 462053	
462055	Rhone-Poulenc	6/10/75	Red phosphorus plus a polyamide from trimellitic anhydride and MDI	Flame-resistant
462246	BASF	7/8/75	Diels-Alder addition product from hexachlorocyclopentadiene and cyclooctadiene, plus antimony sesquioxide plus kaolin or talc	Flame-resistant
462245	Rhone-Poulenc	8/27/75	Zinc borate plus antimony trioxide plus filler	Flame-resistant
462130	Unitika	8/27/75	Melamine sulfate	Flame-resistant
462132	Unitika	9/5/75	Isocyanuric acid	Flame-resistant
462133	Unitika	9/10/75	Isocyanuric and premelt blended with nylon	Flame-resistant
71573	BASF	9/25/75	A concentrate of nylon containing CuBr or CuI and bromide of Ca, Zn, or Mg; nylon 66 is to be blended with this concentrate	Stabilization against light and heat
462134	Mitsubishi Gas Chemical	9/26/75	Condensation product of formaldehyde and tetrachloroisophthalonitrile	Fire-retardant
462135	Asahi Chemical	9/30/75	Aminopurine compound	Fire-retardant
462241	ICI	6/21/76	A master batch of polyamide and organic halogen compound and zinc borate	Fire-retardant

Table 6.4 (Concluded)

ADDITIVES TO NYLON 66 RESIN TO FORM MOLDING COMPOUNDS

PATENT SUMMARY

Reference No.	Assignee	Priority Date	Additive	Purpose
462243	Akzo	6/28/76	Metallic oxalato-complex	Flame retardant
71748	Emery	9/7/76	A polyamide from HMDA and dimer acid, plus zinc stearate	Improve flow characteristics
71759	BASF	9/13/76	Hexachlorocyclopentadiene plus cyclooctadiene plus ZnO	Flameproof
71762	Monsanto	11/19/76	Flame-retardant and a plasticizer (adipate ester or fatty acid ester of pentaerythritol)	Embrittlement due to addition of flame retardant compensated for by the plasticizer
462058	Rhone-Poulenc	11/29/76	Zinc borate plus antimony oxide and halogenated compound	Flame-resistant
462057	BASF	1/28/77	Brominated styrene oligomer plus metal oxide	Flame-resistant
462148	Ube	4/27/77	A carboxylic acid having boiling point higher than the melting point of the polyamide	Flame-resistant
462238, 462239	Rhone-Poulenc	10/11/76	Halogenated compound plus cadmium oxide	Flame-retardant
71862	Bayer	7/28/77	Phenol-formaldehyde resin and red phosphorus, 0.5%-25%	Flame retardant
462151	Velsicol Chemical	1/3/78	Br-substituted polyoxyphenylene plus antimony oxide	Flame-resistant

additives are flame retardants, stabilizers, and agents for improving processibility. In addition, there are fibrous or mineral additives to improve the mechanical properties. They are added in very substantial proportions (30% to 40% additives, 60% to 70% nylon). Such nylon is called reinforced nylon and falls into the scope of PEP Report 48; hence these additives are not included in Table 6.4.

It should be noted that any additive incorporated into nylon to improve a certain property often exerts other effects, which may be favorable or unfavorable. Thus, titanium dioxide added as pigment decreases the light stability (71714). Boron compounds added for soil hiding, and phosphorus compounds added for dyeability increase the melt viscosity of nylon (71874). Polyols added for antistatic effect may cause the formation of nubs in filaments on spinning. Flame-resistant additives generally cause a significant loss of mechanical strength.

In converting nylon melt to chips, pelletizing devices are needed. Table 6.5 lists some patents on pelletizing, as well as other related physical operations. In addition to the band type pelletizer described in the patents in Table 6.5, there are centrifugal type underwater pelletizers and water-ring pelletizers (71631).

Nylon 66 for different uses requires different degrees of polycondensation, represented by molecular weight, and often analytically determined by relative viscosity. Nylon 66 for textile fiber generally has a relative viscosity of 30 to 50 (8.4% in 90% formic acid) corresponding to a number average molecular weight of 11,000 to 18,000. Nylon 66 for injection molding generally has a relative viscosity of 40 to 70, corresponding to a number average molecular weight of 12,000 to 22,000. These two grades can be made in the conventional polycondensation facilities by modifying the temperature and duration of the final finishing stage of polycondensation. High tenacity nylon 66 for spinning into tire cord needs to have a relative viscosity of 60 to 100, corresponding to molecular weight of 19,000 to 25,000. Extrusion molding nylon 66 resin needs a relative viscosity of 80 to 110, corresponding to molecular weight of 24,000 to 29,000. For increasing the molecular weight, the following

means can be taken: (1) heating the nylon melt after the introduction of a specified additive, (2) heating a blend of the nylon 66 melt and an additive, (3) heating the nylon melt in the presence of a specified vapor (formic acid), (4) heating the nylon in solid state above 200°C for a prolonged time, (5) maserating nylon melts in a shear-causing machine, such as a twin-screw extruder. Table 6.6 lists patents received at SRI after the issue of PEP Report 54 on processes for increasing molecular weight. (Some useful and important patents were summarized in Report 54.)

It should be noted that nylon 66 for spinning should have a minimum of cross-linking; and the molecular weight of high tenacity nylon should be increased without undue increase of cross-linking. In the case of molding resin, some degree of cross-linking is allowable and even desirable. Hence some means of increasing molecular weight, such as (4) and (5) are not suitable for making high tenacity nylon, only for making extrusion grade molding.

Table 6.7 lists patents on treatment of nylon resins or chips. Table 6.8 lists some of the patents on blends or copolymers for resin use. Those for fiber use will be described in Section 7.

Many patents in these tables deal with polyamides, and the subject polyamides in the patent examples are nylon 6. But we believe that the examples should be equally applicable to nylon 66.

Table 6.5
PELLETIZING AND OTHER PHYSICAL OPERATIONS ON CHIPS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
A. Pelletizing		
71982	Allied Chemical	9/27/57
	Ribbon protruded from reactor is quenched in a tank, transported through a chute, and cut by rotating knives.	
462226	Du Pont	6/2/64
	Ribbon extruded from the reactor is cooled and cut.	
392204	Toyo Spinning	1/18/69
	Strands from extruder with 1-4 mm diameter are cooled in water or other refrigerant, blown with compressed gas to reduce water, and cut to chips; water content can be reduced to 0.1%.	
462093	Asahi Chemical	9/16/69
	Strands from the reactor are conveyed on a belt to a pelletizer in an inert atmosphere.	
462144	Teijin	10/3/77
	Strands extruded under pressurized gas are cooled by water in an inclined chute and then cut by knives.	
71537	Japan Steel	4/3/72
	Cutting the strands immediately at the front of exit of dyes in water.	
71540	Monsanto	7/28/75
	The positioning of bushings around the cutters.	
B. Other operations		
71590	Toray	6/3/69
	Cooling and drying of nylon 66 pellets by water spraying, inert gas blowing, and vacuum drawing.	
71604	Asahi Chemical	9/27/72
	Heating the chips and rapidly cooling to 40-70°C; powders do not adhere to chips and can be removed by sieving.	
71546	BASF	7/8/75
	Chips are dried by allowing them to flow down in a vertical column in hot inert gas.	

Note: Refer to a Werner Pfeider pamphlet for the water-ring pelletizers (71631).

Table 6.6
PROCESSES FOR INCREASING MOLECULAR WEIGHT
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>	<u>Additives</u>	<u>Purpose</u>
388199	Burrows, H. G., et al.	6/15/65	Add 0.6% alkyl or aryl phosphoric acid to nylon 66; heat nylon 66 melt to 290°C for 10 minutes	For high tenacity spinning grade and extrusion molding
462034	Toray	3/19/69	Polyepoxy compound with terminal epoxy group and one to three vinylene epoxy groups	For extrusion molding
462018	ICI	2/4/72	Diaryl esters added to the nylon melt under nitrogen	For high tenacity spinning grade
388217	Du Pont	6/9/72	Nylon granules heated above 200°C and below mp in a plug-flow, gravity-conveyed zone	For extrusion molding
388734	Inventa	6/29/72	Postcondensation in solid state; phosphoric acid is preferably added during poly-condensation	For extrusion molding
71528	Du Pont	5/10/73	Molten nylon from the polycondensation finisher flows to another finisher blanketed by formic acid vapor	For high tenacity spinning grade
462050	Huels	12/12/74	Nylon melt blended with bisoxazoline derivative	For extrusion molding
462121	Tereda Cotton Spinning	6/2/75	Nylon is blended with Novolac (phenolic resin) and stearic acid, and extruded into pellets	For extrusion molding

Table 6.7

TREATMENT OF RESINS OR CHIPS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
387536	Toyo Rayon	1/17/59
	Resins are treated with an aqueous solution of Se, Cr, or Ag salts, and then irradiated and heated to give colored products.	
392204	Toyo Spinning	1/18/69
	Strands from extruder with 1-4 mm diameter are cooled in water or other refrigerant, blown with compressed gas to reduce water, and cut to chips; water content can be reduced to 0.1%.	
71784	Technochemie GmbH Verfahrenstechnik	5/20/69
	Nylon 66 resin is heated under pressure, and then undergoes an ultrasonic treatment or ionizing radiation; modulus is increased.	
71966	BASF	9/7/73
	Chips impregnated in an aqueous solution of a dye (1-amino-4-arylaminoanthraquinone-2-sulfuric acid); dye is exhaustively absorbed to form a blue-tinted chip.	

Note: For increasing mol wt of resins by solid-phase polymerization, see Table 8.1.

Table 6.8

NYLON 66 COPOLYMERS OR BLENDS AS RESINS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
A. Copolymers		
391097	Toyo Spinning	10/20/65
	A copolymer of nylon 66 and a salt from adipic acid and bis(α -aminopropoxy)ethane; water retentive.	
391850	Asahi Chemical	3/17/67
	Nylon 66 and nylon 6 mixture is melt at 200°C to give block copolymer.	
462084	Unitika	8/11/70
	A copolymer of nylon 66 and nylon 6; good processibility in injection molding.	
462035	Foster Grant	5/27/71
	A copolymer of nylon 66 and a salt made from aliphatic diacid and aliphatic diamine both with high C numbers (30 to 40); product used in tubing in automobiles.	
462059	Hoechst	8/12/72
	A copolymer made from diamines, dicarboxylic acids, and lactams.	
462145	Huels	9/24/75
	Polyester-polyamide by two stage polycondensation.	
462140	Mitsubishi Chem.	7/16/76
	Nylon copolymer produced by concentrating nylon salt solution in presence of lactams.	
B. Blends		
391990	ICI	5/19/69
	Blend of nylon, containing nucleating agent such as CaF ₂ , Na-phenylphosphinate, et al., a copolymer of ethylene, methacrylate, and hydroxyethyl methacrylate, and polyethylene or polystyrene; useful as molding compound.	
462037	Continental Can	3/18/71
	A blend of nylon and polyolefin.	
462037	ICI	11/27/72
	A blend of nylon, polyolefin, and a graft copolymer of maleic anhydride and propylene; compatibility improved between polyolefin and nylon.	
462042	BASF	7/23/74
	A blend of nylon, a rubbery graft copolymer (styrene and acrylonitrile on polyacrylate); higher impact strength.	
462116	Asahi Chemical	9/14/74
	Nylon 66, nylon 6, and nylon 12 are heated in a slight addition of triethyl phosphite to get a copolymer.	
71738	Du Pont	11/13/74
	Nylon, polyethylene, and a graft copolymer of ethylene and acrylic acid; useful for wire jacketing.	
71849	Allied Chemical	2/26/75
	A blend of nylon 6 and nylon 66 containing CuI and CuBr as stabilizer; used for making film.	
462146	Asahi Dow	4/3/75
	A blend of nylon 66 and polyethylene, with addition of 3-8 C carboxylic acid, its salt, and its ester; higher impact strength and dimensional stability.	
462150	Mitsubishi Gas Chemical	11/20/75
	A blend of nylon 66 and a nylon from xylenediamine and dicarboxylic acid; for molding.	
462240	Asahi Dow	12/27/75
	A blend of nylon 66 and ethyl acrylate-ethylene copolymer.	

Table 6.8 (Concluded)

NYLON 66 COPOLYMERS OR BLENDS AS RESINS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71758	Du Pont	6/10/76
	A blend of nylon, polyethylene, and a copolymer of ethylene and methacrylic acid neutralized with Zn or Cd; moldings made therefrom are tough and have high tensile strength; useful for wire jacketing.	
71946	Bayer	7/22/76
	A blend of nylon 66 and a copolymer of acrylonitrile and butadiene; high impact.	
71861	Bayer	3/3/77
	Blend of nylon 66 and nitrile rubber; moldings made therefrom have high impact strength.	
71943	Shell Oil	4/22/77
	Blend of polyamide, polyolefin, and a hydrogenated block copolymer of styrene-butadiene, useful as an engineering plastic.	
462237	Asahi Chemical	8/12/77
	A blend of nylon 66 and ethyl acrylate-ethylene copolymer.	

Manufacture of Nylon 66 Resin

Process Description

The design case is for production of 50 million lb/yr of nylon 66 resin. The base grade is injection grade, natural color. Part of the product can be converted to colored resin or to extrusion grade resin, or it can be blended with additives and extruded to form molding compounds. In the design, the capacity of each of these three conversions is assumed to be 30% of the total production.

The design is based on information compiled from references 70716, 71630, 71631, 366054. The flow sheet is shown in Figure 6.1 (foldout at end of report). The equipment list and utilities summary are given in Tables 6.9 and 6.10.

Figure 6.1 is a continuation of Figure 5.1 or 5.2. Nylon 66 melt from R-203 in Figure 5.1 or Figure 5.2 is extruded by a simple extruder, M-101, into strands. M-101 is only a driving mechanism (a short screw) and a nozzle die. The strands are cut by a rotary knife in a pelletizer into cylindrical pellets, which are thrown by centrifugal force to the ring of the pelletizer, where they are quenched and carried away by a stream of water. The water is removed first in preseparator M-103, and then in screen M-104. The water is collected in a shallow pan and then in a tank, and recycled. The wet nylon 66 resin pellets are elevated pneumatically to a feed bin and then enter a fluidized bed drier. A stream of nitrogen keeps the bed fluidized, and dries the pellets. The dry pellets overflow at the top of the drier to resin bin T-103. This product can be elevated to storage bins.

By carrying out the polycondensation by procedures as given in Section 5, with the reaction time in R-203 increased to 50 minutes, the nylon 66 resin produced would have a relative viscosity of 50 to 55, corresponding to a molecular weight of around 20,000. This is suitable for use in injection molding, which is the major fabrication method for nylon. There are some applications in which nylon articles are molded by extrusion. For this usage the nylon resin must have a relative viscosity of 80 to 110. The most convenient way of producing this grade is to

subject the injection grade resin to an aftertreatment, consisting of steps involving T-201 through T-204 in Figure 6.1. The resin from T-103 or from the storage bins (not shown) is pneumatically transferred to feed bin T-201, and then fed into extruder-reactor R-201. This is a twin-screw extruder, blanketed with nitrogen, heated by electricity, and cooled by cooling water in different sections. The construction and function of such extruders is described in references 70716 and 71957. In a residence time of 5 to 10 minutes, the molecular weight of nylon 66 resin is increased up to 30,000. The extrudate is then pelletized and dried by procedures similar to those described earlier.

Sometimes colored resins are needed either for the injection grade or extrusion grade. These are made by blending the proper grade of resin with pigments in blenders (M-205). Silicone oil is usually added to facilitate the coating of pigments on the pellets.

Some additives, notably flame retardants, are desirably added after the polycondensation (Table 6.4). Such additives may be introduced to compounding extruder S-201, to which nylon resin is also added. Alternatively, the addition may be blended and then fed into the extruder. The pellet formation is similar to that described before.

Off-grade resin, as well as degraded nylon recovered in cleaning of equipment in the polycondensation (Section 5), can be treated in a twin-screw extruder to upgrade it to a useful product (70716). This equipment is not shown on the flow sheet.

A machine should be provided for packing the resins into drums. This is also not shown on the flow sheet.

Table 6.9

NYLON 66 RESIN FROM MELT

MAJOR EQUIPMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Resin
 at 0.90 Stream Factor

Equipment Number	Name	Size	Material of Construction	Remarks
<u>Reactors</u>				
R-201	Extruder reactor	9 in. dia, L/D = 20	304 ss	Twin-screw, 110 hp.
<u>Size (bhp)</u>				
<u>Compressors</u>				
K-101	Air blower	10	Carbon steel	
K-102	Air blower	20	Carbon steel	
K-201	Air blower	6	Carbon steel	
K-202	Air blower	12	Carbon steel	
K-203	Air blower	12	Carbon steel	
K-204	Air L > FN9	6	Carbon steel	
K-205	Air blower	12	Carbon steel	
<u>Area (sq ft) Heat Load (million Btu/hr) Material of Construction</u>				
<u>Shell Tubes</u>				
<u>Exchangers</u>				
K-101	Heater	200	0.65	Carbon steel Carbon steel
K-201, 2	Heaters	50 ea	0.15 ea	Carbon steel Carbon steel
<u>Volume (gal) Material of Construction</u>				
<u>Tanks</u>				
T-101	Water tank	2,000	Carbon steel	
T-102	Feed bin	5,000	304 ss	
T-103	Resin bin	10,000	304 ss	
T-151A,B	Storage bins	60,000 ea	304 ss	Not shown on flow sheet.
T-201	Feed bin	1,500	304 ss	
T-202	Water tank	1,000	Carbon steel	
T-203	Feed bin	1,500	304 ss	
T-204	Resin bin	10,000	304 ss	
T-205	Feed bin	1,500	304 ss	
T-206A-C	Resin bins	5,000 ea	304 ss	
T-207	Feed bin	1,500	304 ss	
T-208A-C	Additive feed bins	500 ea	304 ss	
T-209	Water tank	1,000	Carbon steel	
T-210	Feed bin	1,500	304 ss	
T-211A-C	Resin bins	10,000 ea	304 ss	
T-251A-H	Storage bins	10,000 ea	304 ss	Not shown on flow sheet.
<u>Size</u>				
<u>Special Equipment</u>				
S-201	Compounding extruder	6 in. dia, L/D = 20.	304 ss	Twin-screw, 200 hp.
<u>Miscellaneous Equipment</u>				
M-101	Extruder	6 in. dia, L/D = 4	304 ss	
M-102	Pelletizer		304 ss	
M-103	Water preseparatot		304 ss	
M-104	Dewatering screen		304 ss	
M-105	Fluidized bed drier		304 ss	
M-201	Pelletizer		304 ss	
M-202	Water preseparatot		304 ss	
M-203	Dewatering screen		304 ss	
M-204	Fluidized bed drier		304 ss	
M-205A-C	Blenders	10,000 gal ea	304 ss	
M-206	Pelletizer		304 ss	
M-207	Water preseparatot		304 ss	
M-208	Dewatering screen		304 ss	
M-209	Fluidized bed drier		304 ss	
M-210	Conveyers			Not shown on flow sheet.
M-301	Packing machine			Not shown on flow sheet.
M-302	Conveyers			Not shown on flow sheet.
M-303	Extruder	2.5 in.	304 ss	60 hp for treating waste, not shown on flow sheet.
<u>Pumps</u>				
10G Section: 2, including 1 operating, 1 spares; 4 operating bhp				
200 Section: 4, including 2 operating, 2 spares; 2 operating bhp				

Table 6.10
NYLON 66 RESIN FROM MELT
UTILITIES SUMMARY

**Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Resin
 at 0.90 Stream Factor**

	<u>Battery Limits</u>	<u>100</u>	<u>200</u>	<u>300</u>
	<u>Total</u>	<u>Section</u>	<u>Section</u>	<u>Section</u>
Average consumptions				
Cooling water (gpm)	6		6	
Electricity (kw)	474	139	290	45
Steam at 100 psig (lb/hr)	1,100	700	400	
Inert gas, low pressure (scfh)	260,100	160,000	100,100	
Peak demands				
Cooling water (gpm)	20		20	
Electricity (kw)	662	165	430	67
Steam at 100 psig (lb/hr)	1,500	900	600	

Process Discussion

The production scheme starts with nylon 66 melt which in turn is made from nylon salt. This is the practice of major producers of nylon resin. There are some minor resin producers using nylon waste from fiber manufacture as raw material. In such cases, M-101 cannot be a simple short extruder; rather, it must be able to melt and knead, and have a length-to-diameter ratio greater than 20.

In the design case, the larger pelletizer (M-201) is an underwater type, and the smaller (M-206) is a water-ring type. Other ways of pelletizing use strand cutting, i.e., cooling the continuous band or strand from the extruder in water, and then cutting by knife, and drying with a nitrogen flow. One type is described in reference 392204.

An alternative way of making extrusion grade resin is to use solid phase polymerization such as is described in reference 388217. The product is expected to be less uniform than that made by the process using a twin-screw extruder for increasing the molecular weight.

Cost Estimates

Tables 6.11 and 6.12 give the capital investment and the production cost. This is based on a plant with equipment as listed in Table 6.6. Actually, the resin production is always integrated with polycondensation, and often also integrated with nylon salt production.

The pricing of nylon 66 melt at a constant price of 66¢/lb for several capacities of nylon 66 resin production, as is done in Table 6.12, is for convenience only. Nylon 66 melt is always captively produced in a resin plant; hence, the price assigned to nylon 66 melt should vary with the capacity. A more straightforward way is to evaluate the production of nylon 66 resin starting from HMDA and adipic acid. Tables 6.13 and 6.14 give the capital investment and production cost for such a plant, with the polycondensation unit using the conventional process (Figure 5.2).

The product value given in Table 6.14 is lower than that given in Table 6.12, by 3.4¢/lb in the case of 50 million lb/yr capacity. This

is partly because of the lower overall working capital and partly because of the lower overall capital investment in an integrated plant.

The production cost is a weighted average of the production of several grades of resin, i.e., 30% extrusion grade, partly natural color and partly colored; 30% colored resin (including injection grade and extrusion grade); and 30% resin compounded with additives. The balance is natural color injection grade. The total production is 50 million lb/yr. The production cost and product value of the individual grades, if made alone at full plant capacity, are estimated in Table 6.15.

It should be noted that in the above-evaluated production cost, no additive (other than acetic acid for molecular weight control) has been included. For most grades, additives are introduced during the polymerization; and in the compounding, of course, additives are used. The effect of such additives on production costs will be discussed later.

Table 6.11

NYLON 66 RESIN FROM MELTCAPITAL INVESTMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Resin
 at 0.90 Stream Factor
 PEP Cost Index: 320

	Total				Resin Formation				After Treatment				Packing			
	Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent		Cost	Capacity Exponent		
		Up	Down		Up	Down		Up	Down		Up	Down		Up	Down	
Battery limits equipment, f.o.b.																
Reactors	\$ 320,000			\$ 120,200	0.39	0.35	\$ 320,000	0.60	0.60	\$ 658,000	0.35	0.35				
Vessels and tanks	778,200			12,400	0.37	0.28	18,400	0.15	1.38							
Exchangers	30,800			32,300	0.76	0.76	57,600	0.76	0.76							
Compressors	89,900									496,000	0.60	0.60				
Special equipment	496,000									255,400	0.63	0.63	60,800	0.65	0.65	
Miscellaneous equipment	511,400			195,200	0.61	0.61				5,800	0.17	0.12				
Pumps	9,800			4,000	0.30	0.24										
Total	\$ 2,236,100	0.53	0.52	\$ 364,100	0.54	0.51	\$ 1,811,200	0.52	0.52	\$ 60,800	0.65	0.65				
BATTERY LIMITS INVESTMENT	\$ 8,383,000	0.53	0.51	\$ 1,575,000	0.54	0.52	\$ 6,444,000	0.52	0.51	\$ 364,000	0.58	0.58				
Off-sites																
Cooling tower	\$ 86,600			\$ 23,400	0.82	0.82	\$ 86,600	0.28	0.28	\$ 15,600	0.82	0.82				
Steam generation	39,000			1,026,800	0.91	0.95	665,600	0.91	0.95							
Inert gas	1,692,400			272,400	0.95	0.35	582,000	0.35	0.35							
Tankage	854,400															
Warehouse facilities	1,324,800															
Utilities and tankage investment	\$ 4,797,000	0.79	0.74	\$ 1,587,000	0.92	0.80	\$ 1,620,000	0.66	0.61	\$ 1,590,000	0.80	0.80				
General service facilities	2,636,000															
Waste treatment	659,000															
OFF-SITES INVESTMENT	\$ 8,092,000	0.79	0.74													
TOTAL FIXED CAPITAL	\$16,475,000	0.63	0.59													
Start-up costs	\$ 2,557,000															
Working capital	<u>\$ 6,552,000</u>															
TOTAL CAPITAL INVESTMENT	\$25,584,000															

Table 6.12

NYLON 66 RESIN FROM MELT

PRODUCTION COSTS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Resin
 at 0.90 Stream Factor
 PEP Cost Index: 320

	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost (¢/lb)	66		
Raw materials			
Melt	66¢/lb	1.005 lb	<u>66.33</u>
Gross raw material cost			66.33
Utilities			
Steam	\$5.00/1,000 lb	0.173 lb	0.09
Electricity	2.65¢/kwh	0.074 kwh	0.20
Inert gas, low pressure	60¢/1,000 scf	41 scf	<u>2.46</u>
Total utilities			2.75
Labor			
Operating, 5 men/shift	\$14.20/hr	0.0009 man-hr	1.24
	<u>Million lb/yr</u>		
	<u>25</u>	<u>50*</u>	<u>100</u>
Investment (\$ million)			
Battery limits	5.9	8.4	12.1
Off-sites	<u>5.1</u>	<u>8.1</u>	<u>13.4</u>
Total fixed capital	11.0	16.5	25.5
Scaling exponents	0.59	0.63	
Production costs (¢/lb)			
Raw materials	66.33	66.33	66.33
Utilities	2.75	2.75	2.75
Maintenance materials, 3%/yr of BL cost	0.70	0.50	0.36
Operating supplies, 10% operating labor	<u>0.25</u>	<u>0.12</u>	<u>0.06</u>
Variable costs	70.03	69.70	69.50
Operating labor	2.49	1.24	0.62
Maintenance labor, 3%/yr of BL cost	0.70	0.50	0.36
Control laboratory, 20% operating labor	<u>0.50</u>	<u>0.25</u>	<u>0.12</u>
Total direct costs	73.72	71.69	70.60
Plant overhead, 80% of total labor	2.95	1.60	0.89
Taxes and insurance, 2%/yr of fixed capital	0.88	0.66	0.51
Depreciation, 10%/yr of fixed capital	4.38	3.30	2.55
Interest on working capital, 10%/yr	<u>1.39</u>	<u>1.31</u>	<u>1.26</u>
Plant gate cost	83.32	78.56	75.81
G&A, sales, research, 10% of annual sales	<u>10.00</u>	<u>10.00</u>	<u>10.00</u>
NET PRODUCTION COST	93.32	88.56	85.81
25%/yr return on fixed capital, before taxes	<u>11.00</u>	<u>8.25</u>	<u>6.38</u>
PRODUCT VALUE	104.32	96.81	92.19

*Base case.

Table 6.13
NYLON 66 RESIN FROM HMDA AND ADIPIC ACID

CAPITAL INVESTMENT			
	<u>Cost</u>	<u>Capacity Exponent</u>	
		<u>Up</u>	<u>Down</u>
Battery limits equipment, f.o.b.			
Reactors	\$ 732,800		
Vessels and tanks	1,243,700		
Exchangers	80,100		
Furnaces	83,200		
Compressors	89,900		
Special equipment	688,000		
Miscellaneous equipment	562,600		
Pumps	<u>184,900</u>		
Total	\$ 3,665,200	0.58	0.52
BATTERY LIMITS INVESTMENT	\$12,281,000	0.55	0.51
Off-sites			
Cooling tower	\$ 349,500		
Process water treatment	4,800		
Steam generation	214,300		
Inert gas	1,791,100		
Tankage	1,046,100		
Warehouse facilities	1,324,800		
Utilities and tankage investment	\$ 5,677,000	0.78	0.70
General service facilities	3,592,000		
Waste treatment	<u>898,000</u>		
OFF-SITES INVESTMENT	\$10,167,000	0.78	0.70
TOTAL FIXED CAPITAL	\$22,448,000	0.63	0.56
Start-up costs	\$ 2,990,000		
Working capital	<u>\$ 6,257,000</u>		
TOTAL CAPITAL INVESTMENT	\$31,695,000		

Table 6.14
NYLON 66 RESIN FROM HMDA AND ADIPIC ACID

PRODUCTION COSTS			
Plant Capacity: 50 Million lb/yr (23,000 Metric Tons/yr) Resin at 0.90 Stream Factor PEP Cost Index: 320			
	Unit Cost	Consumption/lb	¢/lb
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Adipic acid	38.3¢/lb	0.65353 lb	25.03
HMDA	55.5¢/lb	0.51981 lb	28.85
Acetic acid	20.7¢/lb	0.00175 lb	<u>0.04</u>
			53.92
Gross raw material cost			
Utilities			
Cooling water	4.5¢/1,000 gal	18.6 gal	0.08
Steam	\$5.00/1,000 lb	1.4 lb	0.70
Process water	\$1.10/1,000 gal	0.312 gal	0.03
Electricity	2.65¢/kwh	0.097 kwh	0.26
Fuel oil	\$3.30/million Btu	1,761 Btu	0.58
Inert gas, low pressure	60¢/1,000 scf	42.3 scf	2.54
Inert gas, high pressure	80¢/1,000 scf	0.189 scf	<u>0.02</u>
			4.21
Total utilities			
Labor			
Operating, 9.5 men/shift	\$14.20/hr	0.0017 man-hr	2.36
	<u>Million lb/yr</u>		
	25	50*	100
Investment (\$ million)			
Battery limits	8.6	12.3	18.0
Off-sites	<u>6.6</u>	<u>10.1</u>	<u>16.7</u>
Total fixed capital	15.2	22.4	34.7
Scaling exponents	0.56	0.63	
Production costs (¢/lb)			
Raw materials	53.92	53.92	53.92
Utilities	4.21	4.21	4.21
Maintenance materials, 3%/yr of BL cost	1.04	0.74	0.54
Operating supplies, 10% operating labor	<u>0.47</u>	<u>0.24</u>	<u>0.12</u>
Variable costs	59.64	59.11	58.79
Operating labor	4.73	2.36	1.18
Maintenance labor, 3%/yr of BL cost	1.04	0.74	0.54
Control laboratory, 20% operating labor	<u>0.95</u>	<u>0.47</u>	<u>0.24</u>
Total direct costs	66.36	62.68	60.75
Plant overhead, 80% of total labor	5.37	2.86	1.57
Taxes and insurance, 2%/yr of fixed capital	1.22	0.90	0.69
Depreciation, 10%/yr of fixed capital	6.07	4.49	3.47
Interest on working capital, 10%/yr	<u>1.40</u>	<u>1.25</u>	<u>1.17</u>
Plant gate cost	80.42	72.18	67.65
G&A, sales, research, 10% of annual sales	<u>10.00</u>	<u>10.00</u>	<u>10.00</u>
NET PRODUCTION COST	90.42	82.18	77.65
25%/yr return on fixed capital, before taxes	<u>15.20</u>	<u>11.20</u>	<u>8.67</u>
PRODUCT VALUE	105.62	93.38	86.32

*Base case.

Table 6.15
NYLON 66 RESIN, VARIOUS GRADES

PRODUCTION COST AND PRODUCT VALUE

PEP Cost Index: 320

	Capacity (million lb/yr)		
	<u>25</u>	<u>50</u>	<u>100</u>
Production cost* (¢/lb)			
Injection, natural color	85	78	74
Injection, colored	87	80	75
Extrusion	93	85	80
Compound	95	86	81
Product value* (¢/lb)			
Injection, natural color	94	85	80
Injection, colored	98	88	82
Extrusion	108	95	90
Compound	113	99	91

* In addition, adjustments have to be made for material cost changes due to additives.

Manufacture of Spinning Chips

For making spinning chips, used for carpet and textile fibers, the polycondensation follows the procedures and conditions described in Section 5, and then the melt is extruded and pelletized as shown in the Resin Formation Section of Figure 6.1 (foldout at end of report).

Tables 6.16, 6.17, and 6.18 give the utilities summary, the capital investment and production cost of a chips plant, starting from HMDA and adipic acid. The production costs at different levels are given in Figure 6.2. In the production cost, the additives are not accounted for. The cost effect of additives will be discussed later in this section.

For making spinning chips useful for tire cord, there are two alternatives. One is to after-treat the chips in R-201 of Figure 6.1. The procedure would then be similar to those used in the manufacture of extrusion grade resin. A better way is to make changes in the polycondensation; the temperature in R-203 is increased from 520°F (271°C) to 536°F (280°C), and formic acid vapor is added above the surface of molten nylon 66 in R-203 (71528).

Table 6.16

NYLON CHIPS FROM HMDA AND ADIPIC ACID

UTILITIES SUMMARY

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Resin
 at 0.90 Stream Factor

	Battery Limits <u>Total</u>	100 <u>Section</u>	200 <u>Section</u>	300 <u>Section</u>
Average consumptions				
Cooling water (gpm)	2,500	1,100	1,400	
Electricity (kw)	263	240	11	12
Process water (gpm)	30	30		
Steam at 50 psig (lb/hr)	800	800		
Steam at 100 psig (lb/hr)	14,000	13,700	300	
Inert gas, low pressure (scfh)	168,000	168,000		
Inert gas, high pressure (scfh)	300		300	
Fuel oil (million Btu/hr)	21			21
Peak demands				
Steam at 50 psig (lb/hr)	2,500	2,500		
Inert gas, high pressure (scfh)	600		600	

Table 6.17
NYLON CHIPS FROM HMDA AND ADIPIC ACID

CAPITAL INVESTMENT			
Plant Capacity: 50 Million lb/yr (23,000 Metric Tons/yr) Resin at 0.90 Stream Factor PEP Cost Index: 320			
	<u>Cost</u>	<u>Capacity Exponent</u>	
		<u>Up</u>	<u>Down</u>
Battery limits equipment, f.o.b.			
Reactors	\$ 350,400		
Columns	17,500		
Vessels and tanks	523,100		
Exchangers	163,300		
Furnaces	137,000		
Compressors	32,300		
Special equipment	112,000		
Miscellaneous equipment	265,600		
Pumps	<u>253,800</u>		
Total	\$ 1,855,000	0.62	0.49
BATTERY LIMITS INVESTMENT	\$ 6,187,000	0.57	0.48
Off-sites			
Cooling tower	\$ 396,100		
Process water treatment	8,000		
Steam generation	311,100		
Inert gas	1,223,400		
Tankage	464,100		
Warehouse facilities	1,324,800		
Utilities and tankage investment	\$ 4,474,000	0.80	0.70
General service facilities	2,132,000		
Waste treatment	<u>533,000</u>		
OFF-SITES INVESTMENT	\$ 7,139,000	0.80	0.70
TOTAL FIXED CAPITAL	\$13,326,000	0.67	0.57
Start-up costs	\$ 2,530,000		
Working capital	<u>\$ 6,014,000</u>		
TOTAL CAPITAL INVESTMENT	\$21,870,000		

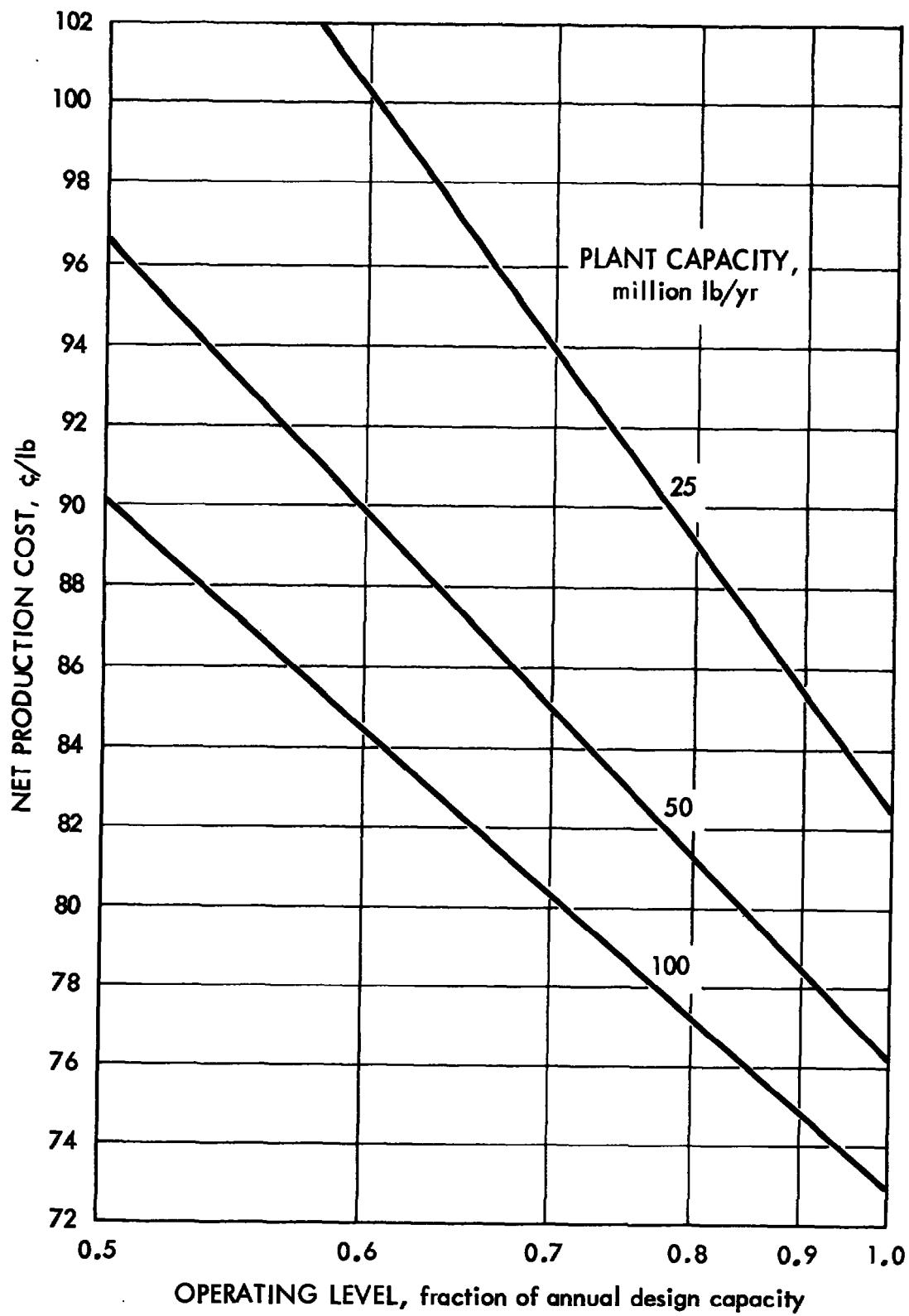
Table 6.18
NYLON CHIPS FROM HMDA AND ADIPIC ACID

PRODUCTION COSTS			
	Unit Cost	Consumption/lb	¢/lb
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Adipic acid	38.3¢/lb	0.65353 lb	25.03
HMDA	55.5¢/lb	0.51981 lb	28.85
Acetic acid	20.7¢/lb	0.00175 lb	<u>0.04</u>
Gross raw material cost			53.92
Utilities			
Cooling water	4.5¢/1,000 gal	22.5 gal	0.10
Steam	\$5.00/1,000 lb	2.33 lb	1.17
Process water	\$1.10/1,000 gal	0.284 gal	0.03
Electricity	2.65¢/kwh	0.04 kwh	0.11
Fuel oil	\$3.30/million Btu	3,311 Btu	1.09
Inert gas, low pressure	60¢/1,000 scf	26.5 scf	1.59
Inert gas, high pressure	80¢/1,000 scf	0.047 scf	<u>negl</u>
Total utilities			4.09
Labor			
Operating, 8 men/shift	\$14.20/hr	0.0014 man-hr	1.99
	Million lb/yr		
	25	50*	100
Investment (\$ million)			
Battery limits	4.4	6.2	9.2
Off-sites	<u>4.6</u>	<u>7.1</u>	<u>12.0</u>
Total fixed capital	9.0	13.3	21.2
Scaling exponents	0.57	0.67	
Production costs (¢/lb)			
Raw materials	53.92	53.92	53.92
Utilities	4.09	4.09	4.09
Maintenance materials, 3%/yr of BL cost	0.53	0.37	0.28
Operating supplies, 10% operating labor	<u>0.40</u>	<u>0.20</u>	<u>0.10</u>
Variable costs	58.94	58.58	58.39
Operating labor	3.98	1.99	1.00
Maintenance labor, 3%/yr of BL cost	0.53	0.37	0.28
Control laboratory, 20% operating labor	<u>0.80</u>	<u>0.40</u>	<u>0.20</u>
Total direct costs	64.25	61.34	59.87
Plant overhead, 80% of total labor	4.25	2.21	1.18
Taxes and insurance, 2%/yr of fixed capital	0.72	0.53	0.42
Depreciation, 10%/yr of fixed capital	3.60	2.67	2.12
Interest on working capital, 10%/yr	<u>1.26</u>	<u>1.15</u>	<u>1.09</u>
Plant gate cost	74.08	67.90	64.68
G&A, sales, research, 10% of annual sales	<u>8.30</u>	<u>8.30</u>	<u>8.30</u>
NET PRODUCTION COST	82.38	76.20	72.98
25%/yr return on fixed capital, before taxes	<u>9.00</u>	<u>6.65</u>	<u>5.30</u>
PRODUCT VALUE	91.38	82.85	78.28

*Base case.

Figure 6.2

NYLON 66 CHIPS FROM HMDA AND ADIPIC ACID
EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCTION COST



Additives--Cost Effects

Commercially, there are various grades of nylon 66 resins, marked as color stabilized (not liable to discolor), heat stabilized, weather stabilized, hydrolysis resistant, nucleated (for fast cycling in injection molding), and lubricated (easier to fabricate). For chips there are also many grades. Table 6.19 lists some examples of compositions. On the basis of unit prices as listed in Table 6.18, and a value of nylon melt at 66¢/lb, the effect of such additions on the material costs can be calculated, as also shown in Table 6.19.

Note that in most cases the effect on material costs is quite insignificant, in comparison with the total cost at 80¢ to 100¢/lb. Far more significant in cost effects is the fact that for making several different grades it would either be necessary to change the formulation during polycondensation, hence breaking the continuity of operation and causing some off-grade production; or, batch polycondensation has to be used, leading to higher labor costs. Hence, the volume of the market for a particular grade often has more bearing on the cost, and hence the sales price, than the composition.

Table 6.19
ADDITIVES TO NYLON RESINS AND CHIPS

		Additive			Change in Material Cost (¢/lb product)
		Compound	%	Price (¢/lb)	Reference
Resins					
Color stabilized	KBr		0.4	67	71036
	Na ₂ HPO ₄		0.1	32	
Heat stabilized	KI		1	376	70974
	H ₃ PO ₄		0.25	18.5	
	Cu(OAc) ₂ ·H ₂ O		0.015	80	
Weather stabilized	Carbon black		0.3	17	70947, 420069
	Lenkanol®		0.01	300	
	Casein		0.015	72	
	NH ₃		0.03	9	
Hydrolysis resistant	CuCl ₂		0.05	90	70106
	Cu(OAc) ₂ ·H ₂ O		0.05	80	
	2-Mercaptobenzothiazole		0.22	94	
Nucleated	Kaolinite		2	10	70174
	Na ₄ B ₂ O ₇		0.6	32	
	CaF ₂		0.1	16	71552
	Ethylenediamine		0.2	68	
	Zn-stearate		0.3	86	
Lubricated	Zn-stearate		0.12	86	71206
	Na-phenylphosphinate		0.25	400	
Chips					
Heat stabilized	Cu(OAc) ₂ ·H ₂ O		0.023	71	71536
	KBr		0.12	67	
	KI		0.06	376	
	K-phenylphosphinate		0.19	420	
Dull	TiO ₂		0.5	49	32253
Antistatic	Na-phenylphosphinate		0.7	400	70822
	3-Aminopropylphenylphosphinate		0.8	500	
	Polyethylene glycol		5	70	

7 NYLON 66 FIBER

Review of Processes

Fiber is made from nylon 66 by melt spinning. The melt may either come directly from the polycondensation, or be made from chips. The melting device used nowadays is an extruder; no longer used are the various types of electric- or Dowtherm®-heated grid melters.

The fiber can be in various forms: filament yarn (textured or not), for apparel, staple for apparel, filament yarn for carpet, staple for carpet, cord for tires, and monofilament for hosiery, etc.

Various substances are added to impart desirable properties (stable in heat, light, and weather; antistatic; easily dyed; flame-retardant; etc.). Some additives are incorporated during polycondensation, as mentioned in Section 6. Some are blended with chips before the chips are melted, or are added to the extruder together with chips. Patents relating to such additives are summarized in Table 7.1.

Table 7.2 lists the patents relating to the supply of nylon 66 melt to the spinning packs from the polycondensation unit (in the case of direct spinning), or from the extruder (in the case of chip spinning). Table 7.3 lists the patents relating to spinning packs. A spinning pack is a built-in unit consisting of a filter and a spinneret (having numerous spinning orifices) with a metering pump either built into or preceding the pack.

The melt from the orifices of a spinneret is quenched by air, and congeals into filaments. Table 7.4 lists the patents relating to quenching.

The filaments are combined into a yarn. The yarn is pulled by a spinning roll. From there on, there are two ways, a split process or a coupled process. In a split process, the yarns are wound, and then transferred to another machine, unwound and drawn for further elongation,

Table 7.1
ADDITIVES TO CHIPS OR TO MELT SHORTLY BEFORE SPINNING
PATENT SUMMARY

Reference No.	Assignee	Priority Date	Additives	Purpose
389418	Du Pont	12/9/60	Poly(oxyethylene) added to nylon chips that were then melt-spun into filaments.	Fabric made therefrom is cross-linked with NH_4BF_4 solution; it is resilient and wrinkle-resistant.
71894	ICI	9/14/65	Nylon salt and nylon 6T salt are copolymerized; the copolymer is blended with nylon 66 in a 90% phenol aqueous solution, and precipitated in methanol; this powder is mixed with a pigmented low mol wt nylon 66 in a slurry, which is used for coating of nylon 66 chips.	Nucleating enables high draw ratio of the filament, and hence increases productivity.
71801	Ciba Geigy	10/28/65	Rutile 0.3% and N-heterocyclic compound containing an ethylene double bond 0.02%.	Brightening.
388178	Toyo Spinning	12/4/65	A complex of caprolactam and a copper salt 0.001%-1%.	Improved thermal stability.
71839	Ciba	4/11/67	Bis-oxalic acid diamide 0.1%-10%	Stabilization against ultraviolet light.
71891	Du Pont	9/14/67	Part of additive polyetherpolyol is added during polycondensation to saturation and the balance is added to the melt-extruder.	
71845	Teijin	9/18/67	Polyalkylene glycol-diisocyanate 1%-30%.	Durable antistatic property.
71588	Toray	12/5/67	Phthaliamide 0.2%-0.5%.	Improved heat stability.
71597	Toyoba	12/5/67	Dimethyl terephthalate 1.5% in methanol solution.	Melt stabilizer.
392597	Matsumoto Yushi-Seigaku	5/28/68	A styrene-phenol-ethylene oxide adduct.	Antistatic property.
462108	Unitika	7/2/68	Polyoxyethylene monoester of a dicarboxylic acid.	Antistatic property.
462099	Kanebo	4/29/69	Reaction product of polyester and diisocyanate.	Antistatic property.
462189	Allied Chemical	9/3/69	A reaction product of polyglycol and aliphatic dibasic acid.	Antistatic property.
71565	Celanese	11/25/69	Copper acetate or KI aqueous solution; extruded nylon passes through this solution, and the granules made therefrom are extruded again.	Heat stabilization.
462188	Monsanto	5/11/70	Tertiary amine.	Antistatic property.
71837	Chem. Fabrik. Pfersee	7/17/70	Adipic acid-caprolactam-polyethylene glycol graft copolymer.	Antistatic property.
392571	Toray	8/4/70	An addition product of ethylene oxide, enantholactan, and phosphoric acid; fiber washed with hot water to remove the polyether.	Fiber has silky luster.
392575	Toray	8/6/70	An addition product of ethylene oxide, enantholactan, and phosphoric acid.	Fiber has silky luster.
71803	Ciba-Geigy	10/20/70	Manganese salt of 3,5-di-tert-4-hydroxy-berzyl phosphoric acid mono-n-butyl ester.	Stabilizer against heat and light.
71979	BASF	9/20/71	Ethyoxylated polyamide.	Antistatic property.
392605	Toyobo	9/27/71	Ethylene oxide-propylene oxide-polysiloxane.	Good drawing processability.
71941	ICI	10/26/71	Boric acid plus polyoxalkylene.	Antistatic property (without impairing the dye-fastness).
462200	Weeden, G. C., et al.	12/21/71	Tris(β-hydroxyalkyl)isocyanurate-alkylene oxide adduct.	Antistatic property.
462086	Toray	3/23/72	Tin oxide plus zinc oxide plus organic halogen compound.	Fire-resistance.
462202	Emery Industries	3/30/72	Reaction product of a dimer acid and ethylenediamine and polyethylene glycol.	Antistatic property.
462029	Snia Viscosa	3/31/72	Polyethylene glycol with a mol wt of 20,000 and a very narrow mol wt distribution.	Antistatic property.
71666	Rohm & Haas	12/4/72	Methyl methacrylate-ethyl acrylate copolymer 10%-20%.	Soil-hiding and soil-resistant property (for carpet yarn).
462154	Teijin	12/27/72	Adduct of polyethylene glycol bis(2-aminoethyl) ether-xylene diisocyanate.	Antistatic property.
462206	Akrona	1/19/73	O-carboxyalkylated and an ethoxylated diamine.	Antistatic property.
406632	Akrona	3/29/73	Similar to 71845.	
71939	Bayer	5/16/73	Polyoxalkylene plus a tertiary diamine.	Antistatic property (durable).
71654	Monsanto	6/29/73	Polyethoxylated glycerol tri(hydroxystearate) blended in a melt mixer with molten nylon 66.	Antistatic property.
462205	Du Pont	8/14/73	N-alkyl-substituted polycarbonate.	Antistatic property.
71658	BASF Farben & Fasern	9/7/73	Polystyrene 0.2%.	Monofilament, 70.5 mm thick, free of bubbles.

Table 7.1 (Concluded)

ADDITIVES TO CHIPS OR TO MELT SHORTLY BEFORE SPINNING

PATENT SUMMARY

Reference No.	Assignee	Priority Date	Additives	Purpose
71732	Akzo	10/9/73	Polystyrene 0.1%–6% in trilobal fiber.	Antisoiling property (for carpet yarn).
71619	Soc. Viscose Suisse	5/24/74	1,6-Bis(3,5-di-tert-butyl-4-hydroxy-phenoxy) hexane.	Stabilization against thermal and oxidative deterioration (alleviated loss of strength on heating in air).
462128	Kanebo	8/18/75	N-acylated aromatic amine.	Fire-resistance.
462008	BASF-Wyandotte	9/24/75	Polymer from diethylene triamine plus methyl isobutyl ketone plus propylene oxide.	Durable antistatic property.
462006	Phillips Fiber	10/6/75	Reaction product of a block copolymer of propylene oxide and ethylene oxide on ethylene diamine plus a dicarboxylic acid ester.	Antistatic property.
462139	Tetjin	4/9/76	Polyvalent amine plus a magnesium compound.	Improved affinity for acid dyes and reduced breakage.
71745	Phillips Petroleum	5/27/76	Reaction product of a block copolymer of ethylene oxide, propylene oxide, and an alkylene diamine, and a dicarboxylic acid.	Antistatic property.
71750	Allied Chemical	9/22/76	Zinc borate 2% and a chlorine-containing flame retardant 2%.	Flame-retardance.
71743	Akzo	11/29/79	Hydantoin polyamide-poly(oxyethylene) block copolymer.	Antistatic property.

Table 7.2

SUPPLY OF MELT TO SPINNING PACKS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71898	Du Pont	12/21/66
	A melt-extruder in which a small portion of the melt is recycled from a high pressure point to a low pressure point; the power of the driving motor is reduced.	
71893	Glanzstoff AG	11/21/67
	Pigment dispersed in butyrolactam is added to polyamide melt, and immediately cut by pitched blades; the mixture is withdrawn at the bottom by a gear pump and sent to spinnerets.	
71899	Du Pont	10/10/68
	A filter on the line before the spinning packs.	
388057	Asahi Chemical	5/4/70
	Melting wet chips of polyamide in a screw extruder and delivering the melt from the extruder to molten nylon 66 pool in a separator tank; the melt from the tank goes to spinnerets.	
71782	Celanese	3/28/74
	A melt reservoir provided with dual, parallel lines from the melt source (extruder or polycondensation reactor; the lines are alternately inactivated for cleaning of filters.	
71661	Du Pont	9/23/74
	The pressure differential between the polycondensation finisher and the spinnerets is monitored, and this differential is used to control the temperature of the evaporator for the nylon salt solution before the polycondensation. The amine end group is thus maintained constant and hence the dyeability of the fibers is constant.	

Table 7.3

SPINNING PACK

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71904	Monsanto	9/23/65
	<p>Relays are connected to motors driving metering pump and booster pump to actuate alarm when power consumption deviates from preselected limits.</p>	
71901	ICI	1/3/66
	<p>Polyamide melt is collected from filter in the spinning pack to a central orifice, then flows from the central orifice to the spinning orifices through channels. The flow to all spinning orifices is uniform.</p>	
71905	Monsanto	4/7/67
	<p>Nylon 66 of low relative viscosity (≤ 25) flows through a sand bed in the spinning pack; because of the shear, the relative viscosity is increased to a level to enable the production of satisfactory filaments.</p>	
71657	Zimmer	6/22/73
	<p>Construction of a spinning pack containing pump and nozzle and their connections.</p>	

Table 7.4
QUENCHING OF MOLTEN FILAMENTS FROM SPINNERETS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71902	Monsanto	12/28/66
	Quenching through a closed refrigerated zone of relatively still air.	
71903	Monsanto	3/28/67
	Quenching through a liquid metal.	
71653	Du Pont	4/18/74
	Melt-extruded filament passes through a steam blanketed zone, followed by a short inert-gas blanketed zone, and then an air quenching zone.	

and then rewound. In a coupled process, the drawing follows the spinning without intermediate winding. The coupled process is the simpler. It saves labor and gives a product with higher strength and modulus and greater depth of dyeing. However, since there is a maximum limit of winding speed (7,000 meters/minute for fine denier, and 4,000 meters/minute for coarse denier) for a given output, the coupled process would require more spinning positions.

In recent years, high speed direct spinning (up to 5,500 meters/minute in the latest development) has been introduced. The yarn spun at such a speed and then wound is "preoriented" and needs to be drawn only slightly (draw ratio 1:1.2 to 1:1.3), and this degree of drawing is often achieved in texturing (crimping), without an explicit drawing step. Such high speed spinning followed by texturing-winding is a split process, but the product is of much higher quality than that made by the conventional split process. The productivity is just as high as, or higher than it is in the conventional coupled process. Furthermore, the preoriented yarn is quite stable and can be used, as such, in textile processing, without further drawing or texturing. In this sense, the high speed spinning is equivalent to a coupled process.

Steaming, heating, and cooling are used throughout the spinning and drawing operations. The operations are very delicate. The relevant properties of the yarn or filament are not only tensile strength, elongation, and modulus, but also uniformity, surface condition, freedom from nubs, and freedom from breakage. These properties are affected by temperature, moisture content, tension applied to the yarn, rate of change of tension, surface that the yarn contacts, etc. These relationships can only be ascertained empirically and can at best be rationalized by theory in a qualitative way (71513, 71514, 71687, 71697, 71703, 71712, 71791, 71872, 71873, 71877, 372313, 388615, 389309, 392466, 406733).

Table 7.5 lists the patents relating to melt spinning. Table 7.6 lists the patents relating to coupled spinning-drawing. Table 7.7 lists patents relating to drawing.

Table 7.5

SPINNING OF NYLON 66 FIBERS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71884	British Nylon Spinners	5/25/63
	Filaments from spinnerets → air cooling → guide (combining the filaments) → nip rolls (running at a speed a few percent slower than the wind-up) → steaming → wind-up. If the spinneret output changes, and the draw ratio changes correspondingly to maintain the same denier, the properties of the final yarn remain constant.	
70848	Toyo Rayon	7/22/66
	Spinning conditions relate to relative viscosity.	
388155	Du Pont	4/5/68
	Monofilaments pass through saturated steam at 40-90 psig for 10 milliseconds to 5 seconds, the knot strength of the monofilaments is improved.	
392270	Teijin	4/25/68
	Melt-spun fiber is taken up while the moisture is maintained at 1.3%, and aged at a humidity of less than 50% and a temperature less than 30°C. The fiber has a low birefringence, and hence can be drawn at a high draw ratio.	
71857	Toray Industries	10/14/69
	Melt-spinning through T-shaped orifices connected to a cooling chimney heated in such a way that the temperature of the atmosphere 0-75 mm from the orifices is greater than 150°C and higher than the mp of nylon 66, and the temperature 75-85 mm from the orifices is 50-150°C. Fiber obtained has a silky appearance.	
462067	Unitika	12/4/69
	Oxidation of polyamide during melt spinning is minimized by injecting an inert gas in place of air for quenching.	
392206	Sobico Inc.	3/20/70
	Notched, lobe-shaped filament.	
462081	Asahi Chemical	5/18/70
	Chips are screw-extruded through nozzles into a dehydration vessel blanketed with nitrogen; the dried mass is then screw-extruded to form fiber. Spun fiber is free of gel.	
71858	Toray Industries	8/3/70
	Very fine filaments are obtained by melt spinning, coagulating, taking-off at 2,500-4,500 m/min, treating on an oiling roller, heat-treating and drying at 150-220°C, or heat-treating with steam at 90-180°C under tension.	
462112	Unitika	12/25/70
	Nylon with high relative viscosity is blended with 0.1Z-1% an alcohol with a boiling point of 190-295°C, and melt-spun into hot atmosphere to evaporate the alcohol. On cooling and drawing, a high tenacity filament is obtained.	
392384	Karebo	6/29/71
	Spinning to give undrawn filament with high tensile strength.	
71777	Toray Industries	10/26/71
	Nylon 6 in an amount twice the inside volume of the spinneret is first melt-spun; then nylon 66 is melt-spun; breakage is reduced.	
71859	Teijin	2/7/72
	Melt-spun filaments are cooled, treated by aqueous lubricant emulsion at 25°C to get 3% water, passed through an air jet zone at 110°C, and wound. The package is stable and shows no change on storage.	
71520	Teijin	2/8/72
	Melt-spun filaments are cooled, bundled, treated with a steam jet, water mist, or aqueous emulsion spray, dry-heat-treated at 60-180°C for 0.012-0.18 second, and wound.	

Table 7.5 (Concluded)

SPINNING OF NYLON 66 FIBERS

PATENT SUMMARY

Reference No.	Assignee	Priority Date
71521	Toray Industries Nylon 66 is melt-spun at 278°C, and the undrawn package is steamed at 55°C.	5/4/72
71662	Barmag Barmer Maschinenfabrik Tire cord yarn is produced by melt-spinning, cooling, wetting with a finish, guided by a godet at a speed more than 3,500 m/min and wound. The yarn is then pretwisted, plied, and after-twisted into cord ply yarn.	11/10/72
71771	BASF Farben u. Fasern Bubble-free monofilaments, greater than 0.5 mm thick, are made by quenching the melt-spun filaments in a silicone oil bath at 20-45°C.	6/19/73
71853	Teijin The melting spinning of filaments with proper position of collecting guide.	7/9/74
71954	Metallgesellschaft High speed spinning at 3,000-6,000 m/min take-off speed, and a stretch ratio of 200:1 to 2,000:1, through an air cooling duct, and then a steam duct.	1/6/75
71664	Du Pont High speed spinning at 3,000-3,500 m/min attained by using a long quench chimney, steam duct, a finishing roll, a high speed puller roll, and a wind-up.	2/7/75
71665	Du Pont A mixture of two sizes of trilobal filaments; quenched by air, combined into tow, drawn at a ratio of 3.75, crimped in a stuffing box, and cut. Staple for carpet.	3/20/75
71955	Zimmer High speed spinning. Filaments, after being air cooled are subjected to a heat treatment in a duct, with a minimum wall temperature related to spinning speed.	4/5/75
71854	Teijin Multifilament yarn with controlled degree of fluffiness obtained by changing the proportion of small denier filaments and large denier filaments.	5/12/75
71675	Monsanto Spinneret → air quenching → finishing roll → feed roll (3,800 m/min) → heated draw roll (4,500 m/min) in an insulated chamber → interlacing device → roll (4,800 m/min) → wind-up.	5/22/75
71669	Bolitsin, M. N., et al. Yarn made of filaments with complex cross-section.	7/17/75
462010	Allied Chemical Below the spinneret is a short zone with still air, then a quenching zone with air drawn-in from one side and drawn-off at upper part of the opposite side; production capacity is increased.	10/28/75
462236	Monsanto Filaments after being quenched are passed around a heated roller, and then around a second roller for drawing at a ratio of 4; the yarn becomes textured when exposed to dry heat at 180°C.	12/23/77
462213	Monsanto The productivity for producing undrawn carpet and tire yarns is increased by utilizing a heat feed roll (40-150°C) and by eliminating the steam conditioning and convergence guide associated therewith.	12/27/77

Table 7.6

HIGH SPEED SPINNING AND COUPLE SPINNING**PATENT SUMMARY**

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71907	Snia Viscosa	4/17/63
	A coupled spinning-drawing process consisting of exposing filaments to a steam-air mixture at about 100°C for 1-3 sec in one chamber, heating them, in a second chamber, at 60-70°C for 1-6 sec, and then drawing.	
71829	Toyo Rayon	8/2/63
	The spun filament is directly drawn in two stages, at 65°C and 210°C respectively.	
406162	Rhodiaceta	6/10/67
	Direct spinning-stretching, speed 1,200 m/min.	
391991	ICI	3/15/68
	Filaments after being congealed are contacted with a finish containing less than 10% water and then are drawn directly; drawing is more uniform than when a finish having a high water content is used.	
71908	Du Pont	9/10/69
	A coupled spinning-drawing with steaming after quenching and before drawing; the yarn has a rougher surface than an unsteamed, coupled-process yarn.	
71776	Viscousuisse	4/1/77
	Spinnerets → air quenching → guide, to a bundle → finish roll in a bath → draw roll → steam channel → wind-up, speed 1,200-6,000 m/min.	

Table 7.7

DRAWING
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
33116	Whitin Machine Works	7/6/55
	Slippage of yarn on the feed roll is prevented by a presser roll mounted on an arm pivoted to swing freely about a stud.	
71812	Bayer	1/14/58
	Monofilament, yarn, or tow is subjected to a vibrational stress while being stretched; higher strength is attained than when stretching is used without vibration.	
71811	Du Pont	1/22/58
	Melt-spun filament is cooled to crystallization state, heated to 216-220°C for 10 seconds, and then drawn at a ratio of 4:1.	
71797	Du Pont	3/28/58
	Drawn fiber passes through a heating zone at constant speed, and then through another heating zone with allowance for residual retraction.	
71798	Leesona Corp.	4/23/58
	A winding device is used after drawing-stretching, to maintain a constant speed of winding.	
71819	Canadian Industries Ltd.	3/13/59
	Yarn is wound around the feed roll several times, contacts an idler roll, and is wound around a heated draw roll several times.	
71809	Vereinigte Glanzstoff	7/4/59
	Heat drawing effected on a helical surface.	
71810	British Nylon Spinners	9/18/59
	The feed roll is located between the snubbing pin and drawing roll, so that a sufficiently long path can be attained between the snubbing pin and drawing roll, without overly increasing the total height of the whole set.	
71821	Du Pont	9/20/60
	Drawing occurs over a heated tube, in which flowing oil serves as a means of heating in the bottom portion and a means of cooling in top portion.	
71823	Monsanto	4/10/61
	The draw roll has a polished surface with several roughened strips; slippage and flitting of filaments are avoided.	
71825	Bayer	5/9/61
	Heating between draw roll and feed roll is carried out on a rod, on which the filament is wound helically.	
71827	Monsanto	5/31/61
	Tire cord is drawn on a snubbing pin and after it passes a heating block.	
71824	Monsanto	6/23/61
	Drawing of tire cord takes place in a snake-shaped heating channel, so that all filaments of the cord are heated uniformly.	
71826	Hoechst	7/12/61
	Thermal treatment for drawing is done on a flat iron which has several surfaces, exchangeable by turning.	
71828	British Nylon Spinners	4/24/63
	A device for temporary suppression of drawing at the point of knotting.	
71913	Monsanto	3/13/65
	The filaments are heated by a gas vortex at 250-325°C, and simultaneously stretched; draw ratio can be as high as 5.5:1.	

Table 7.7 (Concluded)

DRAWING
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71799	ICI	3/25/65
	<p>Yarns travelling on a heating plate between the feed roll and the drawing roll, oscillate transversely to avoid forming an abrasive crust on the surface of the plate.</p>	
71830	Fielder Electronics	9/13/65
	<p>Electric temperature controller used on draw-twister roll.</p>	
71914	Celanese	10/1/65
	<p>Filaments and bobbin are immersed in phenol aqueous solution at 95°C for 2 hr, then are washed and dried. The filament is drawn at 100°C to extend it by 100%, and then is annealed at 120°C for 30 minutes; the product has a low density, 1 gm/cc.</p>	
71831	ICI	4/10/67
	<p>Feed roll has a surface with both flat and round microprotuberances substantially parallel to axis; less breaking of filaments.</p>	
392573	ICI	6/12/68
	<p>Yarn is drawn between rolls turning at various speeds and is brought into contact with a narrow jet of hot gas; a yarn of various deniers is formed.</p>	
462065	Teijin	9/26/68
	<p>Yarn is heated to crystallization temperature (but below its melting point) and then drawn.</p>	
71910	Du Pont	10/9/68
	<p>Drawing of monofilament with 15-30 denier, using appropriate tensions before and after the draw zone, an absolute draw ratio greater than 5.4 can be obtained by drawing on a pin and a hot plate.</p>	
71912	Du Pont	3/12/69
	<p>Yarns for tire cord are drawn at constant tension between 75% and 98% of its breaking tension at 200-260°C for 5-120 sec.</p>	
71856	Toray	10/2/69
	<p>Multiple-step drawing.</p>	
71519	Asahi Chemical	10/22/70
	<p>Tire cord is produced by three-step drawing after melt-spinning at 80°, 190°, and 190°C with draw ratios of 1.1, 3, and 1.7, making a total draw ratio of 5.7.</p>	
71765	BASF	1/3/72
	<p>Integrated spinning, drawing, and texturing process: melt-spinning is followed by drawing in three pairs of jacketed godets, and then texturing by air jets on collected filaments at 1,600-2,000 m/min.</p>	
462094	Teijin	4/20/72
	<p>Spun fiber is cooled to 40°C, lubricated at 80°C, and drawn 520% in two stages.</p>	
71667	Du Pont	7/4/73
71806	Du Pont	9/13/76
	<p>Heavy denier polyamide monofilaments are produced by coupled steps of spinning, quenching (through an air gap and water bath), drawing (first stage drawing uses steam heating, and second stage drawing uses radiant heat), and winding.</p>	
71746	Monsanto	5/2/75
	<p>Stretching a tow of filaments under tension through a chamber, and forcing a stream of heated fluid transversely through the tow.</p>	

Crimping (texturing) produces bulkiness in the fiber, thus giving a warm feeling to the ultimate product. This is achieved either by false-twisting (i.e., twisting, followed by heat-setting and releasing or reversing the twist) or by compressing the fiber in a stuffing box or between rolls. Table 7.8 lists patents relating to the crimping of nylon 66 fibers.

Blends containing nylon 66, or a copolymer made from several monomers including HMDA and adipic acid (and therefore containing nylon 66 units in the copolymer chain) can be melt-spun. Table 7.9 lists patents relating to this topic.

The different polyamides (both may be nylon 66, differing in amine end groups, or one may be nylon 66 and the other a copolymer) may be extruded from different orifices in the same spinneret. The result would be a bicomponent yarn. Or, two different polyamides may be extruded through the same orifice (side by side, or as a core and sheath) to form bicomponent filaments. Yarns of such structure often have special desirable properties. Patents relating to this topic are listed in Table 7.10. Reference 71927 in Table 7.10 relates to a nylon 66-polyurethane bicomponent fiber, once produced by Monsanto under the trademark Monvelle® for hosiery use. It performed superbly but was abandoned because of its high production cost.

In the spinning process, the yarn is often treated with a finishing agent (an oil or an aqueous solution containing a lubricant to facilitate processing), or various other chemicals to impart desirable properties. Patents on this topic are listed in Table 7.11.

Fibers are generally used to make fabric by weaving or knitting. A small part of the total output of nylon fiber is made into nonwoven fabrics. Patents relating to the manufacture of nonwoven fabric from nylon 66 are summarized in Table 7.12. In this process, the filament or staple is laid on a web-forming belt. Lurgi has such a process for licensing--the DOCAN process (462216). The fiber on the web is then bonded by a resin or an activated agent. The most important activating agent is hydrogen chloride (see reference 71876 and Monsanto's patents in

Table 7.8

CRIMPING

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71818	British Nylon Spinners Heating under zero tension after crimping.	10/22/60
71883	Allied Chemical Crimping of at least two filaments of light and dark contrasting colors and subjecting them to twisting and entangling.	4/4/67
71846	Rhodiaceta Twisting of yarn on a ring between a heating element and a winding system.	12/12/69
71660	ICI A yarn of nylon 66 staple fiber containing some nylon 6 filaments is false-twisted by a fluid vortex and then is wound on a heated roll. The yarn becomes a compact bundle.	5/20/70
71865	Teijin Bulky nylon 66 yarn made by melt-spinning at 1,200 m/min, gelled, dry-treated at 140°C, drawn 280%, and false-twisted at 210-245°C to give crimped fiber with better crimp rigidity than one prepared by wet heat treatment.	3/15/71
71860	Teijin Cooled melt-spun yarn is lubricated with 90% water-in-oil emulsion, false-twisted, heat set, cooled on a plate at 5°C, drawn, and wound; crimp rigidity is better than that for a yarn lubricated with aqueous emulsion and drawn without cooling.	9/27/72
71768	Phillips Petroleum Tow after drawing is crimped in a stuffing box in the presence of saturated steam.	12/29/72
71847	Montedison Crimping on corrugations of a plane.	10/27/72
462105	Toray Bulky yarn made by twisting, heat treating, and tension winding.	5/15/73
71783	Barmag Barmer Maschinenwerk A yarn consisting of two different polymers (polyamide and polyester) is melt-spun at high speed (2,700-4,500 m/min at draw-off); the package is then heated, and stretched to a ratio of 1:1.25. A crimping effect is achieved.	7/18/73
71781	Ernest Scragg & Sons A friction false twist device consists of three parallel equiangularly spaced shafts each having a set of equiaxially spaced friction discs; the discs are arranged so that they overlap substantially when viewed axially; a strand passing through the center of the device followed a zigzag path.	11/3/73
71739	Toray Industries Manufacture of crimped polyamide yarns: melt-spinning → air quenching → nonaqueous oiling → feed roll → (greater than 200 m/min) → doubling pins → heated roll (170-250°C) → heated draw roll (greater than 800 m/min) → steam jet (200-350°C), impinging on a metallic screen for crimping → tensioning guide → take-up roll → air jet for tangling → take-up roll → winding.	2/26/74

Table 7.9
FIBERS FROM MELT BLENDS OR COPOLYMERS CONTAINING NYLON 66
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71886	Allied Chemical <i>Filaments prepared from nylon having dispersed therein microfibers of polyesters.</i>	5/18/64
391097	Toyo Spinning <i>Bis(α-aminopropyl) ether or bis(α-aminopropyl) ethane and adipic acid or sebacic acid are condensed to form a salt; and this is copolymerized with nylon salt; product is moisture retentive.</i>	10/20/65
392477	Teijin <i>Fiber made from a blend of nylon-polyester-aromatic polyamide has a high Young's modulus.</i>	1/29/66
71889	Teijin <i>Yarn spun from the melt of a blend of nylon 66, polyester, and an aromatic polyamide; Young's modulus is higher than that of fiber made from nylon 66 alone.</i>	1/29/66
392561	Allied Chemical <i>Tire cord is made from a polyamide blend consisting of nylon 66 or nylon 6, and a copolymer of nylon 66 or 6 and an aromatic containing polyamide.</i>	2/3/66
391111	Toyo Rayon <i>Melt spinning of a mixture of polyester and polyamide.</i>	4/20/66
71888	Toyo Rayon <i>Block copolymer of polyamide and polyester, made by solid polymerization at a temperature higher than their glass temperatures and lower than their melting points; fiber produced has a high tenacity and a high initial modulus.</i>	5/18/66
71867	Toyo Rayon <i>Filaments made from nylon 66/6/10 incorporated with p-HOC₆H₄COOBu can be laminated to polyester-cotton by ironing.</i>	7/8/66
71885	Esso Research & Engineering <i>Copolymer of HMDA, adipic acid, and β-vinyladipic acid; tire cord made therefrom has good adhesion to rubber.</i>	7/19/66
71844	Toyo Rayon <i>A terpolymer of nylon salt, caprolactam, and a salt of a dimer acid and HMDA; softening point 70-124 °C.</i>	8/8/66
71843	Toyo Rayon <i>Yarn made of a polyamide and a polyester containing sulfonated polystyrene; antistatic, high modulus, and less yellowing tendency.</i>	12/5/66
462062	Asahi Chemical <i>Spinnable copolymer made from nylon salt and caprolactam and a C₄ or lower diamine and a diacid.</i>	12/23/66
71892	Kanegafuchi Bosei <i>Filaments made from a melt blend of polyamide, polyester, and polyester-ether have improved tenacity, dye affinity, elasticity, and resilience.</i>	2/3/67
347603	Firestone Tire & Rubber <i>Block copolymer of a polyamide and polyester with mp above 200°C is used for making tire cord which has less flat-spotting.</i>	2/16/67
392553	Teijin <i>Filaments made from polyamide, polyester, and nylon 66/6T; high Young's modulus.</i>	3/7/67
71733	Fiber Industries <i>Chips of nylon 66 and nylon 6 are blended, heated below their mp while nitrogen is passed over them to reduce the moisture; on melting, a spinnable block copolymer forms.</i>	3/9/67
391850	Asahi Chemical <i>Nylon 66 and nylon 6 of low relative viscosity are melted together to form a block copolymer having a mp of 200-205°C.</i>	3/17/67
392073	Snia Viscosa <i>A polyamide is mixed with a copolymer of caprolactam and a salt of adipic acid and ethylenediamine; and extruded into filaments, drawn to 4.2 times their original length, and crimped in water at 95°C for 15 minutes; filaments have good latent crimpability.</i>	4/10/67

Table 7.9 (Concluded)

FIBERS FROM MELT BLENDS OR COPOLYMERS CONTAINING NYLON 66

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71562	Toray Industries	7/27/67
	A blend of nylon 66 and a copolymer of nylon salt and a salt of HMDA and polyethylene ether dicarboxylic acid (or a salt of polyethylene ether diamine and adipic acid). Product has permanent antistatic property.	
392508	Kanegafuchi Spinning	9/28/67
	Nylon blended with a mixture of polyethylene terephthalate and polyethylene oxybenzoate.	
392031	Teijin	10/28/67
	Nylon is blended with a polyester containing 2% 3,5-bis(methoxycarbonyl)benzenesulfonate, and spun to form a fiber with a high Young's modulus.	
392554	Teijin	12/8/67
	A blend of nylon, polyester, and polyalkylene ether used for making fiber with a high Young's modulus and antistatic property.	
392550	Teijin	2/8/68
	A blend of nylon, polyester, and a Na-salt of alkyl-polyethoxy-benzene sulfonate is spun to form an antistatic fiber.	
392019	Kanegafuchi Spinning	2/24/68
	Nylon chips containing polyester side by side are melt-spun to form fibers.	
392014	Kurray	5/17/68
	Nylon and polystyrene are spun; the yarn is impregnated with a toluene aqueous suspension and drawn.	
392551	Teijin	5/22/68
	Filaments made from a blend of chips of nylon and polyester.	
391854	Teijin	6/7/68
	Filaments made from nylon and polypropylene with a varying composition along the fiber direction gives nonuniform color on dyeing.	
392010	Teijin	1/8/69
	Chips with nylon core and polyester sheath are melt-spun to form yarns.	
392549	Allied Chemical	4/16/69
	Filaments made from a blend of polyamide and polyester, with 0.1%-5% of sterically hindered phenol added have increased whiteness.	
392547	Allied Chemical	4/29/69
	Same as above, with an additional 0.05%-3% of an organic phosphorus compound.	
462073	Unitika	2/10/70
	A blend of nylon, polyolefin, and a copolymer of nylon 66/6; fiber is immersed in acetic acid for swelling and drawn in water at 50°C; the product is porous and hygrometric.	
392546	Unitika	3/10/71
	Same as above, but without addition of sterically hindered phenol.	
462040	Sun Ventures	11/14/73
462041	Sun Ventures	11/14/73
	Filaments made from a blend of nylon and poly(oxaheptamethylene adipamide); product has high moisture regain.	
71880	Asahi Chemical	1/24/74
	Copolymer of nylon 66/610/6.	
462119	Ube	12/28/74
	Copolymer containing aromatic groups in the chain; used in tire cord.	

Table 7.10
COMPOSITE YARNS AND BICOMPONENT FILAMENTS
PATENT SUMMARY

Reference No.	Assignee	Priority Date
71929	Du Pont	6/30/55
	Core has high amine group end, sheath has low amine group end. Core material is protected from sheath, so dripping and bending during spinning is avoided, while the dyeability is still retained.	
71895	Snia Viscosa	12/23/55
	Composite filaments with two components (one is nylon 66 or nylon 6, the other is a copolymer of nylon 66, or nylon 6 and another polyamide such as nylon 6T) side by side over the cross-section.	
71897	Du Pont	5/26/67
	Copolymer and homopolymer are extruded through orifices of the same spinneret, with the copolymer being extruded through larger orifices; both polymers have the same relative viscosity but the copolymer has a higher melt viscosity. Fiber produced has enhanced bulk.	
462017	Toray	6/9/67
	Polyamide as sheath and polyester as core; more dimensionally stable than nylon alone.	
71882	Du Pont	9/5/67
	Two polymers having different dyeability (one is nylon 66 and the other is a copolymer) are extruded through different orifices of the same spinneret, and combined into a yarn.	
392069	Kurashiki Rayon	7/27/68
	Two polyamides having different intrinsic viscosity are spun simultaneously to give a composite yarn.	
462191	ICI	7/28/69
	Sheath-core filaments with sheath made of a copolymer containing polyalkylene oxide radicals; antistatic.	
462064	Toray	8/15/69
	Nylon 66 and a copolymer of nylon 66 and nylon 6, side by side; crimping effect developed by drawing and heat treating.	
71900	Du Pont	12/17/69
	Eccentrically disposed bicomponent filament made from nylon 66 and nylon 6T or nylon 6I; drawing, heat relaxing, cooling, and stretching produce a crimpable filament.	
462077	Toray	1/13/70
	Nylon and styrene-acrylonitrile copolymer cospun, drawn, then treated with trichloroethylene, and then drawn again to give fine high tenacity filaments.	
462074	Asahi Chemical	3/5/70
	A bicomponent crimpable fiber made from nylon and a block copolymer of nylon 66 and nylon 6.	
462075	Toray	3/10/70
	Nylon sheath and a mixture of polyester containing a secondary amine as core; good crimpability.	
71736	Vickers-Zimmer	4/15/70
	Two polymers of different color or luster are extruded into filaments and combined with a yarn.	
462076	Teijin	6/26/70
	Conjugate fiber made from nylon and a copolymer of caprolactam-naphthalene dicarboxylic acid-diamine; crimpable.	
462080	Kanebo	7/21/70
	Filaments of polyamide and polyester are separately spun, combined into a yarn, treated with an emulsion containing polyurethane and an antistatic agent, and stretched. The yarn is suitable for knitting.	
462079	Asahi Chemical	12/20/70
	Eccentric sheath-core made from nylon containing epichlorohydrin piperazine and polyester; crimped fiber produced by drawing and heating.	

Table 7.10 (Concluded)

COMPOSITE YARNS AND BICOMPONENT FILAMENTS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71926	Monsanto	4/1/71
	Side-by-side filament of nylon and polyurethane (Monsanto's Monvelle® used in hosiery).	
462085	Asahi Chemical	1/28/72
	Side-by-side filament made from a nylon and a copolymer of nylon 66/6/612; fiber has latent crimpability.	
71996	Kanebo	2/24/72
	Polyester and polyamide in a single filament with polyamide dividing polyester into several sections; yarn has natural-fiber feel.	
462096	Asahi Chemical	4/19/72
	Nylon is cospun with nylon 66/6/612; drawing, heating, and steaming gives a crimped fiber.	
71649	Asahi Chemical	7/27/72
	A filament with two eccentrically dispersed components (one is nylon 66 or other homo-nylon, the other is a random copolymer of nylon 66/6, 66/6/6T, or 66/6/610) has superior crimpability.	
462103	Unitika	2/22/73
	A copolymer of caprolactam, nylon salt and Na-di-methyl-sulfoisophthalate is spun together with nylon 66, and later extracted with water; a fiber with good hand and dyeability is obtained.	
71917	Du Pont	6/19/73
	A filament consisting of a polyethylene-carbon black or a nylon 6-carbon black core and a nylon 66 sheath; the filament is conductive and therefore antistatic.	
462111	Asahi Chemical	9/4/73
	Bicomponent fiber of nylon 66 and nylon 66/6/6T; drawing and heating gives latent crimpability.	
462110	Asahi Chemical	9/4/73
	Bicomponent fiber of nylon 66 and nylon 66/6/610; drawing and steaming gives a crimped fiber.	
462109	Asahi Chemical	9/4/73
	Similar to 462096.	
71663	Du Pont	2/15/74
	Yarn made of homofilaments and sheath-core filaments. The core and the homofilaments have the same polymer composition and are fed from one source; the sheath has another polymer composition and is fed from another source. By changing the spinneret pack, the ratio of the two kinds of filaments in the yarn can be changed without changing the ratio of throughput of the two kinds of polyamides.	
71852	Asahi Chemical	7/22/74
	Two yarns made from polyamides with different amounts of amine end groups are twisted and dyed. The dye contrast is excellent.	
71972	Akzona	6/6/75
	Blending nylon and polystyrene and extruding through Y-shaped spinnerets; fiber is antisoiling.	
71757	Du Pont	9/12/75
	Filaments made of acid-dyeable core (amine-ending) and basic-dyeable sheath (containing sulfonate groups); when such filaments are combined with acid-dyeable and basic-dyeable monocomponent filaments, versatile cross-dye styling effect is achieved.	
71754	Du Pont	7/6/76
	Sheath made of nylon 66 or nylon 6 or nylon 612, core made of nylon 6/612/610; the core is eccentric; the spun and drawn two-filament yarn is knit into hose or pantyhose; tumble-steaming of the knitted goods develops the crimping.	
71674	Du Pont	5/11/77
	Bicomponent filaments of nylon 66 and polyester modified with 5-sodium sulfo-isophthalate, with two components side by side in oblong filament cross-sections, are drawn in steam and crimped with steam jet; heating the yarn in aqueous caustic soda causes the components to split apart, forming crimped polyester filaments surrounded by arched polyamide filaments.	

Table 7.11
AFTERTREATMENT OF FILAMENTS OR YARNS
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
392615	Sun Chemical Corp.	8/28/51
	An aqueous sizing composition of polyvinyl acetate containing casein and Na-O-phenylphenate for sizing.	
392572	Phrix-Werke	3/16/53
	A finishing solution containing glycerol, sugar, glycol, et al.	
71863	Pirelli Soc. per Azioni	8/5/53
	Fiber treated by magnetite, powdered C, or metallic sulfite to render it conductive.	
392616	British Nylon Spinners & Shell Development	12/29/53
	A composition made of a hydroxylated polyvinyl resin, mineral oil, soap, and a partial ester of a polyhydric alcohol, with a fatty acid containing more than 8 C atoms.	
71816	Du Pont	8/26/58
	Filaments in unorientated form pass through ethanol containing a dye, and then are drawn to form numerous incipient cracks.	
392556	Horzek, M.	8/15/59
	15%-20% HCHO in ethanol and methanol as sizing, later hardened by citric acid or maleic acid.	
392578	Schiedewitz, H., et al.	10/20/60
	Twist of fiber is stabilized by treating with a solution 25% of which is the reaction product of adipic acid and triethanolamine.	
462162	Onyx Chemical	7/7/61
	An aqueous finish containing an addition product of aliphatic polyamines and polyalkoxy compounds; antistatic.	
392558	British Nylon Spinners	10/27/61
	A finish consisting of an aqueous solution of an aliphatic diester containing at least 12 C, and a nonionic surfactant containing polyalkenyl groups.	
462165	Monsanto	7/10/64
	An aqueous antistatic finish containing an acetylated nonoglyceride, a methoxylated alcohol, and an alcohol emulsifier.	
462168	Monsanto	11/23/64
	An aqueous emulsion containing imidazolinium alkylsulfate, an alkyl ester of a fatty acid and an emulsifier; excellent anti-static and lubricant properties.	
392579	Toyo Rayon	5/11/65
	Filaments immersed in SnCl ₄ solution, and then washed and dried; product has high light stability.	
392585	Kurashiki Rayon	8/31/65
	A mixture of K-ethyl phosphate, polyethylene glycol thioether esters, polyethylene glycol ether esters, polyethylene glycol amine esters, and polyethylene glycol amide esters is a good lubricant for fibers.	
462175	Monsanto	1/6/66
	Filaments pass through a zone exposed to light having wave lengths from 2,700 to 4,500 angstroms in an atmosphere of chlorine and oxygen; static-electrification is reduced and wettability is enhanced.	
462179	Friedlander, H. N., et al.	1/6/66
	Fiber surface rapidly halogenated; result is similar to that in 462175.	
71731	Monsanto	7/6/66
	Yarn is treated with a toluene solution of adipoylchloride; affinity to basic dyes is improved.	
392584	Asahi Chemical	8/26/66
	Nylon 66/6T filaments oiled with CCl ₄ containing nonionic surfactant, paraffin, and an antistatic agent.	
392582	Asahi Chemical	8/26/66
	Same as above, except that methylethylketone is used instead of CCl ₄ .	
392583	Asahi Chemical	8/26/66
	Same as above, except that iso Pr ₂ O is used.	

Table 7.11 (Continued)

AFTERTREATMENT OF FILAMENTS OR YARNS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
392565	Vahala, J., et al.	12/7/66
	Antistatic lubricating composition for undrawn nylon fibers consisting of 14%-23% aqueous emulsion of mineral oil, polyglycol alkyl ethers, Na, K, or ethanolamine salts of Cl-4 alkyl esters of hydroxystearylsulfonic acid, ethanolammonium ricinoleate, ethylene glycol, and a copper salt; light stability is increased.	
392566	Vahala, J., et al.	12/7/66
	Fibril coherence, smoothness, and antistatic properties are imparted to undrawn and untwisted polyamide fibers by applying a 14%-23% aqueous solution of mineral oil, polyglycol alkyl ether, Na, K, or ethanolamine salts of Cl-4 alkylesters of hydroxystearylsulfonic acid, wool wax, benzyl alcohol, and polyethylene glycol.	
392567	Vahala, J., et al.	12/7/66
392563	Vahala, J., et al.	12/7/66
	Long-term antistatic effects and thermal stability are obtained on undrawn nylon fibers with a spinning oil consisting of 92-93% aqueous emulsion of mineral oil, polyglycol ether, K, or Na salts of Cl-4 alkyl esters of hydroxystearylsulfonic acid, K, or Na alkyl phosphoric acid salt, benzyl alcohol, polyethylene glycol, and wool wax.	
392564	Vahala, J., et al.	12/7/66
	Twin undrawn nylon fibers are made smooth, thermally stable, and antistatic by application of 12%-20% emulsion of mineral oil, polyglycol alkyl ester, and K, Na, or ethanolamine salts of Cl-4 alkyl esters of stearylsulfonic acid.	
392590	Toray Industries	2/14/67
	A mixture of Bu oleate, sorbitol dioleate, and a sperm oil alcohol-polyethylene glycol adduct is applied to a polyamide fiber and the fiber is crimped to give a bulky yarn.	
462183	Du Pont	4/21/67
	Fiber is treated with salts of polyoxyalkylene amines and phosphoric esters of monohydroxy alkyl alcohols or polyoxyalkylene monoalkyl ethers; antistatic.	
462178	Du Pont	5/4/67
	An aqueous antistatic emulsion containing n-butyl monoether of a polyoxyalkylene glycol and potassium salt of a mixture of phosphoric monoesters and diesters or a polyol from $C_6H_5CH(CH_3)C_6H_4OH$ and polyalkylene oxide.	
392612	ICI	5/9/67
	Nylon yarn treated with a lubricant consisting of Bu-stearate an ionic surfactant and a nonionic surfactant, has very low friction variation.	
392613	Du Pont	7/6/67
	Cocoanut oil or tricetyl stearate plus an esterified ethylene oxide-sorbitol copolymer plus 0.35%-1% KOH and 2% water; this lubricant for nylon does not form hard, insoluble resin which otherwise would form if KOH is omitted.	
392595	Yuinickika	9/22/67
	Fiber treated with a reaction product of polyoxyethylenated stearylamine and triphenyl cyanurate has washfast antistatic property.	
462180	Du Pont	11/8/67
	An aqueous antistatic emulsion containing a soft paraffin wax, a hard microcrystalline wax, a salt of partial phosphate ester, a polyoxyalkylene derivative of a fatty alcohol and potassium hydroxide.	
392589	Matsumoto Yushi	11/21/67
	Fiber treated with 0.1%-3% of a condensate of an aminophenol with ethylene oxide shows antistatic property.	
392588	Teijin	1/17/68
	Nylon fiber is treated, before it is drawn with a paste compound of polyethylene, a nonylphenol-ethylene oxide adduct, KOH, and water, and then with a mixture of Bu-oleate, decaethylene glycol monolaurate, pentaethylene glycol monooleate, glycerol monooleate, and water; the filament is antistatic.	
462187	Witco Chemical	3/6/68
	An oily antistatic finish containing methyloleate (or stearate), phosphoric ester of Cl0 to Cl4 aliphatic alcohol, KOH aqueous solution, and polyoxyethylene sorbitan tristearate.	
392601	Toray	5/27/68
	A lubricant consisting of polypropylene glycol trimethylolpropane ether trilaureate, ethyl stearate, and an alkylphenol-ethylene oxide adduct, and an alkyl phosphate; it is heat resistant.	
392594	Kanegafuchi Spinning	7/2/68
	A washfast antistatic finish consisting of a xylene solution or dispersion of partially oxidized low mol wt polyethylene.	

Table 7.11 (Continued)

AFTERTREATMENT OF FILAMENTS OR YARNS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
462184	Du Pont	8/9/68
	An antistatic finish consisting of an anionic surfactant, a cationic nitrogen-containing surfactant with at least one 8-20 C chain, and a nitrogen-containing amphoteric surfactant.	
392591	Toray	8/14/68
	A lubricant with heat stabilization action, consisting of lauryl stearate, sperm oil, an alcohol-ethylene oxide adduct, red oil, and tris(4-hydroxyphenyl) phosphate.	
392592	Toray	8/21/68
	Same as above, with benzyl alcohol instead of phosphate.	
462186	Toray	10/18/68
	An antistatic finish containing a lactam dicarboxylic acid.	
392593	Teijin	10/29/68
	Borate-type anionic surfactant plus sulfate or sulfonate anionic surfactant used as fiber lubricant; excellent stabilization action.	
392603	Teijin	4/8/69
	Fiber treated with glycerol, and then with HCl containing HCHO to reduce glossiness and transparency.	
71915	Monsanto	7/7/69
	Fibers are exposed to SO ₃ , which is later removed by washing, fibers become delustered and have improved soil resistance.	
392598	Yunichika	9/9/69
	An ethylene oxide-fatty acid adduct, a polypropylene glycol-ethylene oxide block polymer, and mineral oil used as lubricant for nylon filaments.	
392599	Yunichika	9/11/69
	Cl2-24 fatty acid ester and ethylene oxide Cl2-19 fatty acid adduct and mineral oil used as lubricant.	
392311	Kanebo	11/24/69
	A lubricant emulsion finish for yarns containing octyl palmitate, K-polyethylenated alkylphosphate, and polyoxyethylene sorbitol ether.	
462069	Unitika	1/14/70
462070	Unitika	1/16/70
	Fibers with a wool-like hand and improved dyeability are obtained by dipping the yarn in sulfuric acid and then in an alcohol.	
462193	Du Pont	4/8/70
	Treating with polyoxypolypropylene glycol polyepoxide and a reaction product of epichlorohydrin and glycerin.	
462196	MK Research & Development	4/23/70
	An antistatic finish containing alkoxyxylated ethylenediamine.	
392569	Witco	5/8/70
392574	Witco	5/11/70
	Antistatic emulsifiable fiber softener consisting of mineral oil, Me-oleate or similar ester, K-salt of phosphoric acid ester of linear Cl0-14 aliphatic alcohol-ethylene oxide adduct, and oleic acid diethanolamide.	
392570	Witco	5/13/70
	Similar to above, but containing fatty acid of pine resin oil, and sulfonated spermaceti oil.	
392577	ICI	6/5/70
	Hydrocarbon oil, nonionic surfactant, and a neutralization product of HMDA and lauric acid; antistatic lubricant.	
392604	Toray	11/24/70
	Lubricant consisting of a fatty diol diester, mineral oil, and a castor oil-ethylene oxide adduct.	
392216	Rohm & Haas	12/14/70
	Acrylate polymer containing quaternary ammonium halide group as antistatic component in the finish. Also refer to journal article 392544.	

Table 7.11 (Continued)

AFTERTREATMENT OF FILAMENTS OR YARNS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
462195	Akzona An antistatic finish containing acylaminopropyl dialkylammonium dialkyl phosphate.	12/16/70
71836	ICI A neutralization product of N-alkyl trimethylenediamine and a fatty acid, together with a nonionic surfactant and a hydrocarbon oil, used as a lubricant finish in nylon yarn spinning; yarn has improved antistatic property.	5/24/71
71800	Ciba Geigy Fibers containing fluorescent whiteners are prevented from staining by treating with an emulsion containing a water-soluble fixing agent, an organic solvent, water, and an organo-soluble dispersing agent.	6/7/71
392607	Asahi Chemical An undrawn nylon filament yarn is treated with an emulsion of oleyl oleate, trispolyethylene glycol, monoalkyl ether phosphate (with hydrophilic-lipophilic balance at 7.3), sulfated oil, and polyacrylate paste. Fabrics made therefrom have good scouring properties.	11/5/71
392606 392609	Asahi Chemical Asahi Chemical A sizing composition for undrawn nylon filament yarn consisting of liquid paraffin, polyethylene glycol alkyl phosphate ester, alkyl imidazoline, and acrylate ester polymer.	11/5/71 11/5/71
392610	Kao Soap Lubricant consisting of an aluminum salt of C8-22 fatty acid having 1 or 2 chains of C4-20 branched alkyl groups.	11/12/71
392611	Kao Soap Heat-resistant lubricant containing C8-18 fatty alcohol diesters of C7-15 saturated dibasic fatty acid having 1 or 2 C2-12 side chains.	11/12/71
392608	Asahi Chemical An undrawn nylon fiber containing polyethylene glycol or its derivative is treated with a lubricant containing Na-hypophosphite.	11/12/71
392614	Allied Chemical A yarn to be processed at high temperature is treated with a finish containing cocoanut oil and a sulfonated natural petroleum product.	1/28/72
462204	Teijin An antistatic emulsion finish consisting of a fatty acid ester of a monohydric or polyhydric alcohol, a reaction product of fatty acid and polyethylene polyamine, a quaternary ammonium salt (cationic surfactant), and an emulsion.	1/29/72
392438	Toho Chemical Antistatic finish containing distridecyl tridecylphosphonate, 2(3-oleayloxy-2-hydroxypropyl)-1,3,2-dioxaborane, and polyethylene glycol monooleyl ether.	2/23/72
71645	ICI US Inc. A lubricating finish consisting of trimethylolalkane esters of fatty acids, imidazolinium alkyl sulfate, and polyoxyethylene-nonylphenol.	8/25/72
462038	Hoechst An antistatic aqueous finish containing K-methyl-n-octadecanephosphonate or similar products.	11/20/72
462106	Teijin An emulsion lubricant for drawing consisting of fatty acid alkali salt.	5/18/73
71770	Rhone-Poulenc Textile Immersing the filament in a polyphonol and ammoniacal silver nitrate solution; the fiber becomes antistatic.	8/1/73
462207	BASF An antistatic finish containing quaternary ammonium compounds with hydroxy groups.	3/1/74
71650	Du Pont Filament drawn in an aqueous bath containing chlorendic acid and an anionic detergent; flame resistance is improved.	5/8/74

Table 7.11 (Concluded)

AFTERTREATMENT OF FILAMENTS OR YARNS

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71752	Hoechst Fibers Industries Pentaerythritol tetrapelargonate plus an adduct of ethylene oxide and hydrogenated castor oil plus Na-alkyl sulfate; a non-fuming finish for yarn texturing.	1/20/75
462004	Du Pont Na-dodecyldiphenyl ether disulfonate and sulfated butyl oleate as a dye leveling agent, applied before drawing.	10/9/75
360313	BASF Wyandotte A reaction product of aldehyde, diamine, and alkylene oxide, for treating fiber to make it antistatic.	12/3/76
462247	Kanebo Heating to 95-135°C and contacting with an aqueous solution containing 0.02%-10% N,N'-methylene-bis-acrylamide and 0.05%-3% of acid (formic, hydrochloric, et al.).	1/6/77
71673	Dow Badische An aqueous solution of alkyoxylated alcohol or thiol as spin finish; chemical used does not turn yellow and is biodegraded in scoured water.	8/15/77
71676	Allied Chemical Spin finish for tire cord yarn, consisting of oxidized polyethylene wax, a white mineral oil, a polyoxyethylene oleyl phosphate, and a sulfonated succinic acid ester of decyl alcohol, emulsified in water and adjusted to a pH of 7.1 to 8.0.	1/18/78
71807	Allied Chemical A spin finish consisting of alkanol amide (from coco fatty acid and diethanol amine), a fluorochemical compound, and an alkyl stearate, for polyamide to be processed to bulked textile yarn.	2/2/78

Table 7.12
NONWOVEN FABRICS FROM NYLON 66 FIBER
PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71202	Du Pont	12/1/61
	Nylon 66 filaments and filaments made from a low melting copolymer are guided together to form a sheet, which is treated with steam or hot air.	
71017	BASF	8/14/62
	Bonding by impregnating in an aqueous solution of diamine and then in a benzene solution of adipoyl dichloride.	
387848	Phillips Petroleum	9/3/63
	Partial splitting of a film to form fiber used for making nonwoven fabrics.	
71916	Carl Freudenberg	2/2/64
	Coplanar row of filaments spun from closely spaced nozzles are impinged by air uniformly and in a nonturbulent way; the filaments are collected as fleece.	
462229	Vereinigte Glanzstoff	12/24/64
	Polyamide filaments are extruded into steam, polyester filaments are extruded into hot air (both steam and air at prescribed ranges of temperature and velocity); both filaments are directed toward a moving collecting surface; the polyester filaments are subsequently shrunk in the web.	
462211	Monsanto	6/16/67
	Spun filaments are randomly deposited on a conveyer to form a web, which is then sprayed with a solution of nylon in formic acid, calendered, treated with HCl gas, washed, and dried.	
462230	Du Pont	9/22/67
	Bicomponent fiber is spun, cut, crimped, and annealed; spread into a batt, and heated for bonding.	
71922	Monsanto	4/11/68
	Similar to 462211 above, except that HCl in chloroform is used instead of gaseous HCl.	
462210	Monsanto	6/17/68
	Filaments or yarns are bonded together by exposing them to gaseous HCl or HF ₃ .	
462022	Monsanto	7/10/68
	Similar to above.	
462218	Monsanto	3/21/69
	A lightweight, nonwoven bonded web is formed by collecting nylon filaments on a moving foraminous belt with vacuum underneath, and contacting the web with an activating gas.	
462233	Kendall Co.	10/2/69
	A fibrous fleece is bonded first by heat and pressure and then by a thermoplastic film.	
462217	Monsanto	11/21/69
	HCl as an activating agent.	
462232	Mallonee, W. C.	1/2/70
	A chamber in which HCl gas intimately mixes with the nonwoven fabric.	
387209	Toray	4/2/70
	Filaments from a spinneret are solidified by compressed air in an elongated chamber and withdrawn from a nozzle at the bottom; they are deposited on a belt to form a web.	
462222	ICI	5/19/70
	A continuous-filament nylon web is impregnated with an aqueous emulsion of polyethyl acrylate containing 0.12% benzophenone, and then squeezed between hot rolls, and irradiated to effect cross-linking.	
462212	Monsanto	6/29/70
	Mat from spun filaments is exposed to moisture to raise the water content of the fiber to greater than 3%, and then the mat is treated with HCl gas for bonding.	
71882	Monsanto	12/29/72
	Mat made from spun filaments is first exposed to moisture to increase the water content of the fiber to greater than 2%; it is further exposed to a mixture of dilute HCl (<2%) and water vapor (0.5%) to increase the fiber's water content to above 3% and to cause the fiber to absorb HCl to at least 2%. The mat is pressed for bonding and the HCl is finally desorbed.	

Table 7.12). Monsanto's Corex® is probably made this way. Web bonding can also be attained by using a copolymer in the fiber composition, and heating the web near the melting point of the copolymer. Reference 387848 in Table 7.12 teaches a process for making nonwoven fabric from film by splitting.

Patents relating to other features of nylon fiber production are listed in Table 7.13.

In the following pages, five products are evaluated: carpet staple, carpet yarn, tire cord, textile yarn, and hosiery monofilament. Carpet staple and carpet yarn take up the lion's share of the total nylon 66 production. Tire cord and textile yarn are also produced in large quantities. Monofilaments are produced in smaller quantities. Hence, the production quantities in our design cases are assumed to be 50 million lb/yr for carpet staple, carpet yarn, tire cord, and textile yarn, and 6 million lb/yr for hosiery monofilament. For each kind of product, especially textile yarn, the manufacturer produces several grades, differing not only in denier and number of filaments, but also in additives. For our evaluation we have assumed one composition and one structure.

Also in this evaluation, the carpet staple, carpet yarn, and tire cord are assumed to be made directly from the melt (from the polycondensation reactor), while the textile yarn and the hosiery monofilament are assumed to be made from chips. These choices are not inherently necessary, but they reflect general practice.

Fibers on the market but not evaluated here are staple for textiles, and heavy denier textured yarn for industrial purposes (e.g., Cordure® of Du Pont, 6 or 7 denier filament, 140 to 560 filaments per yarn). The manufacturing procedures for these products are essentially similar to those for carpet staple and textile yarn.

Table 7.13

OTHER FEATURES RELATING TO NYLON FIBER PRODUCTION

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71815	Du Pont	3/4/58
	Production of decorative yarns: unorientated yarn → feed rolls → guide → notched rolls → hot pin → drawing roll → roll → wind-up. Notched rolls cause formation of notches in the fiber; and drawing causes alternative regions of clear transparent regions and opaque regions.	
71788	Burke, D. J.	7/28/67
	Drafting rolls made of sulfur-cured styrene-butadiene rubber containing toluene sulfonate, which migrates to the surface of rolls and prevents sticking of fibers.	
462112	Unitika	12/25/70
	Adding 0.1%-1% of an alcohol to nylon melt, melt-spinning in a hot atmosphere to eliminate the alcohol, and stretching after cooling; high tenacity nylon is obtained.	
71851	Teijin	3/2/71
462095	Teijin	5/27/72
	Nylon is melt-spun, drawn and wound up, and then stored in wound-up condition for 24 hours and longer at 40-90°C and 30%-90% relative humidity.	
71780	Elitex	11/8/73
	Device for controlling winding unit.	
71760	Rohm & Haas	2/3/76
	Yarn on a spool is covered by a template which partly covers the yarn spool surface, and a modifier (a sulfonate) is sprayed. On dyeing variegated yarn is produced.	

Manufacture of Carpet Staple

Process Description

The design bases and assumptions are given in Table 7.14. The flow sheet is shown in Figure 7.1 (foldout at end of report). The major equipment list and utilities summary are given in Tables 7.15 and 7.16 respectively.

Table 7.14

CARPET STAPLE FROM NYLON 66 MELT

DESIGN BASES AND ASSUMPTIONS

References	71662, 71782, 71790, 71897 (melt supply) 70194, 71665 (spinning) 71741, 71917, 71929, 71931 (conductive fiber) 462161 Communications from American Barmag
Fiber structure	18 denier, 7-1/2 in. length; trilobal, 50% having modification ratio* at 1.8, 50% having modification ratio* at 2.3. Blend with 1% conductive fiber, which has polyethylene-carbon as core, and nylon 66 containing 8.5% TiO ₂ as sheath.
Spin-draw-texturing	Coupled process Final speed--3,000 meters/min

* Modification ratio is the ratio of the radius of a circle circumscribing the lobes and the radius of a circle inscribed in the lobes.

The nylon 66 carpet staple to be made is 18 denier, 7.5 in. long, trilobal cross-section, with two different modification ratios--1.8 and 2.3 respectively, mixed in a 1:1 ratio (for definition of modification ratio, see the footnote of Table 7.14). In addition, 1% conductive fiber is blended. This is an 18 denier circular fiber with polyethylene-carbon

black as a core, and nylon 66, highly pigmented with titanium dioxide, as a sheath. (The manufacture of conductive fiber is described later.)

The nylon 66 is polycondensed with additives of 0.52% polyethylene oxide, 0.02% titanium dioxide, and 40 ppm capric acetate, in a continuous polycondensation unit, as described in Section 5. The melt flows by one of two alternative routes through a pump and a filter to a melt reservoir. When the filter plugs, the flow takes the other route. The melt reservoir is constructed in such a way that the flow through it is plug-wise. From there, the melt passes to 24 metering pumps, each of which is followed by a spinning pack containing a filter and spinneret. The spinneret is rectangular, 260 mm X 64 mm, with 330 holes of 0.8 mm (outside diameter of the lobe). Below each position is a quench chamber, where air is blown sidewise. The molten stream from the holes congeals to form filaments. Below the quench chamber is a steaming duct, where steam at 7 psig is injected. The tow of 330 filaments from the duct is oiled by a finish solution and pulled and drawn by several rolls, and then textured in a draw-texturing machine to produce bulkiness. By such an operation, a tow of 330 filaments of 5,940 deniers is formed at each position. These tows, together with one tow of core-sheath fiber (described below) are combined to form a big tow, and fed into a cutting machine at a speed of 3,000 meters/min and cut to 7.5 in. lengths. The fiber from the cutter is baled in a baling machine.

The conductive fiber is made in the following manner: Nylon salt is polymerized in a batch reactor, with additives of 8.5% titanium dioxide, 230 ppm manganese hypophosphate, 55 ppm acetic acid, and 35 ppm silicone antifoam agent. Titanium dioxide is added as a slurry; the others are added as aqueous solutions. The resulting nylon 66 is extruded and pelletized into chips. For spinning, the chips are melted in an extruder and low density polyethylene (70%) and carbon black (30%) are mixed in a small jacketed dough mixer. These two molten streams are separately pumped by metering pumps at a ratio of 29 (nylon):1(PE-C), and fed into a spinning pack. This spinning pack has separate filters for the two

streams, and separate channels leading to 80 holes of special structure, giving a core-sheath configuration (71929, 71931). These filaments are quenched, drawn, and then formed into a tow, before they go to the cutting machine, where they are cut, together with the trilobal tows.

Table 7.15

CARPET STAPLE FROM NYLON 66 MELT

MAJOR EQUIPMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Staple
 at 0.95 Stream Factor

Equipment Number	Name	Size, Each	Material of Construction	Remarks
B-101	Air fans (2)	2,400 cfm, 3/4 hp	Carbon steel	Centrifugal type, one set for spare.
B-102	Air fans (2)	800 cfm, 1/4 hp	Carbon steel	Exhaust fan.
E-101	Dowtherm® evaporator	200,000 Btu/hr	316 ss	Not shown in Figure 7.1.
M-101	Spinning packs (24)	10-1/4 in. x 2-1/2 in.	Special hardened steel	333 holes/spinneret; Y-shaped hole.
M-102	Quench chambers (24)	Length 6 ft	Aluminum	
M-103	Steaming ducts (24)	Length 14 ft	Aluminum	
M-104	Draw-texturing machines (24)		304 ss	7 psig steam is injected. For each position, there are one finish roll, two sets of draw rolls, one set of draw-heaters, and one crimper.
M-105	Cutting machines (2)	250,000 denier, 3,000 m/min	Carbon steel and 304 ss	
M-106	Double baling presses (2)		Carbon steel and 304 ss	Automatic packing, one set for spare.
P-101	Melt transfer pumps (2)	40 hp	316 ss	Screw pumps, one set for spare.
P-102	Metering pumps (24)	3 hp	316 ss	Gear pumps, variable speed.
S-101A, B	Melt filters	2 x 167 ft ²	316 ss	31 candles, jacket Dowtherm® heated.
S-102	Air filters (2)		304 ss	Paper filters, one set for spare.
S-103	Dust filter		304 ss	
V-101	Melt reservoir	50 gal	316 ss	Jacket Dowtherm® heated.
V-102	Finish oil vessels (2)	600 gal	304 ss	Jacket steam-heated, 1 hp agitator.
B-201	N ₂ blowers (2)	100 cfm, 3 hp	Carbon steel	Centrifugal type, one set for spare.
E-201	Cooler	50 ft ²	Carbon steel	Fixed-tube type.
M-201	Chip cutter	1,600 lb/hr, 100 fpm	Carbon steel and 304 ss	With 5 hp drive and 4 knives.
M-202	Vacuum dryer	75 gal, 3/4 hp	304 ss	Double-cone type, jacket steam-heated.
M-203	Extruder	1-3/4 in. dia x 24 D, 66 lb/hr	316 ss	Normal drive power: 7.5 kw; total heating power: 9.8 kw.
M-204	Dough mixer	0.7 gal, 1 hp	316 ss	Double-arm type, jacketed, vacuum design.
M-205	Spinning pack	4 in. dia	Special hardened steel	80 holes/spinneret; circular hole.
M-206	Quench chamber	Length 6 ft	Aluminum	
M-207	Steaming duct	Length 14 ft	Aluminum	Similar to M-103.
M-208	Draw-texturing machine		304 ss	Similar to M-104.
P-201	Melt transfer pump	1/8 hp	316 ss	Screw pump.
P-202	Metering pump	1 hp	316 ss	Gear pump, variable speed.
P-203	Metering pump	1/8 hp	316 ss	Gear pump, variable speed.
R-201	Autoclave	100 gal	316 ss clad	Jacket Dowtherm®-heated, with 1/2 hp agitator.
S-201A, B	Nitrogen filters		304 ss	Candle type.
S-202	Melt filter	2 x 5.4 ft ²	316 ss	Twin-chamber, 1 candle/chamber, jacket Dowtherm®-heated.
S-203	Melt filter	2 x 5.4 ft ²	316 ss	Same as S-202.
T-202	Chip storage silo	1,600 gal	304 ss	
T-203	Chip storage silo	230 gal	304 ss	
T-204	Chip feed bin	40 gal	304 ss	
V-201	N ₂ surge vessel	270 gal	Carbon steel	

Small vessels T-101, T-102, T-201 not listed.

Table 7.16

CARPET STAPLE FROM NYLON 66 MELT

UTILITIES SUMMARY

**Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Staple
at 0.95 Stream Factor**

	Battery Limits <u>Total</u>	100 <u>Section</u>	200 <u>Section</u>
Average consumptions			
Cooling water (gpm)	402	390	12
Refrigeration at 40°F (tons)	300	300	0
Process water (gpm)	11	10	1
Electricity (kw)	925	900	25
Steam at 7 psig (lb/hr)	2,400	2,300	100
Steam at 50 psig (lb/hr)	200	100	100
Fuel oil (million Btu/hr)	1	1	0
Inert gas, low pressure (scfh)	5	0	5
Inert gas, high pressure (scfh)	450	450	0
Peak demands			
Cooling water (gpm)	482	470	12
Refrigeration at 40°F (tons)	360	360	0
Process water (gpm)	27	26	1
Electricity (kw)	1,137	1,100	37
Steam at 7 psig (lb/hr)	2,600	2,500	100
Steam at 50 psig (lb/hr)	3,100	3,000	100
Inert gas, high pressure (scfh)	500	500	0

Note: The battery limits figures include electricity and cooling water requirements of refrigeration.

Process Discussion

The composition and structure of the staple is patterned after the commercial Antron® III produced by Du Pont, but SRI does not claim to have described Du Pont's process.

The process described, with spinning-drawing-texturing at each position, and cutting of the combined tows, is a one-step continuous process. The spinning-drawing-texturizing machine is by Barmag. Another West German firm, Neumag, supplies a machine which handles spinning, drawing, texturing, and cutting in one position, to produce staple directly. The smallest machine supplied by Neumag is a two-position one having a capacity of 4 million lb/yr.

The conventional process of producing staple limits the function at each position to spinning; the spun tows are deposited in cans; the cans are taken to a fiber machine in which tows from the cans are combined, stretched, textured, and cut. The present design would call for two fiber machines, each handling 800,000 deniers and winding at a speed of 300 meters/min.

If conductive fiber is not blended in, higher amounts of antistatic additives would be needed in the nylon 66 to reach the same degree of antisoiling. In this case, a major part of such additives is preferably introduced at the melt reservoir, in a procedure similar to that described later in connection with carpet yarn production.

The spinneret holes, at 0.8 mm diameter, are larger than conventional because of the shape (71879).

Cost Estimates

Estimates of the capital investment and production cost are given in Tables 7.17 and 7.18 respectively.

If the conventional process (split process) is used, the capital investment would be reduced by \$1 million, but the labor requirement would be almost doubled. The net production cost and product value would be higher.

Table 7.17

CARPET STAPLE FROM NYLON 66 MELT

CAPITAL INVESTMENT			
	Cost	Capacity Exponent	
		Up	Down
Battery limits equipment, f.o.b.			
Reactors	\$ 22,400		
Vessels and tanks	131,800		
Exchangers	7,400		
Compressors	31,400		
Special equipment	19,500		
Miscellaneous equipment	224,800		
Pumps	<u>37,900</u>		
Total	\$ 475,200	0.49	0.48
Spin-drawing units*	4,297,000		
Conductive fiber production†	298,200		
Process buildings	1,049,600		
BATTERY LIMITS INVESTMENT	\$10,673,000	0.80	0.76
Off-sites			
Cooling tower	\$ 210,800		
Process water treatment	4,900		
Steam generation	116,400		
Refrigeration	374,700		
Inert gas	56,000		
Warehouse facilities	566,400		
Utilities and tankage investment	\$ 1,595,000	0.73	0.69
General service facilities	2,454,000		
Waste treatment	<u>613,000</u>		
OFF-SITES INVESTMENT	\$ 4,662,000	0.73	0.69
TOTAL FIXED CAPITAL	\$15,335,000	0.79	0.75
Start-up costs	\$ 3,157,000		
Working capital	<u>\$ 5,822,000</u>		
TOTAL CAPITAL INVESTMENT	\$24,314,000		

* Including metering pumps, spinning packs, quench chambers, steaming ducts, draw-texturing units, tow cutting machines, baling presses, Dowtherm® evaporator, and electric control units.

† Including chip cutter, extruder, dough mixer, metering pumps, spinning pack, quench chamber, steaming duct, draw-texturing unit, and electric control units for conductive fiber production.

Table 7.18
CARPET STAPLE FROM NYLON 66 MELT

PRODUCTION COSTS			
	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost (¢/lb)			
Raw materials			
Nylon 66 melt	66¢/lb	0.971 lb	64.09
Nylon 66 salt (50%)	25¢/lb	0.0186 lb	0.46
Polyethylene oxide	30¢/lb	0.0051 lb	0.15
Titanium dioxide	49¢/lb	0.0007 lb	0.03
LDPE	34¢/lb	0.00025 lb	0.01
Carbon black	25¢/lb	0.00011 lb	negl
Finish oil	\$1.00/lb	0.0115 lb	1.15
Packaging materials			<u>0.40</u>
Gross raw material cost			66.29
By-product credit, waste filament	60¢/lb	0.033 lb	<u>-1.98</u>
Total credits			<u>-1.98</u>
Utilities			
Cooling water	4.5¢/1,000 gal	4 gal	0.02
Steam	\$5.00/1,000 lb	0.433 lb	0.22
Process water	60¢/1,000 gal	0.103 gal	0.01
Electricity	2.65¢/kwh	0.153 kwh	0.40
Inert gas, high pressure	80¢/1,000 scf	0.075 scf	<u>0.01</u>
Total utilities			0.67
Labor			
Operating, 12 men/shift	\$11.40/hr	0.0021 man-hr	2.40
	<u>Million lb/yr</u>		
	<u>25</u>	<u>50*</u>	<u>100</u>
Investment (\$ million)			
Battery limits	6.3	10.7	18.6
Off-sites	<u>2.8</u>	<u>4.6</u>	<u>7.9</u>
Total fixed capital	9.1	15.3	26.5
Scaling exponents	0.75	0.79	
Production costs (¢/lb)			
Raw materials	66.29	66.29	66.29
By-product credits	-1.98	-1.98	<u>-1.98</u>
Utilities	0.67	0.67	0.67
Maintenance materials, 3%/yr of BL cost	0.78	0.65	0.57
Operating supplies, 10% operating labor	<u>0.32</u>	<u>0.24</u>	<u>0.18</u>
Variable costs	66.08	65.87	65.73
Operating labor	3.20	2.40	1.80
Maintenance labor, 3%/yr of BL cost	0.78	0.65	0.57
Control laboratory, 20% operating labor	<u>0.64</u>	<u>0.48</u>	<u>0.36</u>
Total direct costs	70.70	69.40	68.46
Plant overhead, 80% of total labor	3.69	2.83	2.18
Taxes and insurance, 2%/yr of fixed capital	0.73	0.61	0.53
Depreciation, 10%/yr of fixed capital	3.65	3.07	2.65
Interest on working capital, 9.5%/yr	<u>1.15</u>	<u>1.11</u>	<u>1.07</u>
Plant gate cost	79.92	77.02	74.89
G&A, sales, research, 10% of annual sales	<u>10.00</u>	<u>10.00</u>	<u>10.00</u>
NET PRODUCTION COST	89.92	87.02	84.89
25%/yr return on fixed capital, before taxes	<u>9.10</u>	<u>7.65</u>	<u>6.63</u>
PRODUCT VALUE	99.02	94.67	91.52

* Base case.

Manufacture of Carpet Yarn

Process Description

The design bases and assumptions are given in Table 7.19. The flow sheet is shown in Figure 7.2 (foldout at end of report). The major equipment list and utilities summary are given in Tables 7.20 and 7.21 respectively.

Table 7.19

CARPET YARN FROM NYLON 66 MELT

DESIGN BASES AND ASSUMPTIONS

References	71662, 71782, 71790, 71891, 71938, 70187 Communications from American Barmag Du Pont's Pamphlet
Yarn structure	1,224 denier, 68 filaments, square, with four hollow square holes
Spin-draw-texturing	Coupled process Winding speed--3,000 meters/min.

The carpet yarn produced is 1,224 denier, with 68 filaments each of 18 deniers. The structure has a square cross-section and four square channels within. The nylon 66 is made by continuous polycondensation; 0.8% polyethylene oxide and 40 ppm cupric acetate are added during the reaction. These procedures are described in Section 5. The melt flows through a pump and filter (with alternates to permit cleaning of the filter) to a melt reservoir. Polyethylene oxide at 1.6% of the nylon 66 passes through the melter and is added to the melt reservoir. From the reservoir the melt flows to 32 spinning positions. At each position, there is one metering pump and one spinning pack. In each spinning pack is a filter and a spinneret. The spinneret is 133 mm in diameter and has 272 sets of holes. By one set of holes is meant the numerous holes (0.2 mm dia.), as shown in Figure 7.2. The melt from neighboring holes

in one set merges together so that the melt from each set forms a filament with a square cross-section and four square channels. Below each spinning position is an air quench chamber, serving four yarns of 68 filaments each from the spinning pack. Below the quench chamber is a steaming duct, where steam at 7 psig is injected. The four yarns from the duct go to a finishing roll, and then to a draw texturing machine with four ends. The yarns are then wound at a speed of 3,000 meters/min.

Table 7.20
CARPET YARN FROM NYLON 66 MELT

MAJOR EQUIPMENT				
Equipment Number	Name	Size, Each	Material of Construction	Remarks
B-101	Air fans (2)	2,800 cfm, 3/4 hp	Carbon steel	Centrifugal type, one set for spare.
E-101	Dowtherm® evaporator	200,000 Btu/hr	316 ss	Not shown in Figure 7.2.
M-101	Additives melter	1 in. dia, 18 lb/hr	316 ss	Screw melter, drive power: 2 kw; total heating power: 3 kw.
M-102	Spinning packs (32)	5-1/4 in. dia	Special hardened steel	4 x 68 sets of holes/spinneret.
M-103	Quench chambers (32)	Length 6 ft	Aluminum	
M-104	Steaming ducts (32)	Length 14 ft	Aluminum	7 psig steam is injected.
M-105	Draw-texturing machines (32)		304 ss	For each position, there are one finish roll, two sets of draw rolls, one set of draw-heaters, and one crimper.
M-106	Take-up heads (32)	4 ends/position	304 ss	Winding speed: 3,000 m/min.
P-101	Melt transfer pumps (2)	40 hp	316 ss	Screw pumps, one set for spare.
P-102	Metering pumps (32)	3 hp	316 ss	Gear pumps, variable speed.
S-101A,B	Melt filters	2 x 167 ft ²	316 ss	31 candles, jacketed, Dowtherm®-heated.
S-102	Air filters (2)		304 ss	Paper filters, one set for spare.
V-101	Melt reservoir	50 gal	316 ss	Jacket, Dowtherm®-heated.
V-102	Finish oil vessels (2)	600 gal	316 ss	Jacket steam-heated, 1 hp agitator.

Small tanks T-101 and T-102 not listed.

Table 7.21
CARPET YARN FROM NYLON 66 MELT

UTILITIES SUMMARY

**Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Yarn
at 0.95 Stream Factor**

	<u>Battery Limits</u>	<u>100</u>
	<u>Total</u>	<u>Section</u>
Average consumptions		
Cooling water (gpm)	460	460
Refrigeration at 40°F (tons)	350	350
Process water (gpm)	5	5
Electricity (kw)	1,200	1,200
Steam at 7 psig (lb/hr)	2,900	2,900
Steam at 50 psig (lb/hr)	500	500
Fuel oil (million Btu/hr)	1	1
Inert gas, high pressure (scfh)	580	580
Peak demands		
Cooling water (gpm)	550	550
Refrigeration at 40°F (tons)	430	430
Process water (gpm)	20	20
Electricity (kw)	1,300	1,300
Steam at 7 psig (lb/hr)	3,200	3,200
Steam at 50 psig (lb/hr)	3,000	3,000
Inert gas, high pressure (scfh)	640	640

Note: The battery limits figures include electricity and cooling water requirements of refrigeration.

Process Discussion

The addition of the antistatic agent at the melt reservoir shortly before the spinning would minimize the time of exposure of this chemical to high temperature. The addition of a fraction of the antistatic agent during the polycondensation gives a more uniform distribution.

The production of yarn needs more careful control than that of staple. A means of temperature control as advocated in reference 71938 is preferably added.

The structure of the yarn is patterned after one grade of Du Pont's Antron® carpet filament, except that Antron® probably contains a small fraction ($\leq 0.5\%$) of core-sheath conductive filaments. The preparation of such conductive filaments is by a method similar to that described under carpet staple.

Cost Estimates

Estimates of the capital investment and production cost are given in Tables 7.22 and 7.23 respectively.

Table 7.22

CARPET YARN FROM NYLON 66 MELT

CAPITAL INVESTMENT			
	Cost	Capacity Exponent	
		Up	Down
Battery limits equipment, f.o.b.			
Vessels and tanks	\$ 46,200	0.50	0.47
Compressors	1,600	0.47	0.47
Miscellaneous equipment	212,000	0.61	0.61
Pumps	<u>29,500</u>	0.40	0.38
Total	\$ 289,300	0.57	0.56
Spin-drawing units*	6,440,000	0.95	0.94
Process buildings	931,200	0.90	0.90
BATTERY LIMITS INVESTMENT	\$12,578,000	0.87	0.84
Off-sites			
Cooling tower	\$ 219,100	0.28	0.28
Process water treatment	4,000	0.77	0.77
Steam generation	124,700	0.82	0.82
Refrigeration	419,400	0.73	0.68
Inert gas	45,100	0.24	0.22
Warehouse facilities	1,132,800	0.90	0.90
Utilities and tankage investment	\$ 2,334,000	0.79	0.75
General service facilities	2,982,000		
Waste treatment	<u>746,000</u>		
OFF-SITES INVESTMENT	\$ 6,062,000	0.79	0.75
TOTAL FIXED CAPITAL	\$18,640,000	0.85	0.83
Start-up costs	\$ 3,157,000		
Working capital	<u>\$ 5,863,000</u>		
TOTAL CAPITAL INVESTMENT	\$27,660,000		

*Including additive melter, metering pumps, spinning packs, quench chambers, steaming ducts, draw-texturing units, take-up heads, Dowtherm® evaporator, and electric control units.

Table 7.23

CARPET YARN FROM NYLON 66 MELT

PRODUCTION COSTS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Yarn
 at 0.95 Stream Factor
 PEP Cost Index: 320

	Unit Cost	Consumption/lb	c/lb
Raw material, labor, and utility cost (c/lb)			
Raw materials			
Nylon 66 melt	66¢/lb	0.958 lb	63.23
Polyethylene oxide	30¢/lb	0.0234 lb	0.70
Finish oil	\$1.00/lb	0.0112 lb	1.12
Packaging materials			<u>1.00</u>
Gross raw material cost			66.05
By-product credit, waste filament	60¢/lb	0.029 lb	<u>-1.74</u>
Total credits			<u>-1.74</u>
Utilities			
Cooling water	4.5¢/1,000 gal	4.58 gal	0.02
Steam	\$5.00/1,000 lb	0.566 lb	0.28
Process water	60¢/1,000 gal	0.05 gal	negl
Electricity	2.65¢/kwh	0.187 kwh	0.50
Inert gas, high pressure	80¢/1,000 scf	0.096 scf	<u>0.01</u>
Total utilities			0.82
Labor			
Operating, 11 men/shift	\$11.40/hr	0.0019 man-hr	2.20
Million lb/yr			
	25	50*	100
Investment (\$ million)			
Battery limits	7.0	12.6	22.9
Off-sites	<u>3.5</u>	<u>6.0</u>	<u>10.8</u>
Total fixed capital	10.5	18.6	33.7
Scaling exponents	0.83	0.85	
Production costs (c/lb)			
Raw materials	66.05	66.05	66.05
By-product credits	<u>-1.74</u>	<u>-1.74</u>	<u>-1.74</u>
Utilities	0.82	0.82	0.82
Maintenance materials, 3%/yr of BL cost	0.86	0.77	0.70
Operating supplies, 10% operating labor	<u>0.28</u>	<u>0.22</u>	<u>0.19</u>
Variable costs	66.27	66.12	66.02
Operating labor	2.80	2.20	1.90
Maintenance labor, 3%/yr of BL cost	0.86	0.77	0.70
Control laboratory, 20% operating labor	<u>0.56</u>	<u>0.44</u>	<u>0.38</u>
Total direct costs	70.49	69.53	69.00
Plant overhead, 80% of total labor	3.37	2.73	2.38
Taxes and insurance, 2%/yr of fixed capital	0.84	0.75	0.67
Depreciation, 10%/yr of fixed capital	4.20	3.73	3.37
Interest on working capital, 9.5%/yr	<u>1.15</u>	<u>1.11</u>	<u>1.09</u>
Plant gate cost	80.05	77.85	76.51
G&A, sales, research, 10% of annual sales	<u>10.00</u>	<u>10.00</u>	<u>10.00</u>
NET PRODUCTION COST	90.05	87.85	86.51
25%/yr return on fixed capital, before taxes	<u>10.50</u>	<u>9.30</u>	<u>8.42</u>
PRODUCT VALUE	100.55	97.15	94.93

*Base case.

Manufacture of Tire Cord

Process Description

The design bases and assumptions are given in Table 7.24. The flow sheet is shown in Figure 7.3 (foldout at end of report). The major equipment and utilities summary are given in Tables 7.25 and 7.26 respectively.

Table 7.24

TIRE CORD FROM NYLON 66 MELT

DESIGN BASES AND ASSUMPTIONS

References	71782, 71662, 71790 (melt supply) 71662 (spinning) Communications from American Barmag
Fiber structure	980 denier yarn, 140 filaments, circular
Composition	Nylon 66, relative viscosity 100
Spin-drawing	Coupled process Spinning speed 800 meters/min. Draw ratio 5 Winding speed 4,000 meters/min.

For making tire cord, nylon 66 needs to have a relative viscosity of 80 to 110 instead of 30 to 50 as for the other fibers. Such nylon 66 is preferably made by polycondensation with the last step being at a higher temperature and under an atmosphere of formic acid vapor, as mentioned in Section 5. The composition of nylon 66 contains a heat stabilizer, but no antistatic agent or delusterers.

The melt passes through pumps, filters, and a reservoir to spinning positions, just as in the manufacture of carpet staple and yarn. There are 32 spinning positions, each with a metering pump and a spinning pack. Each spinning pack contains a filter and a spinneret of 171 mm diameter, with 560 holes. The 560 filaments from one position pass through an air

quench chamber and a steaming duct, and then combine to become four yarns. Each of the four yarns passes through a guide to a finishing roll and drawing rolls, and are then wound at a speed of 4,000 meters/min.

The above procedures (spinning roll to winding) are done in a spin-draw-winding machine. Thirty-two machines with four ends are needed for the design case capacity of 50 million lb/yr. The product is a yarn of 980 deniers, consisting of 140 filaments, each 7 deniers.

Table 7.25
TIRE CORD FROM NYLON 66 MELT

MAJOR EQUIPMENT				
Equipment Number	Name	Size, Each	Material of Construction	Remarks
B-101	Air fans (2)	3,200 cfm, 1 hp	Carbon steel	Centrifugal type, one set for spare.
E-101	Dowtherm® evaporator	200,000 Btu/hr	316 ss	Not shown in Figure 7.3.
M-101	Spinning packs (32)	6-3/4 in. dia	Special hardened steel	4 x 140 holes/spinneret; circular hole.
M-102	Quench chambers (32)	Length 6 ft	Aluminum	
M-103	Steaming ducts (32)	Length 14 ft	Aluminum	7 psig steam is introduced.
M-104	Spin-drawing machines (32)		304 ss	For each position, there are one finish roll, four sets of draw rolls, and one set of draw-heater.
M-105	Take-up heads (32)	4 ends/position	304 ss	Winding speed: 4,000 m/min.
P-101	Melt transfer pumps (2)	40 hp	316 ss	Screw pumps, one set for spare.
P-102	Metering pumps (32)	3 hp	316 ss	Gear pumps, variable speed.
S-101A,B	Melt filters	2 x 167 ft ²	316 ss	31 candles, jacketed, Dowtherm®-heated.
S-102	Air filters (2)		304 ss	Paper filters, one set for spare.
V-101	Melt reservoir	50 gal	316 ss	Jacket Dowtherm®-heated.
V-102	Finish oil tanks (2)	600 gal	304 ss	Jacket steam-heated, with 1 hp agitator.

Small tanks T-101 and T-102 not listed.

Table 7.26
TIRE CORD FROM NYLON 66 MELT

UTILITIES SUMMARY

**Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Cord
at 0.95 Stream Factor**

	<u>Battery Limits</u>	<u>100</u>
	<u>Total</u>	<u>Section</u>
Average consumptions		
Cooling water (gpm)	480	480
Refrigeration at 40°F (tons)	370	370
Process water (gpm)	11	11
Electricity (kw)	1,200	1,200
Steam at 7 psig (lb/hr)	2,900	2,900
Steam at 50 psig (lb/hr)	500	500
Fuel oil (million Btu/hr)	1	1
Inert gas, high pressure (scfh)	630	630
Peak demands		
Cooling water (gpm)	570	570
Refrigeration at 40°F (tons)	440	440
Process water (gpm)	27	27
Electricity (kw)	1,400	1,400
Steam at 7 psig (lb/hr)	3,200	3,200
Steam at 50 psig (lb/hr)	3,000	3,000
Inert gas, high pressure (scfh)	700	700

Note: The battery limits figures include electricity and cooling water requirements of refrigeration.

Process Discussion

The process described is a coupled process. For making tire cord, the split process has been superseded by the coupled process.

The tire cord made can be further heat treated with steam in a long channel for slightly more elongation, to attain improved strength (71912). Another way is to use high speed spinning (say 4,000 meters/min), then weave the cords into a fabric and subject the fabric to a slight stretching (71662).

Cost Estimates

The capital investment and production costs are estimated and given in Tables 7.27 and 7.28 respectively.

Table 7.27
TIRE CORD FROM NYLON 66 MELT

CAPITAL INVESTMENT

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Cord
 at 0.95 Stream Factor
 PEP Cost Index: 320

	<u>Cost</u>	<u>Capacity</u>		
		<u>Exponent</u>		
		<u>Up</u>	<u>Down</u>	
Battery limits equipment, f.o.b.				
Vessels and tanks	\$ 85,300	0.50	0.48	
Compressors	2,700	0.88	0.88	
Miscellaneous equipment	212,000	0.61	0.61	
Pumps	<u>29,500</u>	0.40	0.38	
Total	\$ 329,500	0.57	0.56	
Spin-drawing units*	7,989,000	0.95	0.95	
Process buildings	931,200	0.90	0.90	
BATTERY LIMITS INVESTMENT	\$15,050,000	0.87	0.86	
Off-sites				
Cooling tower	\$ 221,200	0.29	0.28	
Process water treatment	5,000	0.79	0.75	
Steam generation	124,700	0.82	0.82	
Refrigeration	430,400	0.71	0.70	
Inert gas	46,000	0.25	0.22	
Warehouse facilities	<u>1,132,800</u>	<u>0.90</u>	<u>0.90</u>	
Utilities and tankage investment	\$ 2,352,000	0.78	0.75	
General service facilities	3,480,000			
Waste treatment	<u>870,000</u>			
OFF-SITES INVESTMENT	\$ 6,702,000	0.78	0.75	
TOTAL FIXED CAPITAL	\$21,752,000	0.86	0.84	
Start-up costs	\$ 3,033,000			
Working capital	<u>\$ 5,862,000</u>			
TOTAL CAPITAL INVESTMENT	\$30,647,000			

* Including metering pumps, spinning packs, quench chambers, steaming ducts, drawing units, take-up heads, Dowtherm® evaporator, and electric control units.

Table 7.28

TIRE CORD FROM NYLON 66 MELT

PRODUCTION COSTS

Plant Capacity: 50 Million lb/yr
 (23,000 Metric Tons/yr) Cord
 at 0.95 Stream Factor
 PEP Cost Index: 320

	Unit Cost	Consumption/lb	c/lb
Raw material, labor, and utility cost (c/lb)			
Raw materials			
Nylon 66 melt	66¢/lb	0.989 lb	65.27
Finish oil	\$1.00/lb	0.012 lb	1.20
Packaging materials			<u>1.12</u>
Gross raw material cost			67.59
By-product credit, waste filament	60¢/lb	0.039 lb	<u>-2.34</u>
Total credits			<u>-2.34</u>
Utilities			
Cooling water	4.5¢/1,000 gal	4.73 gal	0.02
Steam	\$5.00/1,000 lb	0.566 lb	0.28
Process water	60¢/1,000 gal	0.108 gal	0.01
Electricity	2.65¢/kwh	0.194 kwh	0.51
Inert gas, high pressure	80¢/1,000 scf	0.105 scf	<u>0.01</u>
Total utilities			0.84
Labor			
Operating, 8 men/shift	\$11.40/hr	0.0014 man-hr	1.60
	Million lb/yr		
	<u>25</u>	<u>50*</u>	<u>100</u>
Investment (\$ million)			
Battery limits	8.3	15.1	27.6
Off-sites	<u>3.8</u>	<u>6.7</u>	<u>12.0</u>
Total fixed capital	12.1	21.8	39.6
Scaling exponents	0.84	0.86	
Production costs (c/lb)			
Raw materials	67.59	67.59	67.59
By-product credits	-2.34	-2.34	-2.34
Utilities	0.84	0.84	0.84
Maintenance materials, 3%/yr of BL cost	1.02	0.92	0.84
Operating supplies, 10% operating labor	<u>0.24</u>	<u>0.16</u>	<u>0.15</u>
Variable costs	67.35	67.17	67.08
Operating labor	2.40	1.60	1.50
Maintenance labor, 2%/yr of BL cost	0.68	0.62	0.56
Control laboratory, 20% operating labor	<u>0.48</u>	<u>0.32</u>	<u>0.30</u>
Total direct costs	70.91	69.71	69.44
Plant overhead, 80% of total labor	2.85	2.03	1.89
Taxes and insurance, 2%/yr of fixed capital	0.97	0.87	0.79
Depreciation, 10%/yr of fixed capital	4.86	4.35	3.95
Interest on working capital, 9.5%/yr	<u>1.16</u>	<u>1.11</u>	<u>1.10</u>
Plant gate cost	80.75	78.07	77.17
G&A, sales, research, 10% of annual sales	<u>10.00</u>	<u>10.00</u>	<u>10.00</u>
NET PRODUCTION COST	90.75	88.07	87.17
25%/yr return on fixed capital, before taxes	<u>12.10</u>	<u>10.90</u>	<u>9.90</u>
PRODUCT VALUE	102.85	98.97	97.07

*Base case.

Manufacture of Textured Textile Yarn

Process Description

The design bases and assumptions are given in Table 7.29. The flow sheet is shown in Figure 7.4 (foldout at end of report). The major equipment list and utilities summary are given in Tables 7.30 and 7.31 respectively.

Table 7.29

TEXTILE YARN FROM NYLON 66 CHIPS

DESIGN BASES AND ASSUMPTIONS

References	71794 (chips system) 71664, 71954 (spinning) Communications from American Barmag
Yarn structure	70 denier yarn of 34 filaments, semi-dull, circular
Composition	Nylon 66 with 0.3% TiO ₂ , 1% KI, 0.25% H ₃ PO ₄ , and 0.015% copper acetate added during its polycondensation
Spin-drawing	Split process
Spinning	5,500 meters/min at winding
Draw-texturing	1.25 ratio 700 meters/min at winding

Nylon chips are stored in a silo. The chips are transferred to six feed lines by pneumatic conveyors operated by nitrogen.

From each of the feed bins, the chips enter an extruder. The melt from each extruder passes through a filter and then goes to six metering pumps. Each metering pump supplies the melt to four spinning packs. Each spinning pack contains a filter and a spinneret. The spinneret is 102 mm diameter and has 136 (4 x 34) holes. In an air quench chamber, the filaments from each spinning pack combine to form four yarns, each

having 34 filaments. These four yarns are steamed in a steaming duct by 7 psig steam. Each yarn then passes through a guard, a finishing roll, two drawing rolls, and is then wound at a speed of 5,500 meters/min.

There are altogether 144 (6 x 6 x 4) spin-draw-winding machines, each with four ends. The bobbins are transferred to texturing machines, where the yarn is textured (crimped) and wound. During the texturing, the yarns undergo a moderate draw, at a ratio of 1.25. There are 21 texturing machines, with 216 positions in each machine, and two ends in each position. The product is 70 denier yarn, with 34 filaments.

Yarns of different structures can be produced by using different spinnerets.

Table 7.30
TEXTILE YARN FROM NYLON 66 CHIPS

MAJOR EQUIPMENT

Plant Capacity: 50 Million lb/yr
(23,000 Metric Tons/yr) Yarn
at 0.95 Stream Factor

Equipment Number	Name	Size, Each	Material of Construction	Remarks
B-101	Nitrogen blowers (2)	760 cfm, 30 hp	Carbon steel	Centrifugal type, one set for spare.
B-102	Air fans (2)	7,200 cfm, 2 hp	Carbon steel	Centrifugal type, one set for spare.
E-101	Cooler	390 ft ²	Carbon steel	Fixed-tube type.
E-102	Dowtherm® evaporator	100,000 Btu/hr	316 ss	Not shown in Figure 7.4.
M-101	Extruders (6)	6 in. dia x 24 D, 1.058 lb/hr	316 ss	Normal drive power: 100 kw; total heating power: 75.4 kw.
M-102	Spinning packs (144)	4 in. dia	Special hardened steel	8 x 34 holes/spinneret; circular hole.
M-103	Quench chambers (144)	Length 7 ft	Aluminum	
M-104	Steaming ducts (144)	Length 16 ft	Aluminum	7 psig steam is injected.
M-105	Spin-drawing machines (144)		304 ss	For each position there are one finish roll and two draw rolls.
M-106	Take-up heads (144)	8 ends/position	304 ss	Winding speed: 5,500 m/min.
M-201	Texturing machines (21)	216 positions/set, 2 ends/position 700 m/min	304 ss	Friction-texturing type. Drive power: 45 kw; heating power: 79.2 kw.
P-101	Metering pumps (36)	3 hp	316 ss	Gear pumps, variable speed.
S-101A,B	Nitrogen filters (2)		304 ss	Candle type.
S-102	Melt filters (6)	2 x 37.7 ft ²	316 ss	Twin-chamber, 7 candles/chamber, jacketed, Dowtherm®-heated.
S-103	Air filters (2)		304 ss	Paper filters, one set for spare.
T-101	Chip storage silos (2)	4,800 gal	304 ss	
T-102	Chip feed bins (6)	320 gal	304 ss	
V-101	N ₂ surge vessel	2,050 gal	Carbon steel	
V-102	Finish oil vessels (2)	600 gal	304 ss	Jacket steam-heated, 1 hp agitator.

Small tanks T-103 and T-104 not listed.

Table 7.31
TEXTILE YARN FROM NYLON 66 CHIPS

UTILITIES SUMMARY			
	Battery Limits	100	200
	<u>Total</u>	<u>Section</u>	<u>Section</u>
Average consumptions			
Cooling water (gpm)	1,480	950	530
Refrigeration at 40°F (tons)	1,070	660	410
Process water (gpm)	24	24	0
Electricity (kw)	4,200	2,700	1,500
Steam at 7 psig (lb/hr)	9,100	9,100	0
Steam at 50 psig (lb/hr)	500	500	0
Inert gas, low pressure (scfh)	35	35	0
Inert gas, high pressure (scfh)	990	990	0
Peak demands			
Cooling water (gpm)	1,830	1,200	630
Refrigeration at 40°F (tons)	1,290	800	490
Process water (gpm)	41	41	0
Electricity (kw)	6,600	3,100	3,500
Steam at 7 psig (lb/hr)	10,100	10,100	0
Steam at 50 psig (lb/hr)	3,000	3,000	0
Inert gas, high pressure (scfh)	1,100	1,100	0

Note: The battery limits figures include electricity and cooling water requirements of refrigeration.

Process Discussion

The above process uses high speed spinning. Instead, a slower speed, 1,200 meters/min, can be used, and the yarn can be drawn at a ratio greater than 3. The high speed spinning gives a product of better quality.

This process as described produces a textured yarn. If a draw-twister is used, instead of a draw-texturing machine, the product would be a yarn without the bulky effect.

Cost Estimates

The capital investment and production cost are estimated in Tables 7.32 and 7.33 respectively.

Table 7.32
TEXTILE YARN FROM NYLON 66 CHIPS

CAPITAL INVESTMENT		<u>Capacity Exponent</u>	
Cost	Up	Down	
Battery limits equipment, f.o.b.			
Vessels and tanks	\$ 323,800		
Exchangers	12,700		
Compressors	39,700		
Miscellaneous equipment	466,400		
Pumps	<u>13,800</u>		
Total	\$ 856,400	0.38	0.37
Spinning machines*	17,882,000		
Texturing machines	11,550,000		
Process buildings	7,193,600		
BATTERY LIMITS INVESTMENT	\$54,389,000	0.89	0.87
Off-sites			
Cooling water	\$ 314,000		
Process water treatment	6,900		
Steam generation	230,300		
Refrigeration	1,086,400		
Inert gas	71,400		
Warehouse facilities	1,100,800		
Utilities and tankage investment	\$ 3,372,000	0.82	0.81
General service facilities	11,552,000		
Waste treatment	<u>2,888,000</u>		
OFF-SITES INVESTMENT	\$17,812,000	0.82	0.81
TOTAL FIXED CAPITAL	\$72,201,000	0.88	0.86
Start-up costs	\$ 8,302,000		
Working capital	<u>\$ 9,731,000</u>		
TOTAL CAPITAL INVESTMENT	\$90,234,000		

* Including extruders, metering pumps, spinning packs, quench chambers, steaming ducts, drawing units, take-up heads, Dowtherm® evaporator, and electric control units.

Table 7.33
TEXTILE YARN FROM NYLON 66 CHIPS

PRODUCTION COSTS			
Plant Capacity: 50 Million lb/yr (23,000 Metric Tons/yr) Yarn at 0.95 Stream Factor PEP Cost Index: 320			
	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>\$/lb</u>
Raw material, labor, and utility cost (\$/lb)			
Raw materials			
Nylon 66 chips	82.9¢/lb	0.994 lb	82.40
Finish oil	\$1.00/lb	0.0168 lb	1.68
Packaging materials			<u>1.60</u>
Gross raw material cost			85.68
By-product credit, waste filament	60¢/lb	0.052 lb	<u>-3.12</u>
Total credits			-3.12
Utilities			
Cooling water	4.5¢/1,000 gal	14.7 gal	0.07
Steam	\$5.00/1,000 lb	1.6 lb	0.80
Process water	60¢/1,000 gal	0.232 gal	0.01
Electricity	2.65¢/kwh	0.68 kwh	1.80
Inert gas, high pressure	80¢/1,000 scf	0.165 scf	<u>0.01</u>
Total utilities			2.69
Labor			
Operating, 38 men/shift	\$11.40/hr	0.0067 man-hr	7.59
	<u>Million lb/yr</u>		
	<u>25</u>	<u>50*</u>	<u>100</u>
Investment (\$ million)			
Battery limits	29.8	54.4	100.6
Off-sites	<u>9.9</u>	<u>17.8</u>	<u>32.6</u>
Total fixed capital	39.7	72.2	133.2
Scaling exponents	0.86	0.86	
Production costs (\$/lb)			
Raw materials	85.68	85.68	85.68
By-product credits	-3.12	-3.12	-3.12
Utilities	2.69	2.69	2.69
Maintenance materials, 2%/yr of BL cost	2.42	2.21	2.05
Operating supplies, 10% operating labor	<u>0.84</u>	<u>0.76</u>	<u>0.72</u>
Variable costs	88.51	88.22	88.02
Operating labor	8.39	7.59	7.19
Maintenance labor, 1%/yr of BL cost	1.23	1.13	1.04
Control laboratory, 10% operating labor	<u>0.84</u>	<u>0.76</u>	<u>0.72</u>
Total direct costs	98.97	97.70	96.97
Plant overhead, 40% of total labor	4.18	3.79	3.58
Taxes and insurance, 2%/yr of fixed capital	3.18	2.89	2.66
Depreciation, 10%/yr of fixed capital	15.87	14.44	13.31
Interest on working capital, 9.5%/yr	<u>1.90</u>	<u>1.86</u>	<u>1.82</u>
Plant gate cost	124.10	120.68	118.34
G&A, sales, research, 10% of annual sales	<u>14.00</u>	<u>14.00</u>	<u>14.00</u>
NET PRODUCTION COST	138.10	134.68	132.34
25%/yr return on fixed capital, before taxes	<u>39.70</u>	<u>36.10</u>	<u>33.30</u>
PRODUCT VALUE	177.80	170.78	165.64

*Base case.

Manufacture of Hosiery Monofilament

Process Description

The design bases and assumptions are given in Table 7.34. The flow sheet is shown in Figure 7.5 (foldout at end of report). The major equipment list and utilities summary are given in Tables 7.35 and 7.36 respectively.

Table 7.34

HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

DESIGN BASES AND ASSUMPTIONS

References	387888 (structure) 71794 (chips system) 71733 (copolymer) Communications from American Barmag
Fiber structure	15 denier (average). Each filament is circular and bicomponent, side-by-side.
Composition	One component is nylon 66, with 1% KI, 0.25% H_3PO_4 , and 0.015% copper acetate added during polycondensation. Another component is block copolymer of 70% nylon 66 and 30% nylon 6, made from nylon 66 chips and nylon 6 chips.
Spin-drawing	Coupled process Winding speed 6,000 meters/min.

The product is 15 denier. Each filament has a side-by-side bicomponent configuration, with nylon 66 as one component and a nylon 66/6 copolymer as the other component. The copolymer is made by blending nylon 66 chips (70%) with nylon 6 chips and heating (by a steam jacket) under nitrogen and then feeding into two melt-extruders. At the same time, nylon 66 chips are melt-extruded from another two extruders. From

each extruder the melt feeds three metering pumps. One nylon 66 pump and one nylon 66/6 pump feeds six spinning packs. In each spinning pack, there are separate filters for nylon 66 and nylon 66/6, and a spinneret with channels for both. The spinneret has a diameter of 51 mm and has 16 holes, with each hole being connected to feed channels for nylon 66 and for nylon 66/6 side-by-side. The 16 filaments from each spinning pack pass through an air quench chamber and a steaming duct, and are guided to two spin-draw-winding machines, where they are then wound at a speed of 6,000 meters/min. There are altogether 72 spin-draw-winding machines, each with eight ends.

Table 7.35
HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

MAJOR EQUIPMENT				
Equipment Number	Name	Size, Each	Material of Construction	Remarks
B-101	Nitrogen blowers (2)	180 cfm, 7-1/2 hp	Carbon steel	Centrifugal type, one set for spare.
B-102	Nitrogen blowers (2)	180 cfm, 7-1/2 hp	Carbon steel	Centrifugal type, one set for spare.
B-103	Air fans (2)	1,500 cfm, 1/2 hp	Carbon steel	Centrifugal type, one set for spare.
E-101	Cooler	90 ft ²	Carbon steel	Fixed-tube type.
E-102	Cooler	90 ft ²	Carbon steel	Fixed-tube type.
E-103	Dowtherm® evaporator	50,000 Btu/hr	316 ss	Not shown in Figure 7.5.
M-101	Extruders (2)	3 in. dia x 24 D, 243 lb/hr	316 ss	Normal drive power: 20 kw; total heating power: 20.6 kw.
M-102	Extruders (2)	3 in. dia x 24 D, 243 lb/hr	316 ss	Normal drive power: 20 kw; total heating power: 20.6 kw.
M-103	Spinning packs (36)	2 in. dia	Special hardened steel	16 holes/spinneret; circular hole.
M-104	Quench chambers (36)	Length 6 ft	Aluminum	
M-105	Steaming ducts (36)	Length 16 ft	Aluminum	7 psig steam is injected.
M-106	Spin-drawing machines (72)		304 ss	For each position, there are one finish roll, 4 sets of draw rolls, and one set of draw-heaters.
M-107	Take-up heads (72)	8 ends/position	304 ss	Winding speed: 6,000 m/min.
P-101	Metering pumps (6)	1 hp	316 ss	Gear pumps, variable speed.
P-102	Metering pumps (6)	1 hp	316 ss	Gear pumps, variable speed.
R-101	Tube heaters (2)	4 in. dia x 16 ft	316 ss	Jacket steam-heated.
S-101A,B	Nitrogen filters		304 ss	Candle type.
S-102A,B	Nitrogen filters		304 ss	Candle type.
S-103	Melt filters (2)	2 x 5.4 ft ²	316 ss	Twin-chamber, 1 candle/chamber, jacket Dowtherm®-heated.
S-104	Melt filters (2)	2 x 5.4 ft ²	316 ss	Similar to S-103.
S-105	Air filters (2)		304 ss	Paper filters, one set for spare.
T-101	Mixed chip silo	1,200 gal	304 ss	
T-102	Nylon 66 chip silo	1,200 gal	304 ss	
T-103	Chip feed bins (2)	150 gal	304 ss	
T-104	Chip feed bins (2)	150 gal	304 ss	
V-101	N ₂ surge vessel	500 gal	Carbon steel	
V-102	Finish oil vessels (2)	80 gal	304 ss	Jacket steam-heated, 1/2 hp agitator.

Small tanks T-105 and T-106 not listed.

Table 7.36
HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

UTILITIES SUMMARY		
	Battery Limits <u>Total</u>	100 <u>Section</u>
Average consumptions		
Cooling water (gpm)	430	430
Refrigeration at 40°F (tons)	300	300
Process water (gpm)	3	3
Electricity (kw)	1,300	1,300
Steam at 7 psig (lb/hr)	1,200	1,200
Steam at 50 psig (lb/hr)	100	100
Steam at 250 psig (lb/hr)	700	700
Inert gas, low pressure (scfh)	1,200	1,200
Inert gas, high pressure (scfh)	90	90
Peak demands		
Cooling water (gpm)	500	500
Refrigeration at 40°F (tons)	360	360
Electricity (kw)	1,500	1,500
Steam at 7 psig (lb/hr)	1,400	1,400
Steam at 50 psig (lb/hr)	600	600
Steam at 250 psig (lb/hr)	800	800
Inert gas, low pressure (scfh)	1,300	1,300
Inert gas, high pressure (scfh)	100	100

Note: The battery limits figures include electricity and cooling water requirements of refrigeration.

Process Discussion

The composition and structure follows Du Pont's Cantrece®, but SRI does not claim to have described Du Pont's process.

The blending and heating (in the solid state) under nitrogen of nylon 66 chips and nylon 6 chips causes the formation of a block copolymer which has a higher melting point than a random copolymer obtained by copolymerization of caprolactam, adipic acid, and HMDA (389457, 71692). Another way of producing block copolymer is melt mixing of nylon 66 and nylon 6 with a low relative viscosity (391850). This procedure has the disadvantage that one has to prepare special grades of nylon 66 and nylon 6 as precursors.

Cost Estimates

The capital investment and production cost are estimated in Tables 7.37 and 7.38 respectively.

Table 7.37
HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

CAPITAL INVESTMENT			
	Cost	Capacity Exponent	
		Up	Down
Battery limits equipment, f.o.b.			
Reactors	\$ 23,000	0.60	0.60
Vessels and tanks	117,900	0.58	0.34
Exchangers	16,000	0.27	1.41
Compressors	63,000	0.13	0.13
Miscellaneous equipment	254,400	0.40	0.40
Pumps	<u>5,400</u>	0.14	0.10
Total	\$ 479,700	0.42	0.37
Spin-drawing units*	7,560,000	0.93	0.91
Process buildings	1,216,000	0.90	0.90
BATTERY LIMITS INVESTMENT	\$15,176,000	0.82	0.77
Off-sites			
Cooling tower	\$ 213,400	0.28	0.28
Process water treatment	900	0.85	0.69
Steam generation	65,000	0.82	0.82
Refrigeration	375,400	0.70	0.71
Inert gas	74,600	0.30	0.21
Warehouse facilities	115,200	0.90	0.90
Utilities and tankage investment	\$ 1,013,000	0.62	0.57
General service facilities	3,238,000		
Waste treatment	<u>809,000</u>		
OFF-SITES INVESTMENT	\$ 5,060,000	0.62	0.57
TOTAL FIXED CAPITAL	\$20,236,000	0.81	0.75
Start-up costs	\$ 1,781,000		
Working capital	<u>\$ 1,677,000</u>		
TOTAL CAPITAL INVESTMENT	\$23,694,000		

* Including extruders, metering pumps, spinning packs, quench chambers, steaming ducts, drawing units, take-up heads, Dowtherm® evaporator, and electric control units.

Table 7.38
HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

PRODUCTION COSTS			
Plant Capacity: 6 Million lb/yr (2,700 Metric Tons/yr) Monofilament at 0.95 Stream Factor PEP Cost Index: 320			
	<u>Unit Cost</u>	<u>Consumption/lb</u>	<u>¢/lb</u>
Raw material, labor, and utility cost, ¢/lb			
Raw materials			
Nylon 66 chips	82.9¢/lb	0.8585 lb	71.17
Nylon 6 chips	82.9¢/lb	0.1515 lb	12.56
Finish oil	\$1.00/lb	0.0112 lb	1.12
Packaging materials			<u>1.80</u>
Gross raw material cost			86.65
By-product credit, waste filament	60¢/lb	0.057 lb	<u>-3.42</u>
Total credits			<u>-3.42</u>
Utilities			
Cooling water	4.5¢/1,000 gal	35.1 gal	0.16
Steam	\$5.00/1,000 lb	2.77 lb	1.39
Process water	60¢/1,000 gal	0.2 gal	0.01
Electricity	2.65¢/kwh	1.7 kwh	4.51
Inert gas, low pressure	60¢/1,000 scf	1.58 scf	0.09
Inert gas, high pressure	80¢/1,000 scf	0.125 scf	<u>0.01</u>
Total utilities			6.19
Labor			
Operating, 8 men/shift	\$11.40/hr	0.0117 man-hr	13.32
	<u>Million lb/yr</u>		
	<u>3</u>	<u>6*</u>	<u>12</u>
Investment (\$ million)			
Battery limits	8.9	15.2	26.8
Off-sites	<u>3.1</u>	<u>5.0</u>	<u>8.7</u>
Total fixed capital	12.0	20.2	35.5
Scaling exponents	0.75	0.81	
Production costs (¢/lb)			
Raw materials	86.65	86.65	86.65
By-product credits	<u>-3.42</u>	<u>-3.42</u>	<u>-3.42</u>
Utilities	6.19	6.19	6.19
Maintenance materials, 1.5%/yr of BL cost	4.60	3.90	3.45
Operating supplies, 10% operating labor	<u>2.00</u>	<u>1.33</u>	<u>1.17</u>
Variable costs	96.02	94.65	94.04
Operating labor	19.97	13.32	11.65
Maintenance labor, 1.5%/yr of BL cost	4.60	3.90	3.45
Control laboratory, 10% operating labor	<u>2.00</u>	<u>1.33</u>	<u>1.17</u>
Total direct costs	122.59	113.20	110.31
Plant overhead, 40% of total labor	10.63	7.42	6.51
Taxes and insurance, 2%/yr of fixed capital	8.00	6.75	5.92
Depreciation, 10%/yr of fixed capital	39.97	33.73	29.58
Interest on working capital, 9.5%/yr	<u>2.96</u>	<u>2.66</u>	<u>2.54</u>
Plant gate cost	184.15	163.76	154.86
G&A, sales, research, 10% of annual sales	<u>25.00</u>	<u>25.00</u>	<u>25.00</u>
NET PRODUCTION COST	209.15	188.76	179.86
25%/yr return on fixed capital, before taxes	<u>100.00</u>	<u>84.17</u>	<u>73.96</u>
PRODUCT VALUE	309.15	272.93	253.82

* Base case.

8 NONCONVENTIONAL POLYCONDENSATION PROCESSES FOR MAKING NYLON 66

Commercially, nylon 66 is made from an aqueous solution of nylon salt (hexamethylene diammonium adipate) by heating to evaporate the water and subsequently to polymerize in the molten state. This process has been evaluated in Section 5. Nylon 66 can also be made in other ways: viz., the solid process, the nonaqueous process, the interfacial process, and the bulk process. These processes are briefly discussed in this section.

In the solid process, nylon salt in the solid state is heated below its melting point (197°C) for conversion to nylon 66. The mechanism of this process consists of three steps: the first stage is a recrystallization of nylon salt to form an intermediate compound, which requires 30-60 minutes; a second stage for the formation of comparatively defective polymer structure takes about 2.5-3 hours; and a third stage for ordering of polymer formation with simultaneous crystallization continues for 3-5 hours (71716). The whole process requires a rather long reaction time. Some Russian investigators reported that boric acid, HCl, and oxalic acid can catalyze the reaction (71464, 71725). The solid process has the further disadvantage that additives cannot be uniformly incorporated. Hence, this process is not used, except in a modified way; viz., postpolymerization of nylon 66 to a higher molecular weight product. This has been described in connection with the production of nylon resin in Section 6. Also, copolymers can be formed by heating two polymers in the solid state (71919). This process is described in connection with hosiery monofilament production in Section 7.

The solid process would have the advantage of omitting the water evaporation. Using the process as given in Figure 5 and Tables 5.4-5.9 as the basis, assuming that the evaporation could be omitted, and the duty of the Dowtherm® heater is decreased by an amount corresponding to

the water evaporation, it is estimated that the cost features would be changed by the following amounts:

Battery limits	-\$350,000
Total fixed capital	-\$620,000
Production cost	-1.1¢/lb
Product value	-1.3¢/lb

Since in reality, the processing of solid and molten materials requires different types of equipment, the above assumption is oversimplified. However, the above estimate does give a general concept on the magnitude of the savings. A disadvantage, however, is that the dosage of raw materials is hard to control. Any slight variation may cause nonuniformity of product quality. It seems it is not worthwhile to accept such disadvantages for the slight cost savings.

Recent announcement of BASF's direct casting of fabric from monomer (462250) probably refers to a bulk polymerization. This technique is in the early development stage and little is known about the process.

Patents relating to the nonconventional polycondensation processes for making nylon 66 received by SRI after the issue of PEP Report 54 are listed in Table 8.1.

In Table 8.1 there is one patent (71555) citing adiponitrile instead of adipic acid, to react with HMDA. This approach is interesting in that adiponitrile, unlike adipic acid, can be derived from butadiene or propylene as well as benzene. Therefore, it may be advantageous under the circumstances or in a region where there is a deficiency of benzene and a surplus of butadiene or propylene. However, under the present U.S. price structure, even if one uses the most economic way of producing adiponitrile by butadiene cyanation, adiponitrile is still more expensive than adipic acid, compared on an equal molar basis. This process therefore cannot be economical under the present U.S. price structure.

In addition to the processes mentioned above, there is an emulsion process producing dispersed polyamide particles. These are included in Section 9.

Table 8.1
NYLON 66 BY NONCONVENTIONAL PROCESSES

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
A. Solid Process		
71591	Asahi Chemical	3/18/69
Mol wt of nylon 66 increased by heating under nitrogen; the mol wt is controlled by amount of moisture in nylon 66.		
388217	Du Pont	6/9/72
A continuous process for solid phase polymerization to increase the mol wt.		
B. Bulk Process		
71721	Vereinigte Glanzstoff	11/3/58
Adipic acid and HMDA are added to an extruder through a nitrogen-blanketed feed bin. The extruder melt passes through a line filter to a primary polycondensation vessel and a secondary polycondensation vessel; the latter having a partial reflux condenser to capture volatilized HMDA.		
71602	Toyo Spinning	5/18/72
HMDA containing 5% water is added to molten adipic acid; when temperature has increased by more than 20°C, sample is taken for analysis of end groups; additional diamine or diacid is added for adjustment, and the whole is transferred to a second reactor for completion of reaction.		
71629	Du Pont	8/10/77
A molten mixture of adipic acid with some HMDA is blended with molten HMDA; the whole is heated for reaction.		
462224	Sumitomo Chemical	9/21/77
Bulk polymerization to a low mol wt polymer, and then polymerized in the solid state.		
C. Nonaqueous Solution Processes		
71534	Sumitomo Chemical	10/17/72
Adipic acid and HMDA in dimethylformamide solution, in presence of pyridine and diphenylphosphate; nylon 66 is precipitated.		
71579	Sumitomo Chemical	12/28/74
387943	Sumitomo Chemical	12/28/74
Adipic acid added to a solution of HMDA in pyridine containing phosphorus trichloride; nylon 66 is precipitated; yield 62%.		
D. Other Processes		
71555	Halcon	7/6/72
Nylon 66 from adiponitrile and HMDA.		
71572	BASF	8/28/76
Nylon salt from adipic methyl ester and HMDA.		

9 SPECIAL NYLON 66 PRODUCTS

Aside from the molding plastics and fibers, there are a few other applications of nylon 66. These are described in this section.

Fine Powder

Nylon 66 as a fine powder can form surface coatings by sintering. Such fine-powder nylon 66 can be made in various ways: grinding, spraying, precipitating from a solution or an emulsion. Table 9.1 lists patents relating to the production of nylon 66 fine powder.

Dispersion

Nylon coatings can also be formed by applying an aqueous dispersion of nylon 66. Such a dispersion can be made from nylon 66 or it can be made from a nylon salt, polymerized *in situ* as a dispersion. In the latter case, an emulsion polymerization process is entailed. This constitutes another polymerization process, mentioned in Section 8.

Patents relating to the production of nylon 66 dispersions are listed in Table 9.2.

Melt Adhesives

Some plastics serve as a melt adhesive for textiles. Nylon 66 per se has too high a melting point for this usage, but copolymers of nylon 66, especially nylon 66/6/10 or nylon 66/6/12, are very good adhesives. Patents relating to these copolymers used as adhesives are listed in Table 9.3.

Table 9.1

NYLON 66 POWDER

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
392541	National Distillers & Chemical Corp.	5/25/64
	Heating a polymer under vigorous agitation in water, with addition of a block copolymer of ethylene oxide and propylene oxide, to a temperature well above the melting point of the polymer, under a pressure exceeding the vapor pressure of water at that temperature; on chilling and diluting with water, tiny spheres of polymer are formed.	
462263	Showa Denka	12/6/66
	Nylon is dissolved in N-methyl-2-piperidone or N-2-pyrrolidone by heating at 200°C; and cooled to room temperature to give a gel, which is stirred with 1:1 water-acetone to give powder nylon.	
366201	Sandiz	6/16/71
	Nylon is melted together with naphthalene in an inert gas atmosphere, poured in a thin stream, cooled, and ground at 1400 rpm; naphthalene is removed by extraction.	
409711	Hercules	2/21/73
	Nylon is dissolved in a water-immiscible polar organic solvent, emulsified by water; then a solvent which is miscible with the organic solvent but immiscible with water and a nonsolvent for nylon is added; nylon is precipitated as fine particles.	
462107	Mitsubishi Rayon	5/23/73
	Nylon chips are heat-treated at 100°C for 5 hr in vacuum and then ground with water to form powder.	
462061	Huels	7/9/74
	Cooling a solution of nylon in formamide precipitates the nylon in powder form.	
462137	Nishihara, T.	8/20/75
	Nylon fiber is dissolved in a mixture of C1-5 alcohol and water at high temperature under pressure and cooled to get fine-particle nylon.	
71767	Maruki Shokai	9/24/26
	Similar to above, except that isopropyl alcohol is used.	

Table 9.2
NYLON DISPERSIONS FOR COATING

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71655	ICI	3/30/71
	A 80% HMDA aqueous solution is added to a mixture of adipic acid, aliphatic hydrocarbon and a graft copolymer (12-hydroxymethacrylate/methacrylate) in butyl acetate/ethyl acetate as an emulsifier; water is removed by azeotropic distillation. A stable dispersion of nylon 66 with particle size of 1-5 μ is formed and is useful for coating glass fiber strands.	
71984	FMC	4/27/72
	Nylon is polymerized to low molecular weight polymer and quenched in water to form a dispersion useful for coating.	
71656	Daicel	8/21/73
	A mixture of solutions of nylon 6/66/12 and N-methoxyalkylated nylon; used as a coating.	
71543	FMC	4/30/76
	Same as 71984.	
71774	ICI	5/12/76
	Similar to 71655.	

Table 9.3
NYLON 66 COPOLYMERS AS ADHESIVES

PATENT SUMMARY

<u>Reference No.</u>	<u>Assignee</u>	<u>Priority Date</u>
71890	Inventa	8/14/67
	A tertiary copolymer of nylon 6/66/10 is prepared by melting nylon salt, nylon 10, and amino-caproic acid in the presence of a little sebacic acid at 270°C for 15 hours under agitation, with water vapor continuously removed. The product has a melting point between 110°C and 210°C, depending on composition; useful as an adhesive.	
392517	Inventa	12/3/69
	A tertiary copolymer of nylon 6/66/12 made by heating a blend of three nylons in the presence of sebacic acid.	
462092	Asahi Chemical	5/30/72
	A copolymer of nylon 66/6/6T is made by heating the monomers in water under pressure; useful as an adhesive.	
462028	USM Corp.	9/13/72
	A copolymer of caprolactam, a diamine (including HMDA) and a diacid (including adipic acid), useful as an adhesive.	
462011	Huels	10/10/74
	A nylon 66/612 copolymer to which is added less than 1% acid amide (made from N,N-dimethylpropylamide of tall oil fatty acid, nonylphenol, formaldehyde, and tetraethylene pentamine); adhesive-ness improved by this addition.	

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71966 6 BASF
366054 6 BASF
462042 6 BASF
462046 6 BASF
462056 6 BASF
462057 6 BASF
462246 6 BASF
462248 6 BASF
71017 7 BASF

ACC. CHAP. COMPANY
NO. NO.

71658	7	BASF
71765	7	BASF
71771	7	BASF
71979	7	BASF
462207	7	BASF
71572	8	BASF
360313	7	BASF WYANDOTTE
462008	7	BASF WYANDOTTE
71547	6	BAYER
71861	6	BAYER
71862	6	BAYER
71946	6	BAYER
71973	6	BAYER
462036	6	BAYER
71812	7	BAYER
71825	7	BAYER
71939	7	BAYER
71669	7	BELITSIN, M. N.
462028	9	BOSTIK
71525	5	BRITISH NYLON SPINNERS
71887	5	BRITISH NYLON SPINNERS
71887	6	BRITISH NYLON SPINNERS
71810	7	BRITISH NYLON SPINNERS
71818	7	BRITISH NYLON SPINNERS
71828	7	BRITISH NYLON SPINNERS
71884	7	BRITISH NYLON SPINNERS
392558	7	BRITISH NYLON SPINNERS
392616	7	BRITISH NYLON SPINNERS
388199	6	BURROWS, H. G., ET AL.
71819	7	CANADIAN INDUSTRIES
71916	7	CARL FREUDENBERG, WEINHEIM AN DER PERGSTRASSSE
387536	6	CASSELLA FARBWERKE MAINKUR
71563	6	CELANESE
388175	6	CELANESE
71565	7	CELANESE
71782	7	CELANESE
71914	7	CELANESE
71927	7	CELANESE
387943	8	CELANESE
71839	7	CIBA
71921	6	CIBA-GEIGY
389561	6	CIBA-GEIGY
420399	6	CIBA-GEIGY
420400	6	CIBA-GEIGY
71800	7	CIBA-GEIGY
71801	7	CIBA-GEIGY
71803	7	CIBA-GEIGY
462149	6	CONTINENTAL CAN
71656	9	DAICEL
71673	7	DOW BADISCHE
70608	5	DU PONT
70681	5	DU PONT
70716	5	DU PONT
70791	5	DU PONT
71104	5	DU PONT

ACC. CHAP. COMPANY
NO. NO.

71528 5 DU PONT
71535 5 DU PONT
71544 5 DU PONT
71549 5 DU PONT
71557 5 DU PONT
71624 5 DU PONT
71674 5 DU PONT
71723 5 DU PONT
100356 5 DU PONT
71527 6 DU PONT
71528 6 DU PONT
71533 6 DU PONT
71536 6 DU PONT
71734 6 DU PONT
71738 6 DU PONT
71741 6 DU PONT
71758 6 DU PONT
71998 6 DU PONT
366974 6 DU PONT
388217 6 DU PONT
462007 6 DU PONT
462026 6 DU PONT
462174 6 DU PONT
462226 6 DU PONT
70187 7 DU PONT
70194 7 DU PONT
71650 7 DU PONT
71653 7 DU PONT
71661 7 DU PONT
71663 7 DU PONT
71664 7 DU PONT
71665 7 DU PONT
71674 7 DU PONT
71741 7 DU PONT
71754 7 DU PONT
71757 7 DU PONT
71797 7 DU PONT
71806 7 DU PONT
71811 7 DU PONT
71815 7 DU PONT
71816 7 DU PONT
71821 7 DU PONT
71882 7 DU PONT
71891 7 DU PONT
71897 7 DU PONT
71898 7 DU PONT
71899 7 DU PONT
71900 7 DU PONT
71908 7 DU PONT
71910 7 DU PONT
71912 7 DU PONT
71917 7 DU PONT
71929 7 DU PONT
71931 7 DU PONT
388155 7 DU PONT

ACC. CHAP. COMPANY
NO. NO.

389418 7 DU PONT
392613 7 DU PONT
462004 7 DU PONT
462178 7 DU PONT
462180 7 DU PONT
462183 7 DU PONT
462184 7 DU PONT
462193 7 DU PONT
462205 7 DU PONT
462230 7 DU PONT
71629 8 DU PONT
388217 8 DU PONT
462215 5 DU PONT DEUTSCHLAND
71530 5 DU PONT OF CANADA
71558 5 DU PONT OF CANADA
71621 6 DYNAMIT NOBEL
71780 7 ELITEX ZAVODY TEXTILNHO
71748 6 EMERY INDUSTRIES
462202 7 EMERY INDUSTRIES
71885 7 ESSO RESEARCH + ENGINEERING
71517 5 FIBER INDUSTRIES
71659 6 FIBER INDUSTRIES
71989 6 FIBER INDUSTRIES
71733 7 FIBER INDUSTRIES
71830 7 FIELDEN ELECTRONICS
71960 6 FIRESTONE TIRE + RUBBER
347603 7 FIRESTONE TIRE + RUBBER
71560 5 FISCHER APP ROHRLEI
71543 9 FMC
71984 9 FMC
71974 6 FOSTER GRANT
462035 6 FOSTER GRANT
71550 6 GEIGY, J. R.
71551 6 GEIGY, J. R.
71893 7 GLANZSTOFF
462229 7 GLANZSTOFF
71555 8 HALCON INTERNATIONAL
409711 9 HERCULES
71598 5 HITACHI
71567 4 HOECHST
71840 6 HOECHST
392559 6 HOECHST
462052 6 HOECHST
462053 6 HOECHST
462059 6 HOECHST
462167 6 HOECHST
71826 7 HOECHST
462038 7 HOECHST
71752 7 HOECHST FIBER INDUSTRIES
71580 5 HONDA, T.
392556 7 HROZEK, M.
387538 5 HUELS
462050 6 HUELS
462145 6 HUELS
462011 9 HUELS

ACC. CHAP. COMPANY
NO. NO.

462061 9 HUELS
462153 6 HURT, V., ET AL.
71548 4 ICI
71568 4 ICI
71606 5 ICI
406639 5 ICI
462031 5 ICI
71531 6 ICI
71552 6 ICI
71606 6 ICI
71763 6 ICI
71786 6 ICI
71789 6 ICI
71866 6 ICI
71948 6 ICI
71951 6 ICI
71961 6 ICI
71992 6 ICI
71999 6 ICI
366270 6 ICI
388222 6 ICI
391990 6 ICI
462018 6 ICI
462037 6 ICI
462241 6 ICI
71660 7 ICI
71799 7 ICI
71831 7 ICI
71836 7 ICI
71837 7 ICI
71894 7 ICI
71901 7 ICI
71941 7 ICI
391991 7 ICI
392573 7 ICI
392577 7 ICI
392612 7 ICI
462191 7 ICI
462222 7 ICI
71655 9 ICI
71774 9 ICI
70336 5 ICI FIBERS
366790 5 ICI FIBERS
71645 7 ICI, UNITED STATES
388734 5 INVENTA
71923 6 INVENTA
388734 6 INVENTA
392560 6 INVENTA
462044 6 INVENTA
71890 9 INVENTA
392517 9 INVENTA
71537 6 JAPAN STEEL WORKS
71767 7 KABUSHIKI KAISHA MARUKI SHOKAI
71767 9 KABUSHIKI KAISHA MARUKI SHOKAI
71996 7 KANEBO

ACC. CHAP. COMPANY
NO. NO.

392311 7 KANEBO
392384 7 KANEBO
462080 7 KANEBO
462099 7 KANEBO
462128 7 KANEBO
462247 7 KANEBO
462199 6 KANEAFUCHI SPINNING
71892 7 KANEAFUCHI SPINNING
71895 7 KANEAFUCHI SPINNING
392019 7 KANEAFUCHI SPINNING
392508 7 KANEAFUCHI SPINNING
392594 7 KANEAFUCHI SPINNING
392610 7 KAO SOAP
392611 7 KAO SOAP
462233 7 KENDALL
462152 5 KRASNODAR DESIGN CONSTRUCTION BUREAU
392014 7 KURARAY
392069 7 KURASHIKI RAYON
392585 7 KURASHIKI RAYON
71798 7 LEESONA
462232 7 MALLCNEE, W. C.
392589 7 MATSUMOTO YUSHI-SEIYAKU
392597 7 MATSUMOTO YUSHI-SEIYAKU
71954 7 METALLGESELLSCHAFT
462140 6 MITSUBISHI CHEMICAL
462134 6 MITSUBISHI GAS CHEMICAL
462143 6 MITSUBISHI GAS CHEMICAL
462150 6 MITSUBISHI GAS CHEMICAL
462107 9 MITSUBISHI RAYON
71581 4 MITSUI TOATSU CHEMICALS
462196 7 MK RESEARCH + DEVELOPMENT
71540 6 MONSANTO
71553 6 MONSANTO
71616 6 MONSANTO
71617 6 MONSANTO
71737 6 MONSANTO
71792 6 MONSANTO
71968 6 MONSANTO
71981 6 MONSANTO
71654 7 MONSANTO
71675 7 MONSANTO
71731 7 MONSANTO
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71823 7 MONSANTO
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71827 7 MONSANTO
71902 7 MONSANTO
71903 7 MONSANTO
71904 7 MONSANTO
71905 7 MONSANTO
71913 7 MONSANTO
71915 7 MONSANTO
71922 7 MONSANTO
71926 7 MONSANTO
462022 7 MONSANTO

ACC. CHAP. COMPANY
NO. NO.

462165 7 MONSANTO
462168 7 MONSANTO
462175 7 MONSANTO
462179 7 MONSANTO
462188 7 MONSANTO
462210 7 MONSANTO
462211 7 MONSANTO
462212 7 MONSANTO
462213 7 MONSANTO
462217 7 MONSANTO
462218 7 MONSANTO
462236 7 MONSANTO
71847 7 MONTEDISON FIBRE
71950 6 MUANYAGIPARI
71881 4 MUROMOVA, R. S., ET AL.
392541 9 NATIONAL DISTILLERS + CHEMICAL
462137 9 NISHIHARA, T.
462162 7 ONYX CHEMICAL
71753 6 PHILLIPS FIBERS
462006 7 PHILLIPS FIBERS
71985 6 PHILLIPS PETROLEUM
71745 7 PHILLIPS PETROLEUM
71768 7 PHILLIPS PETROLEUM
387848 7 PHILLIPS PETROLEUM
392572 7 PHRIX-WERKE
71863 7 PIRELLI SOCIETA PER AZIONI
71952 6 RHONE POULENC
462055 6 RHONE-POULENC
462058 6 RHONE-POULENC
462238 6 RHONE-POULENC
462239 6 RHONE-POULENC
462245 6 RHONE-POULENC
71770 7 RHONE-POULENC
71666 7 ROHM + HAAS
71760 7 ROHM + HAAS
392216 7 ROHM + HAAS
462039 6 SANDOZ
366201 9 SANDOZ
392568 6 SANYO CHEMICAL INDUSTRY
71260 5 SCHADE, H., ET AL.
392578 7 SCHIEDEWITZ, H.
71781 7 SCRAGG + SONS
392616 7 SHELL DEVELOPMENT
71943 6 SHELL INTERNATIONAL RESEARCH
462063 9 SHOWA DENKO
71637 4 SMOLYAN, Z. S . ET AL.
71671 6 SNIA VISCOZA
71740 6 SNIA VISCOZA
462029 6 SNIA VISCOZA
71895 7 SNIA VISCOZA
71907 7 SNIA VISCOZA
392073 7 SNIA VISCOZA
462029 7 SNIA VISCOZA
392206 7 SOBICO
71574 5 SOCIETE DE LA VISCOSE SUISSE

ACC. CHAP. COMPANY
NO. NO.

71619	6	SOCIETE DE LA VISCOSE SUISSE
71619	7	SOCIETE DE LA VISCOSE SUISSE
71864	6	SOCIETE RHODIACETA
71983	6	SOCIETE RHODIACETA
71846	7	SOCIETE RHODIACETA
406162	7	SOCIETE RHODIACETA
387216	5	STEHNING, P. R.
462124	6	SUMITOMO CHEMICAL
462127	6	SUMITOMO CHEMICAL
71534	8	SUMITOMO CHEMICAL
71579	8	SUMITOMO CHEMICAL
462224	8	SUMITOMO CHEMICAL
392615	7	SUN CHEMICAL
462040	7	SUN VENTURES
462041	7	SUN VENTURES
71784	6	TECHNOCHEMIE
71589	6	TEIJIN
71622	6	TEIJIN
388556	6	TEIJIN
462066	6	TEIJIN
462144	6	TEIJIN
71520	7	TEIJIN
71845	7	TEIJIN
71851	7	TEIJIN
71853	7	TEIJIN
71854	7	TEIJIN
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71860	7	TEIJIN
71865	7	TEIJIN
71889	7	TEIJIN
391854	7	TEIJIN
392010	7	TEIJIN
392031	7	TEIJIN
392270	7	TEIJIN
392477	7	TEIJIN
392550	7	TEIJIN
392551	7	TEIJIN
392553	7	TEIJIN
392554	7	TEIJIN
392588	7	TEIJIN
392593	7	TEIJIN
392603	7	TEIJIN
462065	7	TEIJIN
462076	7	TEIJIN
462094	7	TEIJIN
462095	7	TEIJIN
462106	7	TEIJIN
462139	7	TEIJIN
462154	7	TEIJIN
462204	7	TEIJIN
462121	6	TERADA COTTON SPINNING
392438	7	TOHO CHEMICAL INDUSTRY
71578	4	TORAY
71594	5	TORAY
71590	6	TORAY

ACC. CHAP. COMPANY
NO. NO.

71593	6	TORAY
389688	6	TORAY
462023	6	TORAY
462034	6	TORAY
462076	6	TORAY
462082	6	TORAY
462383	6	TORAY
462097	6	TORAY
462117	6	TORAY
462235	6	TORAY
71521	7	TORAY
71562	7	TORAY
71588	7	TORAY
71739	7	TORAY
71777	7	TORAY
71856	7	TORAY
71857	7	TORAY
71858	7	TORAY
387209	7	TORAY
392571	7	TORAY
392575	7	TORAY
392590	7	TORAY
392591	7	TORAY
392592	7	TORAY
392601	7	TORAY
392604	7	TORAY
462017	7	TORAY
462064	7	TORAY
462075	7	TORAY
462077	7	TORAY
462086	7	TORAY
462105	7	TORAY
462186	7	TORAY
71785	6	TOYO RAYON
392580	6	TOYO RAYON
70848	7	TOYO RAYON
71829	7	TOYO RAYON
71843	7	TOYO RAYON
71844	7	TOYO RAYON
71867	7	TOYO RAYON
71888	7	TOYO RAYON
391111	7	TOYO RAYON
392579	7	TOYO RAYON
71641	4	TOYO SPINNING
71595	5	TOYO SPINNING
71596	5	TOYO SPINNING
71842	6	TOYO SPINNING
391097	6	TOYO SPINNING
388178	7	TOYO SPINNING
391097	7	TOYO SPINNING
462068	5	TOYOB0
392204	6	TOYOB0
71597	7	TOYOB0
392605	7	TOYOB0
71602	8	TOYOB0

ACC. CHAP. COMPANY
NO. NO.

71518 4 UBE
71603 5 UBE
71778 5 UBE
462148 6 UBE
462119 7 UBE
71577 5 UNITIKA
71605 5 UNITIKA
71582 6 UNITIKA
71586 6 UNITIKA
71587 6 UNITIKA
462084 6 UNITIKA
462130 6 UNITIKA
462132 6 UNITIKA
462133 6 UNITIKA
462067 7 UNITIKA
462069 7 UNITIKA
462070 7 UNITIKA
462073 7 UNITIKA
462103 7 UNITIKA
462108 7 UNITIKA
462112 7 UNITIKA
392563 7 VAHALA, J., ET AL.
392564 7 VAHALA, J., ET AL.
392565 7 VAHALA, J., ET AL.
392566 7 VAHALA, J., ET AL.
392567 7 VAHALA, J., ET AL.
462151 6 VELSICOL CHEMICAL
71809 7 VEREINIGTE GLANZSTOFF-FABRIKEN
71721 8 VEREINIGTE GLANZSTOFF-FABRIKEN
71736 7 VICKERS-ZIMMER
71776 7 VISCOSSUISSE
462200 7 WEEDON, G. C., ET AL.
33116 7 WHITTIN MACHINE WORKS
462045 5 WILTZER, K., ET AL.
392569 7 WITCO CHEMICAL
392570 7 WITCO CHEMICAL
392574 7 WITCO CHEMICAL
462187 7 WITCO CHEMICAL
71583 6 YAMAURA, S.
71584 6 YUNICHIKA
392600 6 YUNICHIKA
392595 7 YUNICHIKA
392598 7 YUNICHIKA
392599 7 YUNICHIKA
71657 7 ZIMMER
71955 7 ZIMMER

Figure 5.1

NYLON 66 BY POLYCONDENSATION
IN A DU PONT CANADA REACTOR

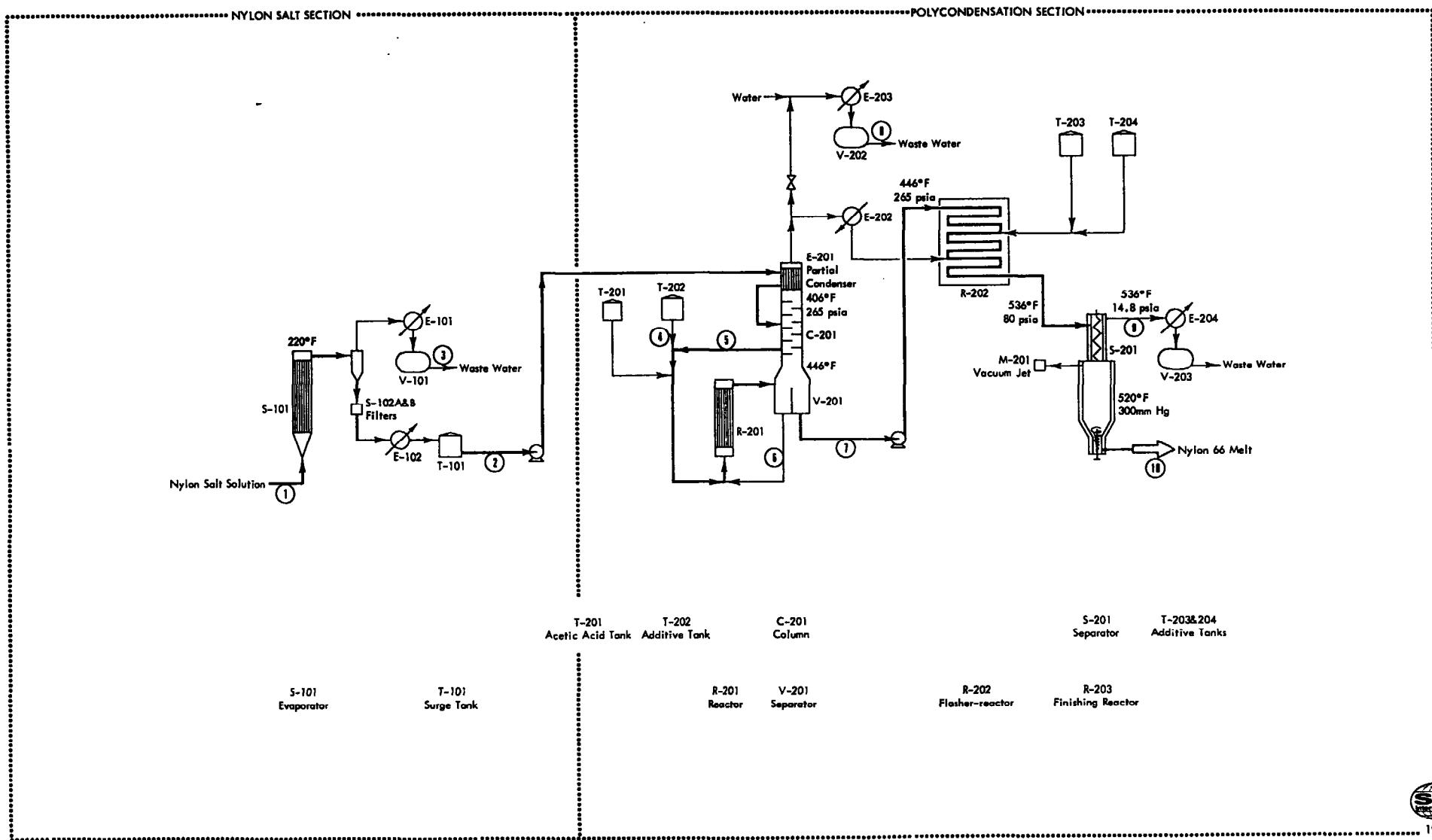


Figure 5.2

NYLON 66 BY POLYCONDENSATION, FIRST STAGE IN A TANK REACTOR

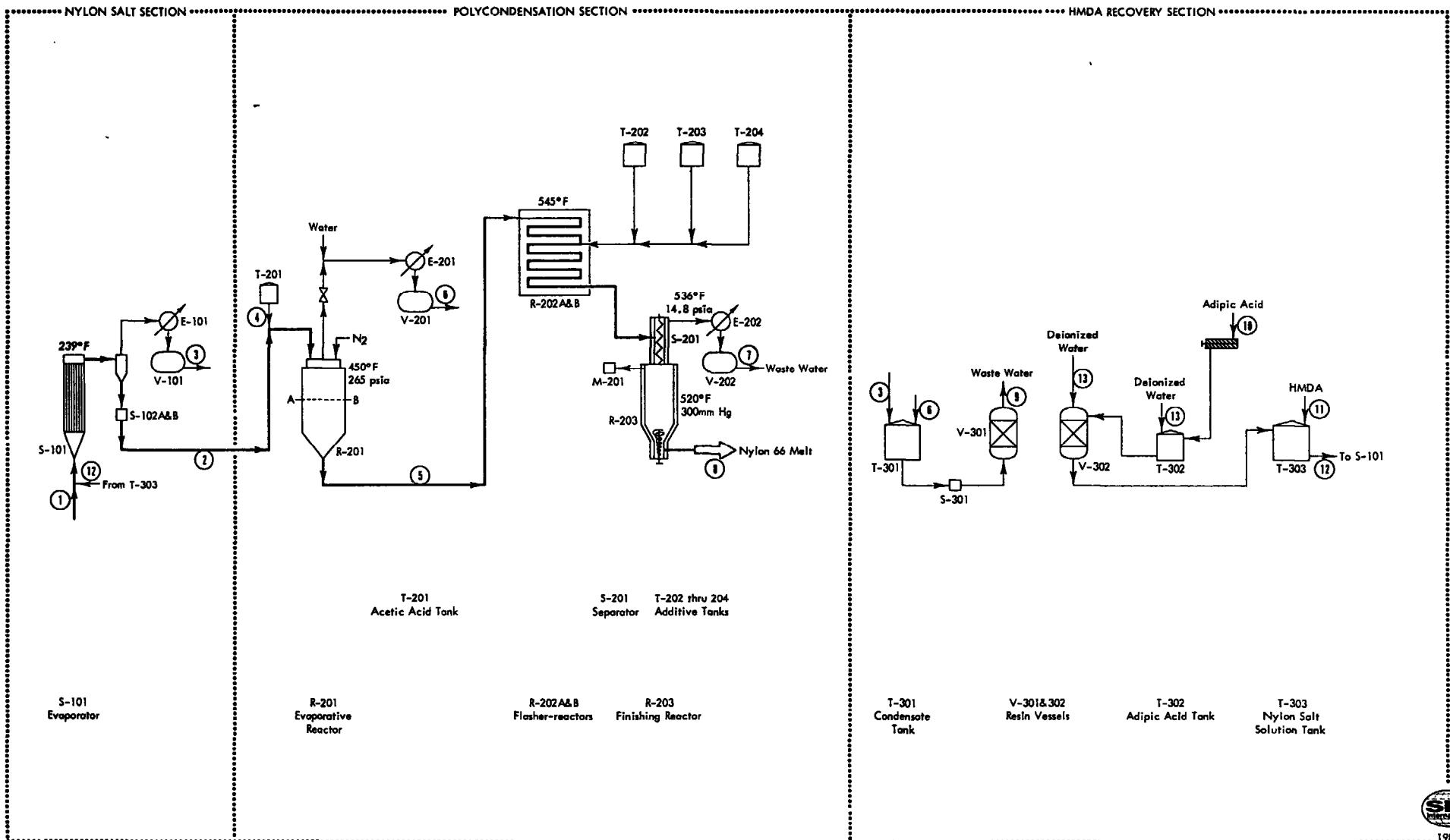
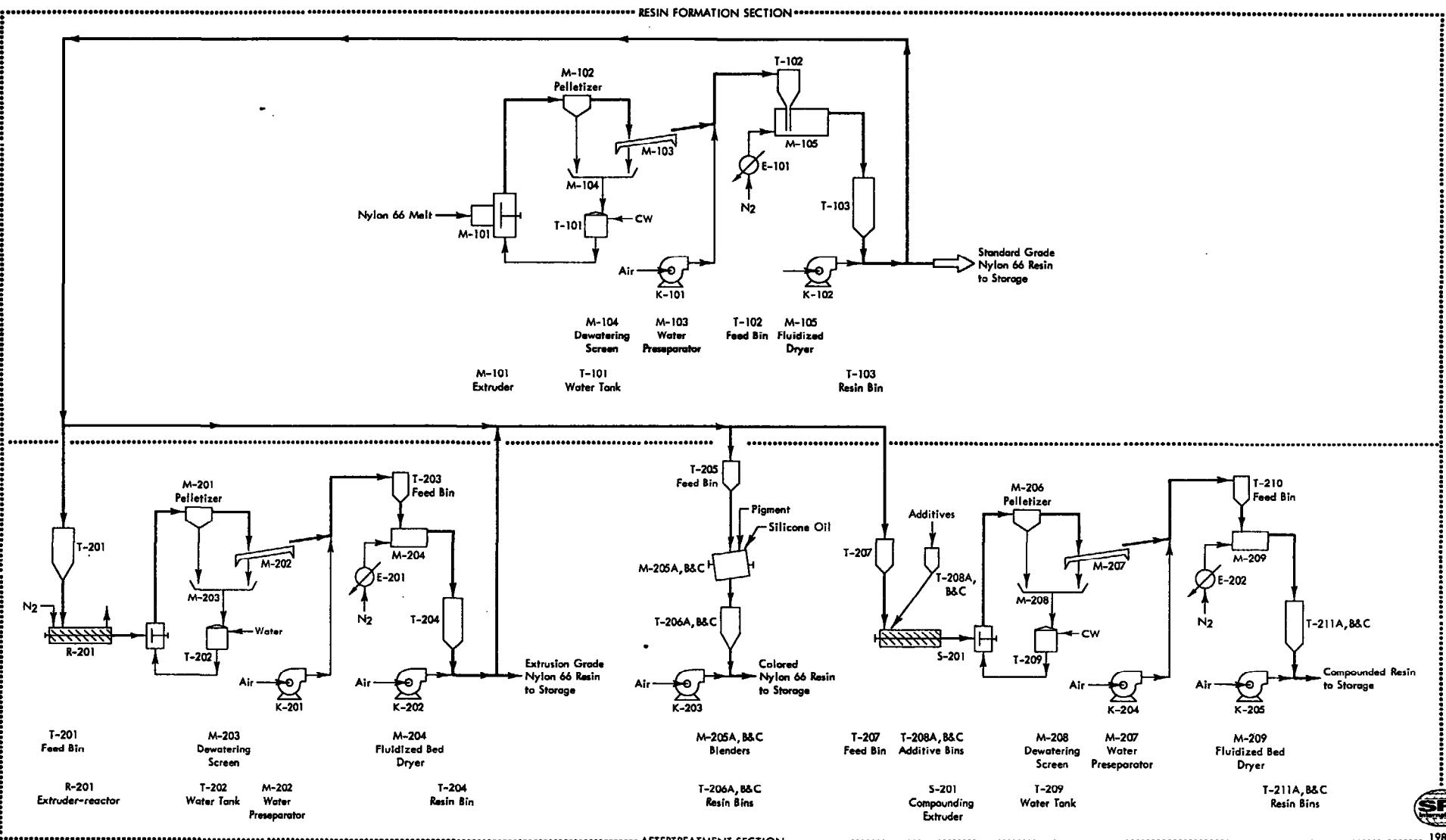


Figure 6.1

NYLON 66 RESIN FROM MELT



SRI
International

1980

Figure 7.1

CARPET STAPLE FROM NYLON 66 MELT

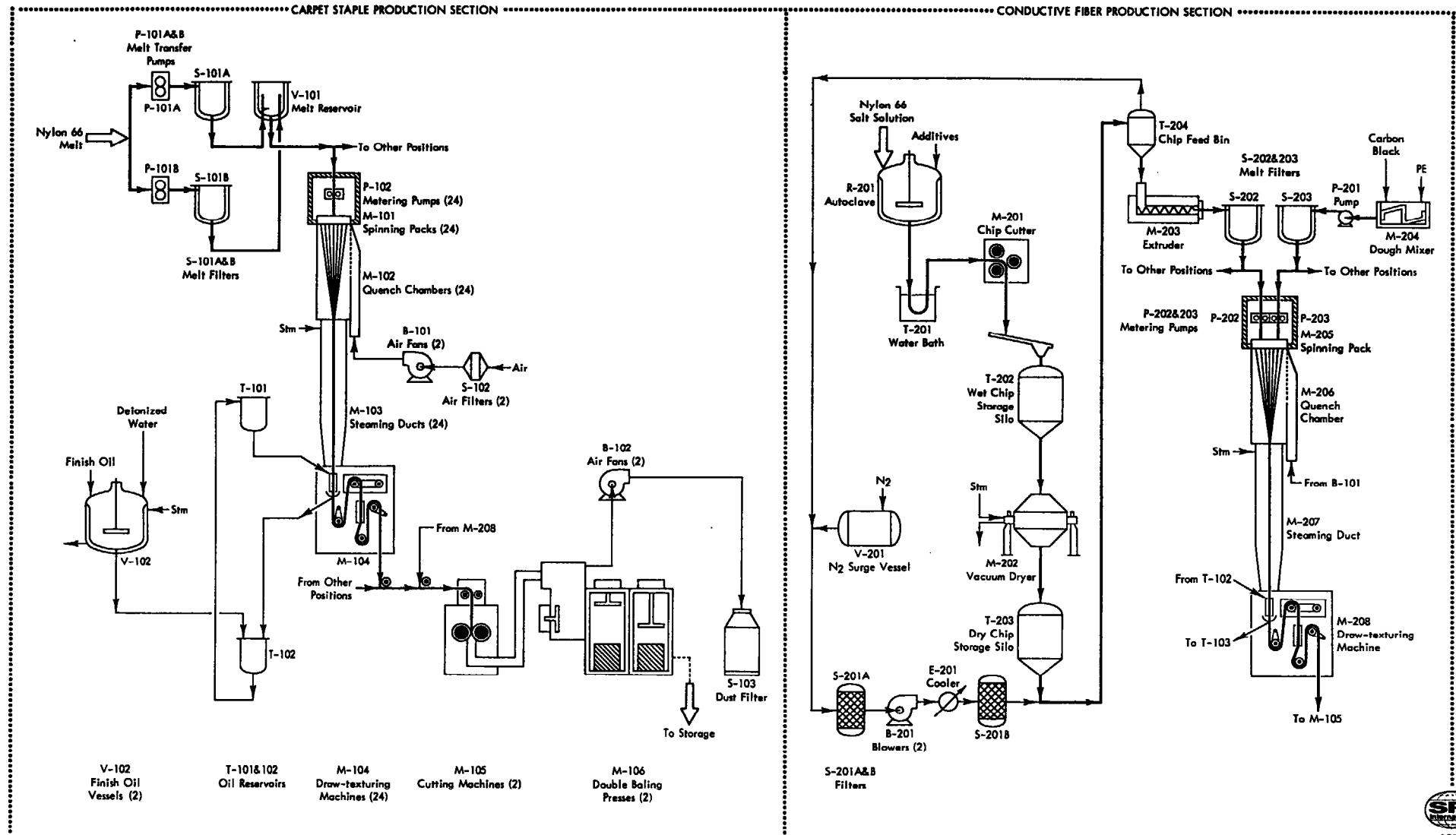


Figure 7.2
CARPET YARN FROM NYLON 66 MELT

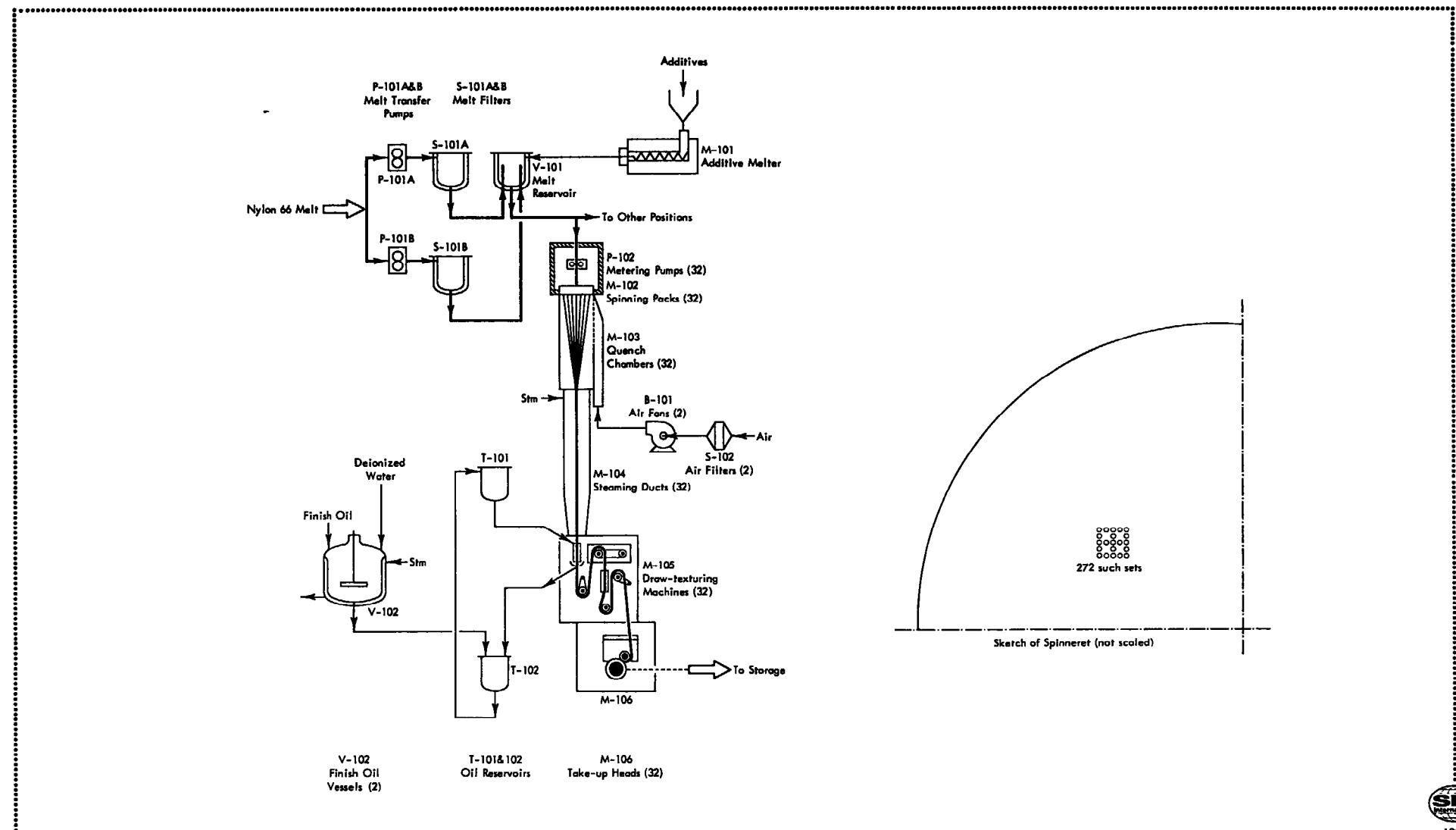
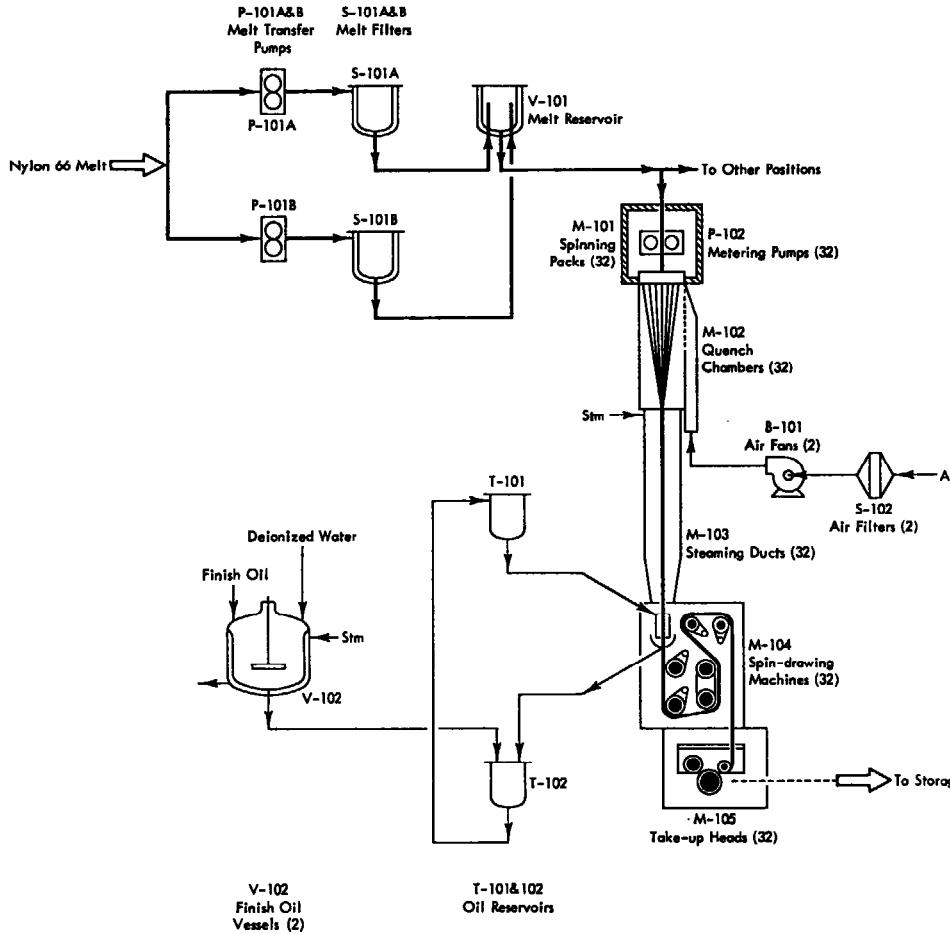


Figure 7.3

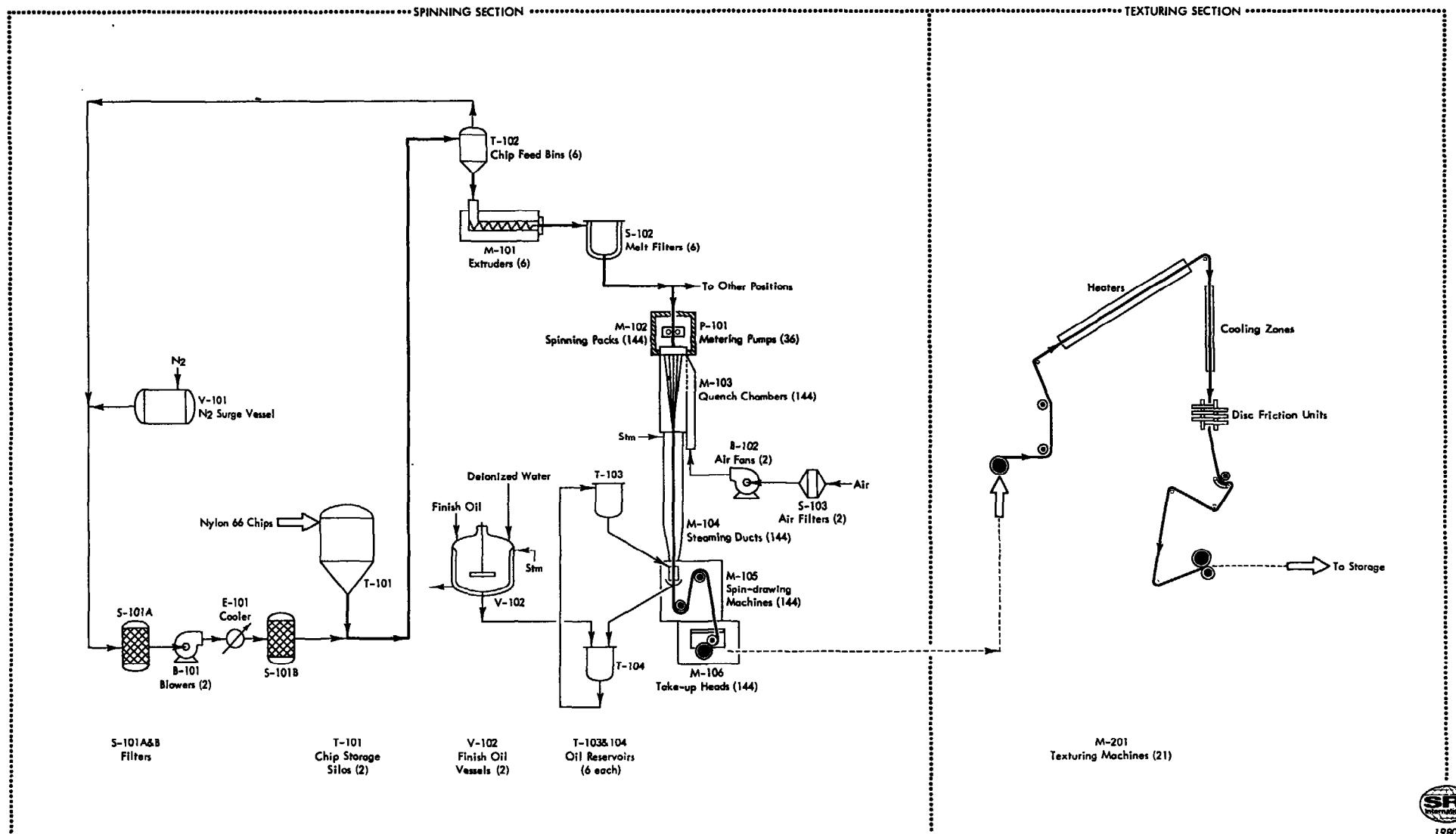
TIRE CORD FROM NYLON 66 MELT



1980

Figure 7.4

TEXTILE YARN FROM
NYLON 66 CHIPS



1980

Figure 7.5

HOSIERY MONOFILAMENT FROM NYLON 66 CHIPS

