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SYNTHETIC FIBERS  
AP-42 Section 5.19  
Reference Number  
24

POLYMER INDUSTRY RANKING BY  
VOC EMISSIONS REDUCTION  
THAT WOULD OCCUR FROM  
NEW SOURCE PERFORMANCE STANDARDS

by

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SECTION 5  
ACRYLIC RESINS

5.1 INDUSTRY DESCRIPTION

Acrylics are a family of vinyl polymers made from acrylic acid and methacrylic acid and their esters. The products range from thermo-plastics to thermosets and from glass-like sheets, through enamels, to resin powders, to latexes. Methyl methacrylate, ethyl acrylate and butyl acrylate are the largest volume acrylic monomers used. Most potential VOC emissions are these monomers plus whatever solvents, modifiers, and volatile organic additives are used. Almost all acrylics are produced in batch processes, and only batch processes will be treated in this report. The four common polymerization methods are all used (bulk or mass, solution, suspension and emulsion) and these may be grouped as "hydrocarbon-based" or "water-based" processes for discussion.

The estimated 1978 U.S. production of all acrylics monomers was 1314 MM PPY for all uses, and indicates 6 to 7% overall annual growth rate over 1977 (some 31 MM PPY (4) used in fiber co-polymers was not included). While nameplate capacity for acrylic resins was unknown, production was 1100 MM PPY in 1977 (5). Using an estimated utilization rate of 85% and an average growth rate of 6.5%, capacity is estimated to be 1468MM PPY in 1979.

The estimated 1980 MMA and acrylate ester consumption markets have been grouped as follows:

<u>Process</u>	<u>% Monomers Consumed</u>
Bulk	25 Hydrocarbon-based
Solution	10
Suspension	10 Water-based
Emulsion	<u>55</u>
	100

As the table indicates, about 35% of production will be hydrocarbon-based, and 65% will be water-based. Within these two groups, the processes have similarities in VOC emissions, emission points, and applicable controls and therefore, they will be treated by group.

Although more than a hundred U.S. manufacturers of acrylics resins are listed (7, pp 21 - 23), only a few are large chemical companies that also produce the monomers. Most of the large monomer producers also make finished products such as cast sheets and/or latex paints. Table 5-I lists all the U.S. acrylic resins manufacturers (ca 1970) and indicates the product distribution they make. Some of the larger U.S. producers are Rohm and Haas, DuPont, and American Cyanamid.

The largest single raw material used is methyl methacrylate (MMA), the second is ethyl acrylate (EA), and the third n-butyl acrylate (n-BA) so these make up the potential monomer VOC. Total use proportions are estimated (by Pullman Kellogg) to be about 75% MMA, 15% EA, and 10% n-BA. Product recipes vary widely from 100% poly MMA (sheets) to 100% poly EA dissolved in toluene

TABLE 5-I.- PRODUCERS OF ACRYLIC RESINS AND RELATED PRODUCTS (Concluded)

Company	Resins	Molding and Extrusion Powder	Solution or Emulsion Or Both	Films and Sheets		Rods, Tubes	
				Cast	Extruded	Standard Cast	Profiles Extruded
Tenneco Chem. (NJ)					X		
Thielex Plastics (NJ)							X
Triangle Conduit & Cable (NJ)							X
Tylac Chem. Div., Int'l Latex & Chemical (DL)			X				
U.S. Plastics & Chem., sub. Kopper Co. (NY)				X			
United Resins Co. (NJ)	X					X	
Union Carbide (NY)			X			X	
Union Oil of California (CA)	X		X				
Upaco Adhesives Inc. (MA)							
Vacuum Plastics Corp. (OH)							X
Vernon-Benshoff Co. (NY)	X						
Westlake Plastics (PA)					X		X
World Plastics Extruders (NJ)							X
Yates Company (PA)							X

TABLE 5-I.- PRODUCERS OF ACRYLIC RESINS AND RELATED PRODUCTS (Continued)

Company	Resins	Molding and Extrusion Powder	Solution or Emulsion Or Both	Films and Sheets		Rods, Tubes	
				Cast	Extruded	Standard Cast	Profiles Extruded
Polymer Industries (CT)			X				
Polytech Co. (MO)	X			X		X	
Polyvinyl Chem. (MA)	X		X				
PPG Industries (PA)			X				
Purethane Div., Easton RS Corp. (NY)			X				
Purex Corp. (CA)			X				
RA Chemical (NY)			X				
Raffi & Swanson (MA)			X				
Rayll Plastics (NY)			X				
Reichhold Chem. (NY)			X				
Research Sales Inc. (NY)			X				
Rohm & Haas (PA)	X	X	X				
Rubba, Inc. (NY)	X		X				
Sandee Mfg. Co. (IL)							X
Sartomer Resins, Inc.	X	X					
Seven-K Color Corp. (CA)			X				
Sherwin-Williams Co. (IL)			X				
Silmar Div., Vistron (CA)			X				
Southern Plastics (SC)				X			
Stanley, A.E. Mfg. Co. (IL)			X				
Standard T Chem. (NY)			X				
Sterling Varnish (PA)			X				
Sun Chemical (PA)			X				
Swedlow, Inc. (CA)				X			

TABLE 5-1.- PRODUCERS OF ACRYLIC RESINS AN RELATED PRODUCTS (Continued)

Company	Resins	Molding and Extrusion Powder	Solution or Emulsion Or Both	Films and Sheets		Rods, Tubes	
				Cast	Extruded	Standard Cast	Profiles Extruded
Jersey State Chem. (NJ)			X				
Jet Plastics (CA)							
Jodee Plastics (NJ)	X		X	X		X	X
Johnson, S.C. & Sons (WI)			X				
Jones-Blair Paint (TX)			X				
Key Polymer Corp. (MA)	X		X				
Koro Corp. (MA)				X			X
Laminations Inc. (PA)							
Landover Mfg. Div.,							
National Lead (MD)				X			X
Leathertone, Inc. (MA)					X		
M.R. Plastics and Coatings (MO)							
3M Co. (MN)	X		X				
McClosky Varnish (PA)			X				
Midland Ind. Finishes (IL)			X				
Milligan, J.G. & Co. (WI)			X				
Mobil Chemical (OH)			X				
Nonsanto (MO)			X				
Morton Chemical (IL)			X				
Murray Prod't. Div., Fanner Mfg. (OH)							
National Lead (NY)			X				
National Starch & Chem (NY)			X		X		
O.C. Adhesives Corp. (NY)			X				
O'Brien Corp. (IN)			X				

TABLE 5-I.- PRODUCERS OF ACRYLIC RESINS AND RELATED PRODUCTS (Continued)

Company	Resins	Molding and Extrusion Powder	Solution or Emulsion Or Both	Films and Sheets		Rods, Tubes Standard Profiles	
				Cast	Extruded	Cast	Extruded
Daylite Industries (NY)	X			X			X
Dennis Chemicals (MO)			X				
De Soto Chem. Coatings (IL)			X			X	
Dimensional Plastics (FL)			X				
Dow Chemical (MI)			X				
Du Pont (DE)		X					
Dura Plastics (NY)						X	X
Electro-seal Glasflex (NJ)							
Extron Corp. (TN)					X		X
Franklin Fibre-Lamitex (DL)					X		X
Freeman Chemical (WI)	X		X				
Fuller, H.B. Co. (OH)			X				
Fusecolor Corp. (NJ)			X				
General Latex & Chem. (MA)			X				
George, P.D. Co. (MO)			X				
Glidden Co. (MD)			X				
Goodyear Aerospace (OH)						X	
Goodyear Tire and Rubber (OH)	X						
Guardian Chem. Coatings (MI)	X		X				
Hand R Plastics Inc. (PA)							X
Heath Tecna Corp. (WA)							
Hunt Foods & Industries (CA)			X				
Hyde, A.L. Co. (NJ)							X
Interchemical Corp. (NJ)			X				
International Coatings (CA)	X						
Isochem Resins Co. (RI)			X				

TABLE 5-I.- PRODUCERS OF ACRYLIC RESINS AND RELATED PRODUCTS (7)

Company	Resins	Molding and Extrusion Powder	Solution or Emulsion Or Both	Films and Sheets		Rods, Tubes Standard Profiles	
				Cast	Extruded	Cast	Extruded
Acco Polymers (MI)	X		X				
Ace Plastics (NY)			X				X
Acro Chemical Prod't (NJ)			X		X		
Adam Spence Corp. (NJ)			X				X
Allied Chemical (NJ)			X				
American Acrylic Corp. (NY)		X	X				
American Cyanamid (U.S.)		X	X				
American Mineral Spirit (IL)		X	X				
American Polymers Inc. (NJ)			X				
Anesite Div., Clow Corp. (IL)			X				X
Armstrong Paint & Varnish (IL)			X				
Ashland Chemical	X	X	X				
Avecor Inc. (CA)			X				
Axel Plastics Res. Lab. (NY)	X		X				
Baltimore Paint & Chem. (MD)			X				
BASF Corporation (NY)			X				
Bay Plastics (CA)			X				X
Borden Chemical (NY)			X				
Cadillac Plastics & Chem. (MI)			X		X		X
Caig Lab. Inc. (NY)			X				
Cast Optics Corp. (NJ)	X		X		X		
Celanese			X				
Chemical Coatings & Engineering (PA)			X				
Clearfloat Inc. (MA)			X				
Colab Resin Corp. (MA)			X				
Colonial Kolonite Co. (IL)			X				
Columbia Technical Corp. (NY)			X		X		X
Columbian Carbon Co. (NY)			X				
Contours Unlimited (MA)		X	X				
Cook Paint & Varnish		X	X				
Crystal-X Corp. (PA)			X		X		X
Custom Chemical (NJ)		X	X				

(laquers) and include many miscellaneous acrylates and organic additives. All present U.S. MMA production uses the acetone cyanohydrin process and is dependent on both the acetone and methanol supply situation.

The most common poly-acrylate solvents and process liquids, and thus potential non-monomer VOC, are toluene, methanol, acetone and methylene chloride. Toluene is likely the plant solvent-of-choice for clean up as well as the most likely process and/or product solvent. The primary use of methanol is to regenerate the ion-exchange resin beds used to remove hydroquinone (or other inhibitor) from monomers before polymerization. Acetone and methylene chloride are alternate solvents.

## 5.2 ACRYLIC RESIN MANUFACTURE BY HYDROCARBON BASED PROCESSES

### 5.2.1 Hydrocarbon Based Process Descriptions

Figure 5-1, Acrylic resins manufacture by bulk/solution processes, is the flow schematic for both bulk and solution processes. Both are completely hydrocarbon based, that is process solvents are monomers or other hydrocarbons. These processes are simpler than water based processes because they do not require emulsification or suspension and have simpler polymer recovery sections (if required at all). Most of Figure 5-1 is for a bulk process making cast sheet (above the heavy dotted line) but below the line alternate equipment and lines are indicated for a solution process that makes lacquer and enamel coatings. For clarity two process descriptions are given (first bulk, then solution) but only one flowsheet, VOC discussion, table of emissions, and "applicable controls" section.

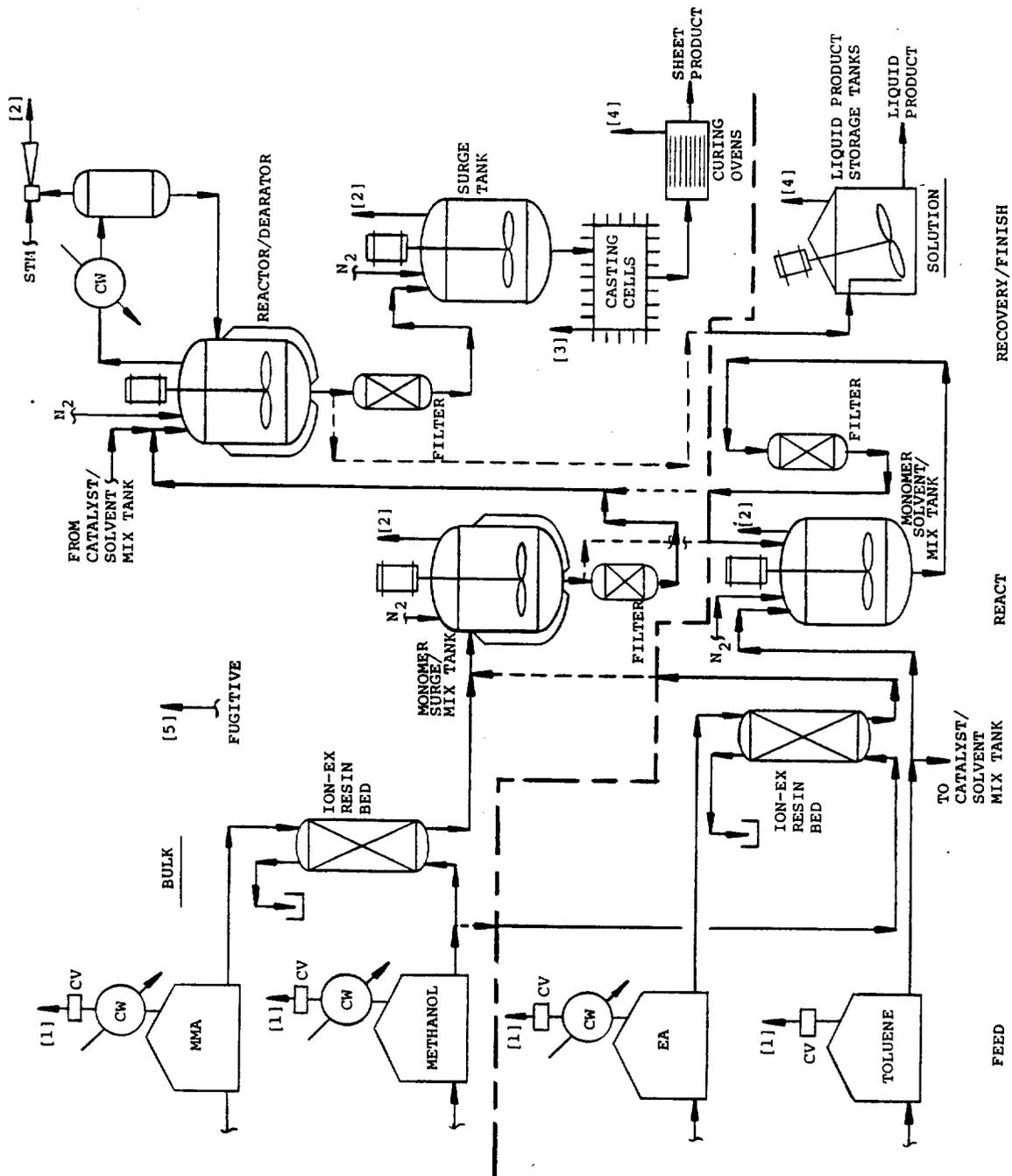


Figure 5-1.- Acrylics resins manufacture by bulk/solution processes.

#### 5.2.1.1 Bulk process.-

A batch process for polymethyl-methacrylate sheets is described but it applies to all batch monomer and polymer-monomer syrup casting processes.

Referring to Figure 5-1, above the heavy horizontal dashed line, the bulk process for cast sheets starts with inhibitor removal from stored MMA via an ion-exchange resin bed system. Purified MMA flows from the resin bed to a monomer surge/mix tank before filtration and subsequent reaction. A catalyst, usually benzoyl peroxide, is dissolved in monomer or solvent in a small tank (not shown) and joins the purified monomer in the reactor. For the bulk process, reaction is started in the presence of the catalyst and (if desired) accelerator by heating to 70-95°C for 5-10 minutes with constant agitation in the reactor. As soon as polymerization is adequate (about 10% solids) the mixture is cooled rapidly to 4°C to halt the polymerization temporarily. Any additional chemicals used are added now (plasticizers, U.V. inhibitors, etc.), and the partially polymerized syrup is deaerated with vacuum to remove bubbles before casting.

Deaerated syrup can be stored temporarily at 4°C. For immediate casting the syrup is reheated, filtered, and cast. Polymerization is completed in the casting cells and the sheets are discharged to curing ovens. Cured sheets are paper coated for protection and sent to storage or sales. Spent ion-exchanger resin beds are regenerated with methanol and reused.

#### 5.2.1.2 Solution process.-

A batch process for copolymer methyl methacrylate/ethylacrylate lacquer is shown. The liquid product is 40% polymer 60% solvent but various recipes could be used.

Figure 5-1, Acrylic resins manufacture by bulk/solution processes, is the flowsheet. Referring to Figure 5-1, both above and below the heavy horizontal dashed line, the solution process for coatings starts with inhibitor removal from stored monomers. Both MMA and EA monomers are fed to ion-exchange resin beds and the purified monomers flow to a surge/mix tank. Toluene solvent is fed from storage to the monomer/solvent mix tank and blended with purified monomers from the monomer surge/mix tank. A separate flow of toluene goes to a catalyst and solvent mix tank (not shown). From the monomer and solvent mix tank the mix flows through a filter to the reactor. Catalyst and solvent mix is fed to the reactor and polymerization is begun by heating. Reactor cycles are long and may be complex as solution polymerization is slower than bulk, suspension or emulsion polymerization. Polymerization is essentially completed in the reactor. Product flows from the reactor to the liquid product storage tank without filtering. Liquid product goes directly to a finishing line (pails) or to bulk shipment.

#### 5.2.2 VOC Emissions For The Hydrocarbon Based Processes

All significant emissions from acrylic-resin manufacturing by hydrocarbon based processes are shown in Figure 5-1 and listed in Table 5-II with bracketed numbers (3). The tabular values in Table 5-II were calculated from industry product distribution data. The

TABLE 5-II.- VOC EMISSIONS FROM ACRYLIC RESINS MANUFACTURED BY BULK/SOLUTION PROCESSES

<u>Stream</u>	Uncontrolled (Bulk Only)		Well Controlled		<u>Composition</u>
	<u>#/1000# Product</u>	<u>Current Practice #/1000# Product</u>	<u>Well Controlled #/1000# Resin</u>	<u>Composition</u>	
[1] Monomer and Solvent Storage and Handling	--	0.09	0.09		Pure VOC
[2] Monomer Mix Tanks, Reactor/De-aerator, Polymer Surge Tank	--	2.55	0.26		VOC in N <sub>2</sub>
[3] Casting, Cells and Shapes	20	2.46	0.25		VOC in air
[4] Curing, Product Storage	30	0.54	0.05		VOC in air
[5] Fugitive, includes Solvent Cleaning of Equipment	--	3.75	3.75		VOC in air
TOTALS	50	9.4	4.4		

distribution was assumed to be (25/35) = 70% bulk, and (10/35) = 30% solution products.

Note that VOC emissions are based on pounds of actual product which may include up to 60% solvent for solution products (lacquers and enamels) but none for bulk since the products are cast sheets and molded shapes.

The major emission points of these processes are:

- [1] Monomer and solvent storage and handling - The emissions are working and breathing losses from tankage as well as valve and line losses and pump seal leaks (storage and handling only).
- [2] Monomer mix tanks, reactor/deaerator and polymer surge tank - Emissions arise from working losses on all tanks and reactors and consist of monomers and, for solution processes, solvent vapors in N<sub>2</sub>. Emissions also arise from deaerating bulk process syrup, from evacuating the reactor to remove oxygen before the batch and from the polymer surge tank.
- [3] Casting, sheets and molded shapes - For bulk processes only, deaerated and partially polymerized syrup is cast or molded then completely polymerized. Emissions are monomer vapors only and arise from filling the molds with syrup and from polymerization. Solution processes have no comparable step.
- [4] Curing and product storage - For sheets, products are oven cured. Lacquers and other liquid solution products are stored for bulk shipment or packaged. Emissions are residual monomers from sheets and solvent vapors from liquid products during packaging.

[5] Fugitive - The majority of these emissions are plant cleaning solvent, usually toluene. Emissions arise from washings required to remove polymerized material from pipes, agitators, coils etc. when changing recipes and cleaning equipment. Some waste materials (syrops) are also polymerized and land filled for disposal and therefore emit some monomers and solvent.

### 5.2.3 Applicable Controls Systems For The Hydrocarbon Based Processes

- [1] Monomer and solvent storage and handling - Present emissions are relatively small. Existing controls are primarily conservation vents on fixed-roof tanks. Some tanks have cooling water condensers on the vent for volatile solvents. Refrigerated vent condensers can be used for methyl methacrylate monomer. No additional controls are presently warranted.
- [2] Monomer mix tanks, reactor/deaerator, polymer/syrup surge tanks - These vent streams constitute one of the largest emission points. Emissions are working losses on tankage, inert gas purges, and vacuum deaeration. All losses are VOC in small flows of N<sub>2</sub>. Existing controls are generally limited to a reflux condenser on the reactor. Applicable controls are refrigerated condensers or incinerators. It was assumed 90% control could be achieved.
- [3] Casting, sheets and molded shapes (Bulk processes only) - One of the largest emission sources for acrylics processes, VOC are monomer vapors arising during mold filling and polymerization. Ventilation is provided for worker health and flows are generally too large for direct control. Applicable controls require tighter hooding to reduce flows; incineration,

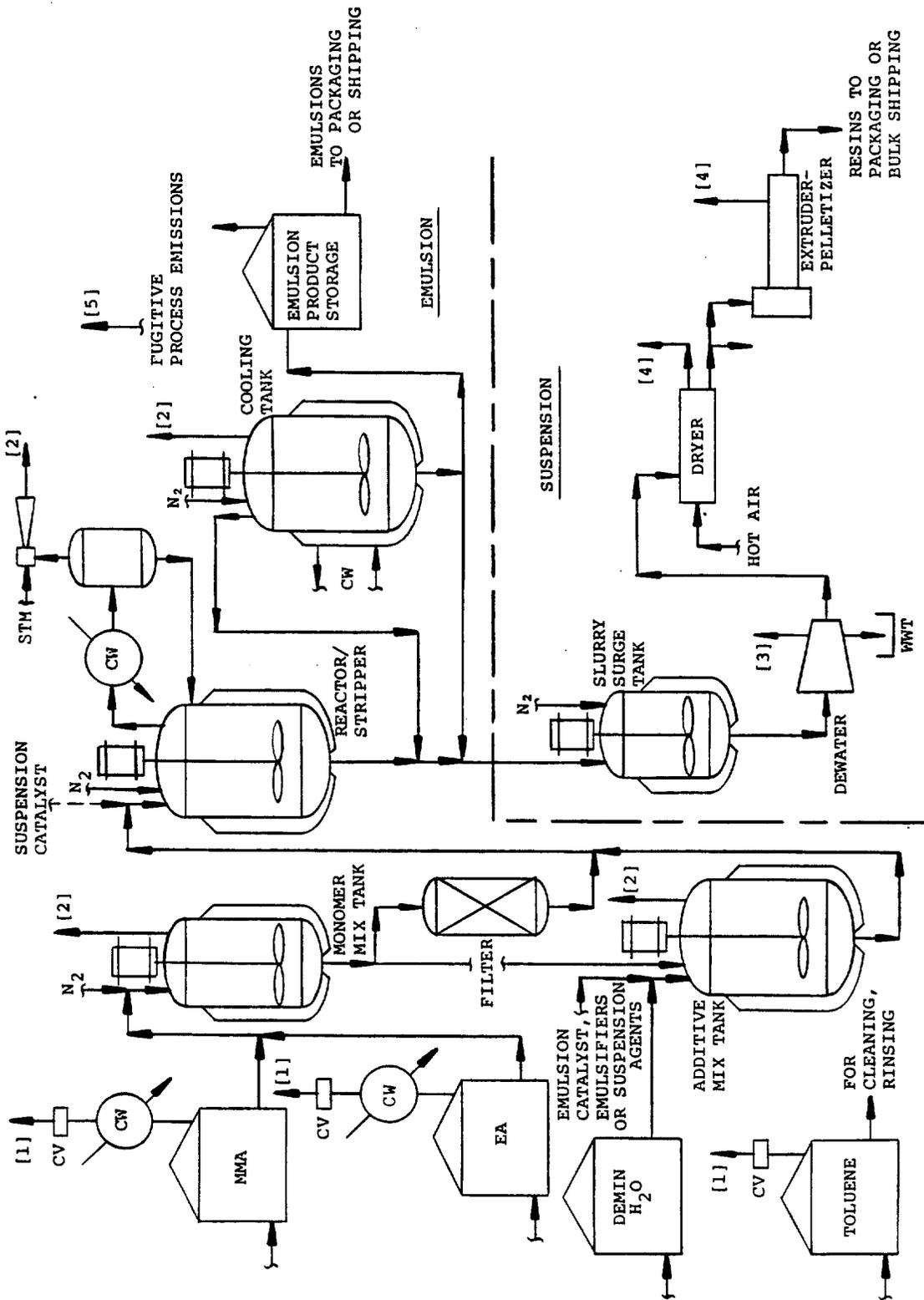
especially in an existing boiler, should be examined. It was assumed 90% control could be achieved.

- [4] Curing and product storage (For sheets and shapes, products are oven-cured) - VOC are unreacted monomers in large flows of air. Relatively small emissions may not warrant additional controls. For solutions warm products are pumped into cooling/surge tanks before packaging or bulk storage. VOC are solvents in air/N<sub>2</sub> from working losses of these tanks. Applicable controls are refrigerated condensers and incinerators and 90% efficiency was assumed.
- [5] Fugitive - Emissions are solvent VOC in air from cleaning and residual monomers in scrap and waste. These are a major VOC emissions point for hydrocarbon-based acrylics resins. Applicable controls include alternate disposal for partially polymerized scrap and waste syrup (incineration instead of landfill) and better housekeeping. No control efficiency was assumed.

### 5.3 ACRYLIC RESIN MANUFACTURE BY WATER BASED PROCESSES

#### 5.3.1 Water Based Process Description

Both emulsion and suspension processes use water as a process fluid and require special steps to achieve emulsification or suspension. Most emulsion process acrylics are sold as a latex product (paints, adhesives etc.) and thus do not require complex recovery systems as do suspension process acrylics. Figure 5-2, Acrylic resins manufacture by emulsion/suspension processes, is a schematic showing both processes. The left side of Figure 5-2 is common to both emulsion and suspension processes. On the right side the upper train is for emulsions only and produces a latex product. The lower right side train



FEED

REACT

RECOVERY/FINISH

Figure 5-2.- Acrylics resins manufacture by emulsion/suspension processes.

shows a brief suspension polymer-recovery system. Two process descriptions have been developed, one for emulsions and one for suspensions; but the other information is combined and only one flowsheet, VOC discussion, table of emissions, and controls section is used.

#### 5.3.1.1 Emulsion process.-

A batch process for a methyl methacrylate/ethyl acrylate emulsion co-polymer latex with 40% solids content is described in this text, but it represents a variety of recipes and emulsion products. Reference to Figure 5-2 will aid in following the discussion.

Demineralized water is emulsified with surfactants, catalyst, small amounts of monomers, and other additives in the additive mix tank. This flows to the reactor. Next, MMA and EA monomers flow to a monomer mix tank then through a filter to the reactor where they join the emulsified water, surfactant, catalyst, and additives. The reactor is heated to initiate polymerization and taken through a batch cycle resulting in about 98-99% monomer conversion. The resulting latex is vacuum stripped in the reactor to remove residual monomers then discharged via a cooling and surge tank to product storage. The final step for latex is packaging or bulk shipment. Latexes are difficult to purify and emulsifiers, catalysts, and other additives cannot be removed and are generally sold with the product.

Although no monomer inhibitor removal steps are shown (low-inhibitor grade monomers are assumed) any of the three classic means could be used, ion-exchange, distillation, and caustic washing.

#### 5.3.1.2 Suspension process.-

A batch process for a methyl methacrylate/ethyl acrylate suspension co-polymer resin is described in this section. There is an extruder-pelletizer in the finishing line, but the process produces resin powder without it. A variety of recipes and resultant resins can be produced. Low-inhibitor grade monomers are assumed.

Reference to Figure 5-2 shows that the description for the suspension process is the same as for the emulsion process up to the cooling tank after the reactor - with two exceptions. One exception is that suspension or dispersion agents are used in place of emulsifiers, and the other is that catalyst is added directly to the reactor rather than the mix tank. Suspension (slurry) leaving the cooling tank is dewatered in a centrifuge, the resulting resin powder is dried in a hot-air drier prior to finishing. Dried resin powder can be the final product and either packaged or bulk shipped or it can be processed into pellets via the extruder-pelletizer. Suspension products are low in residual additives as these are removed with the water during dewatering and sent to waste water treatment (WWT, not shown).

#### 5.3.2 VOC Emissions For The Water Based Processes

All significant emissions from acrylic resin manufacturing by water-based processes are shown in Figure 5-2 and listed with bracketed numbers in Table 5-III. The VOC values in the table were calculated from industry data assuming (55/65) = 85% emulsion and (10/65) = 15% suspension products.

TABLE 5-III.- VOC EMISSIONS FROM ACRYLIC RESINS EMULSION/SUSPENSION PROCESSES\*

Stream	Uncontrolled (Bulk Only) #/1000# Product	Current Practice #/1000# Product	Well Controlled #/1000# Resin	Composition
[1] Monomer and Solvent Storage	0.15	0.15	0.06	Pure Monomers and Solvent
[2] Monomer Mix Tanks, Reactor/Stripper, Surge/Cool	0.48	0.48	0.05	Monomers and Solvent VOC in N <sub>2</sub>
[3] Dewatering, Drying*	0.42	0.42	0.04	Residual Monomers in Air
[4] Extrusion, Finishing, Packaging*	<u>1.26</u>	<u>0.00</u>	<u>0.00</u>	Residual Monomers in Air
TOTALS	2.31	1.05	0.15	

\* Assumes that emulsions are 85%, suspensions 15%, of water based processes; dewatering, drying, extrusion and finishing apply to suspension processes only.

Note that VOC emissions are based on pounds of actual product which includes up to 60% water for emulsions (latex) but none for suspensions since the products are resin powders or extrusions.

The major emission points of these processes are:

- [1] Monomer and solvent storage and handling - Emissions released are working and breathing losses from tankage as well as valve and pump seal and line losses during loading and transfer. A solvent may be used for clean up and for ion-exchange bed regeneration (usually methanol, not shown on Figure 5-2) but only storage and transfer losses are included here. Emissions are pure monomer and solvent vapors, primarily.
- [2] Mix tanks, polymerizer/stripper and latex cooling tanks - Emissions come from working losses on tankage plus residual monomers stripped. All emissions (VOC) are monomers in a flow of N<sub>2</sub>. Both emulsions and suspensions can have these emissions.
- [3] Dewatering, drying - For suspension processes only, because acrylic emulsions are used as emulsions and not subjected to recovery. Suspension process products are recovered by dewatering (screens, centrifuge) and drying. Emissions are residual monomers in air from these operations.
- [4] Extrusion, finishing and packaging - Extrusion and finishing emissions shown are for suspension processes only. Some emulsions are packaged into small cans and have a very small potential VOC from packaging. Emissions are residual monomer vapors in ventilation air.

No data were available on fugitive emissions from either emulsion or suspension processes. However, water-based processes are expected to have much lower fugitive VOC emissions than hydrocarbon-based processes because of the reduced opportunity for VOC emissions from leaks, spills and cleaning.

### 5.3.3 Applicable Control Systems (Water Based Processes)

- [1] Monomer and solvent storage and handling - As with hydrocarbon based acrylics, present emissions are relatively small and existing controls usually are limited to conservation vents on fixed roof tanks perhaps with cooling water condensers for the more volatile substances. Refrigerated (ca 14°F) condensers are sometimes used on MMA and should achieve about 90% reduction in VOC. No additional controls seem presently warranted.
- [2] Monomer and additive mix tanks, polymerizer/ stripper and latex cooling tanks - Presently there are few controls on the mix tanks and cooling tanks and cooling water or refrigerated condensers would be applicable and could achieve up to 90% VOC reduction. Most polymerizer/strippers presently have cooling water condensers for economic reasons. High (>90%) emissions reductions have been achieved for steam ejector vacuum systems in similar service by spray condensers. This system (spray condensers for steam-jet evacuators) seems attractive for control where applicable but creates a waste-water.
- [3] Dewatering and drying - For suspension processes only. Emissions are machine ventilation and dryer exhaust and are presently unabated. Again, as in storage, controls do not seem warranted at present. However

one means of control that may be available is incineration in an existing boiler. If incineration is used actual combustion efficiency of VOC reduction will exceed 90%. However, recycle of dryer air and purges and/or flow splitting will probably limit reductions to <90%.

- [4] Extrusion, finishing and packaging - Extrusion and finishing only apply to suspension processes. Emissions of residual monomer vapors are collected by ventilation equipment. If uncontrolled, these emissions can be the largest VOC source in water-based acrylics manufacture. Tightly hooded or enclosed (as in an extruder- devolatilizer) equipment can be evacuated and controlled by a steam-jet evacuator and spray condenser. Well over 90% VOC reduction can be achieved; but, again, a waste water will be produced.

SECTION 8  
NYLON 6 FIBER

8.1 INDUSTRY DESCRIPTION

8.1.1 General

Nylon is the common name given to any of a group of commercially important synthetic linear polyamides of high molecular weight. Polyamides are synthetic resins having recurring amide groups in the polymer chain; these resins may be formed into fibers, bristles, moldings, sheets, and coatings. The U.S. International Trade Commission has divided the class of polyamide fibers into two groups - nylon fibers and aramid fibers based on the percentage of amide linkages attached directly to two aromatic rings.

Nylons are identified by the number of carbon atoms in the monomers used; hence nylon 6 is a homopolymer of a six carbon compound - caprolactam. Nylon 66 indicates that the polymer is made from two monomers, each having a six-carbon chain. Nylon 66 was the first major fiber made entirely of synthetic polymer. Nylon 66 and nylon 6 accounted for 98% of all domestic nylon fiber production in 1976. Other commercial nylon fibers include nylon 610, 612, 11, 12 and Qiana nylon. Less commercially attractive nylons include nylon 3, 5, and 8. Nylon 66 is discussed more thoroughly in Section 9 of this report.

today. Nylon also exhibits elastic properties; it will return to its original length after stretching up to 8%. This characteristic is used advantageously in manufacturing clothing with satisfactory dimensional stability. Nylon is not attacked by insects, mildew, or perspiration.

Differences between nylon 6 and nylon 66 are slight. The principal difference between the two is that nylon 6 has a lower softening and melting point. The minor property differences between nylon 6 and nylon 66 give one or the other the advantage in given applications, and they compete in many applications (18), (19).

#### 8.1.2 Nylon 6

The primary market for nylon 6 is in fibers with applications in all major fiber markets, including carpeting, hoisery, wearing apparel, and tire cord. There is a much smaller market in thermoplastics applications. High tenacity nylon 6 is used in industrial applications, including fabrics, and for home furnishings.

Most domestic nylon 6 is manufactured by the "chip" process in which fiber spinning is carried out as a separate operation after remelting the "chips". Two polymerization processes are of industrial importance - hydrolytic or water-catalyzed polymerization and anionic or base-catalyzed polymerization. The water-catalyzed process is the overwhelming choice for fibers because it is more suitable for large-scale operation and because it is easier to control.

General consensus in the industry is that nylon 6 develops by a reaction mechanism involving opening the lactam ring by heat, hydrolyzing by water, and chain growth by joining the exposed functional groups by polycondensation (two polymer chains react and combine) with elimination of water and with polyaddition (a molecule of monomer adds on to a polymer chain). Special reagents in the reaction mix, such as acetic acid or amines, serve to control chain length. The polymerization is an equilibrium reaction with approximately 10% water extractable at completion. These are lower molecular weight compounds, including monomer and oligomers.

About 70% of all nylon 6 polymer is produced by continuous polymerization. The subsequent chip extrusion, extraction (to remove the 10% water extractables remaining), and drying operations are carried out normally on a continuous basis regardless of whether continuous or batch polymerization is used. Emissions data per pound of nylon 6 chips produced are believed to be very similar for both the continuous and batch manufacturing processes. Future plants are expected to have approximately the same 70/30% split between continuous and batch processing.

Ten to twenty percent of nylon 6 production uses a method known as "direct spinning" to make fibers. The hot melt polymer is vacuum-stripped to remove unreacted monomers and oligomers before it is sent directly to spinning. Chip extrusion is eliminated.

### 8.1.3 Production Levels for Nylon and Aramid

In 1976, U.S. production of nylon and aramid fibers amounted to 2,169 million pounds, a quantity equal to 27%

of the total U.S. man-made fiber production. On a poundage basis, nylon ranked second of the six most important man-made fibers consumed domestically. Of the total nylon and aramid fiber produced in 1976, nylon 66 fiber accounted for 1,360 million pounds (63%wt); nylon 6 accounted for 667 million pounds (31%wt); other types of nylon accounted for 26 million pounds (1%wt); aramid fibers accounted for 23 million pounds (1%wt); and all types of nylon and aramid waste accounted for 93 million pounds (4%wt).

Data concerning consumption of nylon 66 and nylon 6 by end use are not available, but estimates in the percentage split of major markets can be made from the amounts of production capacity designated for various products. The following table presents these estimated percentages for 1976:

ESTIMATED CONSUMPTION OF NYLON 66 AND NYLON 6 BY END USE  
1976 (Percent)

	NYLON 66	NYLON 6
Total Yarn and Staple	67	33
Total Yarn	70	30
Total Staple	61	39
Textile Yarn and Staple	79	21
Textile Yarn	78	22
Textile Staple	100	0
Carpet Yarn and Staple	60	40
Carpet Yarn	60	40
Carpet Staple	60	40
Industrial Yarn and Staple	76	24
Industrial Yarn	78	22
Industrial Staple	45	55

Nylon 6 demand is projected to grow from 652 MM#/Yr in 1976 to 880 #MM/Yr in 1982, an average rate of 5.1%/Yr. As of October 1977 there were eleven U.S. producers of nylon 6 fiber (yarn, staple, and tow) with a total of fourteen plants and total nylon 6 production capacity of 919 million pounds per year. (Nylon 6 capacity represented 33% of total nylon capacity and nylon 66 accounts for 64%. Monofilaments and other nylons accounting for the remainder, or approximately 3%. Three of the eleven manufacturers, Allied, Akzona, and Dow Badische, have 84% of the total spinning capacity.

The capacity data given in Table 8-I refer to spinning capacity, not polymerization capacity. Only five of the manufacturers listed (Akzona, Allied, Dow Badische, Firestone, and Rohm and Haas) have polymerization capability. The others purchase merchant chip for their spinning operations (18).

## 8.2 NYLON 6 MANUFACTURE BY THE CONTINUOUS CHIP PROCESS

### 8.2.1 Process Description

This process uses a tower or vertical tube reactor, strand die pelletization, a continuous countercurrent chip extraction column, and a recirculating nitrogen drying system. Figure 8-1 describes the process schematically.

Caprolactam monomer is stored with agitation and under a nitrogen blanket at approximately 175°F. It is metered continuously into the reactor along with catalyst (water), the chain terminating agent (acetic acid), and additives such as delusterants and antistatic agents. The reactants flow down through the reactor at approximately 500°F

TABLE 8-I.- NYLON 6 - YARN, STAPLE, AND TOW  
ANNUAL CAPACITY AS OF OCTOBER 1977  
(Millions of Pounds)

PRODUCING COMPANY AND AKZONA INCORPORATED	CONTINUOUS FILAMENT YARN		STAPLE AND TOW		TOTAL
	TEXTILE	CARPET	TEXTILE	CARPET	
American Enka Company, division Central, SC	X	X	X	X	
Enka, North Carolina	X	X	X	X	
Lowland, Tennessee	X	X	X	X	
	<u>38</u>	<u>106</u>	<u>0</u>	<u>2</u>	<u>239</u>
ALLIED CHEMICAL CORP. Fibers Division Columbia, SC	X	X	X	X	
Hopewell, Virginia	X	X	X	X	
	<u>36</u>	<u>105</u>	<u>0</u>	<u>8</u>	<u>309</u>
CAMAC CORPORATION Bristol, Virginia	4	6	0	0	10
COURTAULDS NORTH AMERICA, INC. (100% owned subsidiary of Courtaulds, Limited (United Kingdom))	5	0	0	0	5
Le Moyne (Mobile), Alabama					
DOW BADISCHE COMPANY (jointly owned by Dow Chemical U.S.A. and BASF AG [Federal Republic of Germany])	23	55	0	55	135
Anderson, South Carolina					
THE FIRESTONE TIRE & RUBBER CO. Firestone Synthetic Fibers Company, division Hopewell, Virginia	0	0	0	0	48
GULFORD MILLS, INC. Gainesville Division Gainesville, Georgia	4	0	0	0	4
HANOVER MILLS, INC. (100% owned subsidiary of Falk Fibers & Fabrics, Inc.)	4	0	0	0	4
Yanceyville, North Carolina					
ROHM AND HAAS CO. Fibers Division Fayetteville, NC	0	50	0	0	50
STAR FIBERS, INC. (100% owned subsidiary of Star Textile and Research, Inc. a subsidiary of Dayco Corporation)	0	0	0	25	25
Edgefield, South Carolina					
SUNBURST YARNS, INC. (100% owned subsidiary of Tulex Corporation)	1	0	0	0	1
Afton, Virginia					
<b>TOTAL</b>	<b>115</b>	<b>322</b>	<b>0</b>	<b>358</b>	<b>919</b>

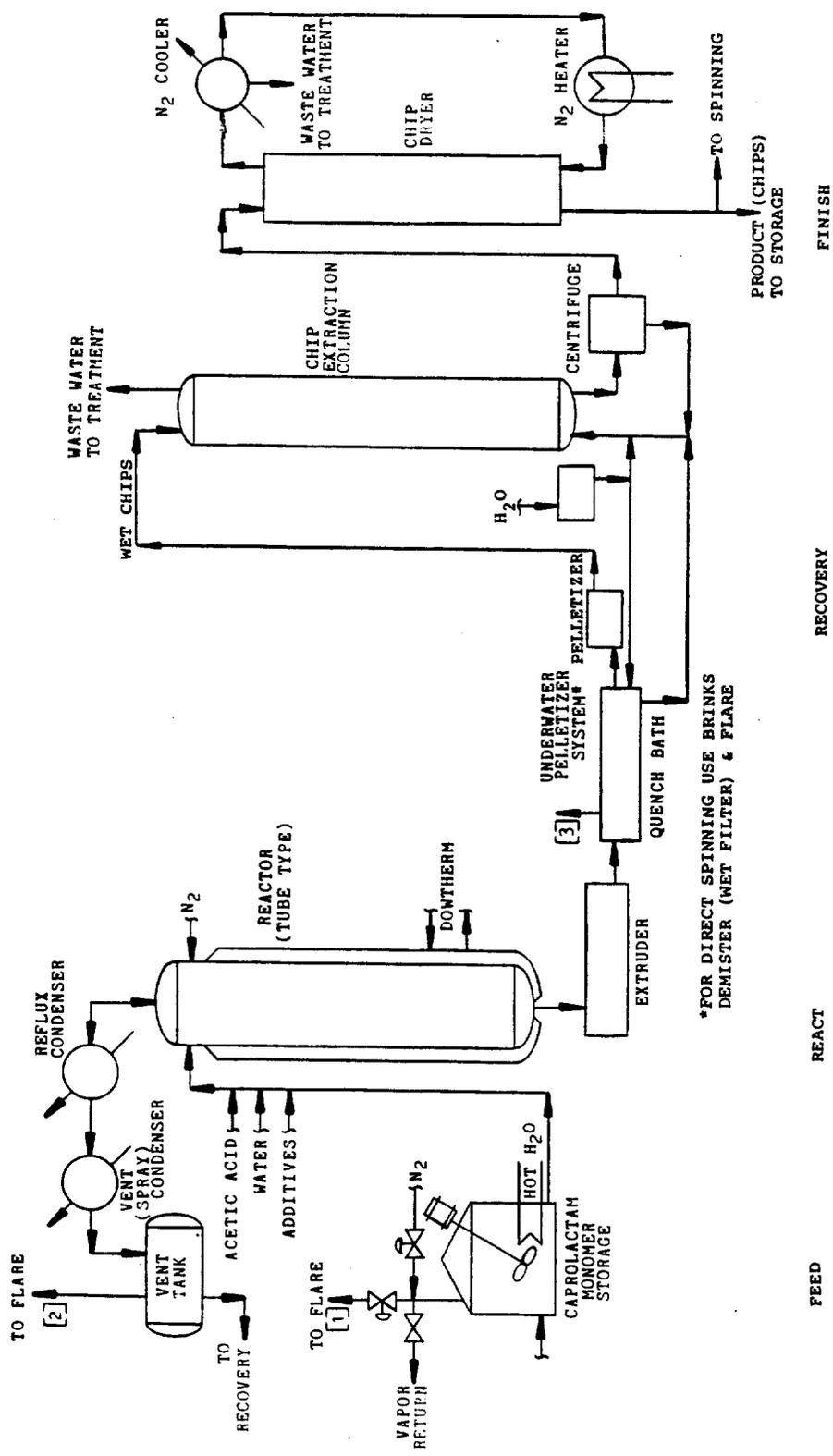


Figure 8-1.- Nylon 6 - Continuous chip process.

during a residence time of approximately 18 hours. Under these conditions the polymer approaches equilibrium. The molten polymer flowing out of the bottom of the reactor is extruded, water quenched, and pelletized to a proper physical form for extraction of residual monomer and oligomer. The top of the reactor contains a boiling polymerization reaction mixture. The reflux condenser serves to return caprolactam and other vaporized reactants to the reactor, while excess water taken overhead is removed.

Oligomer and unreacted monomers are removed from the chips, by continuous countercurrent extraction with water, at approximately 200°F. The extraction process reduces the content of oligomers plus monomers (mainly caprolactom) from 10% to 3%, yielding a product with approximately 0.5% residual monomer. The chips are centrifuged next, but they still contain 10 to 12% internal moisture. The moisture remaining in the chips is removed in a continuous, circulating, hot-nitrogen dryer. The cool wet nitrogen exhausted from the dryer is cooled further to condense out the water, and then it is compressed, reheated, and returned to the dryer. The dried nylon chips are transferred to silo storage for subsequent sale or remelt and spinning.

Several variations of the process described above exist (20), (21). They use different types of reactors, chip extraction equipment, and/or dryers. Examples of such variations are:

- o Using three, stirred-tank reactors in series (one plant).

- o Using stirred tanks in series rather than countercurrent extraction.
- o Using vacuum drying instead of inert gas.
- o Using a thin-film evaporator for monomer/oligomer removal when direct spinning is carried out.

### 8.2.2 VOC Emissions

All significant emission rates and sources for this product are shown on Table 8-II. The schematic flowsheet (Figure 8-1) for the product includes the emission streams and their sources, and the same stream number is used for a given stream throughout these discussions. Nylon 6 chip dryer and storage have not been included because no VOC emissions were reported from these sources. Emission figures include both continuous and batch process emissions - prorated according to the reported nylon 6 production poundage. The estimated U.S. production split was 70% continuous and 30% batch. VOC emissions from the two types of processes are believed to be nearly equal on a per pound of nylon 6 produced basis.

The largest emissions from nylon 6 manufacturing plants actually come from the fiber spinning facilities downstream from the chip manufacturing facilities described here. However, these spinning emissions are outside the scope of this study. Conversely, this study does include spinning emissions when evolved from "direct spinning", where fibers are spun directly from the reactor hot melt without a separate or intermediate chip-making step. The estimates are that 10 to 20% of U.S. nylon 6 fibers are manufactured by "direct spinning".

A description of the emission streams follows:

TABLE 8-II.- VOC EMISSIONS FROM NYLON 6 MANUFACTURE BY THE CONTINUOUS  
CHIP PROCESS

<u>Stream</u>	<u>Uncontrolled #/1000# Resin</u>	<u>Current Practice #/1000#Resin</u>	<u>Well Controlled #/1000# Resin</u>
[1] Caprolactam Monomer Storage	0.01	0.01	nil
[2] Polymerization Reactor	0.02	0.01	nil
[3] Extrusion/Pelletizing Sections (includes spinning if direct spinning)	0.65	0.22	nil
Totals	<u>0.68</u>	<u>0.24</u>	<u>nil</u>

[1] Caprolactam monomer storage tanks - This stream emits vapor with blanket nitrogen from the fixed roof tanks or from cylinders storing molten caprolactam. Normal breathing, filling, and withdrawing of monomer are the emission causes. Caprolactam is kept molten by water heated internal coils and agitators or mixers are generally provided. Internal pressure in the tanks is either atmospheric or slightly positive and a nitrogen blanket is required. Storage temperature normally is 160 to 170°C. The same tanks can serve batch and continuous processes, if both are present.

[2] Polymerization reactor - This stream emits caprolactam vapor diluted by blanket nitrogen and traces of water vapor which taken overhead from the polymerization reactor. This reactor typically is a continuous UK vertical tube vessel heated by Dowtherm in the jackets. The stream normally passes through a reflux condenser, a vapor condenser, and a K.O. drum, from which it is emitted directly.

In the less common batch process case, the reactor usually is an autoclave with an overhead condenser. A vacuum is drawn during part of the reaction cycle and part of the cycle proceeds as a closed system at elevated pressures. The stream components are the same as for continuous processing but in somewhat different proportions.

[3] Extrusion/pelletizing sections - This stream is potentially the largest VOC emission source from a nylon 6 plant. Molten nylon 6 polymer from the bottom of the reactor is extruded through a die to form heavy

strands which are quenched in water, and pelletized. Pellets are slurried with water for further processing. Vapors are produced by the extrusion, quenching, and pelletizing operations and normally are collected by hoods. Steam or a water spray is commonly added to the exhaust vapor stream to prevent crystallization.

The stream is composed of caprolactam and water vapors in a large volume of air. These operations are usually continuous and this emission is essentially unaffected by the type of upstream process (batch or continuous). Additional caprolactam emissions are generated by the direct spinning process and included in this stream, but direct spinning is only used for an estimated 10 to 20% of production.

### 8.2.3 Applicable Control Systems

The following control technologies are recommended for the emission streams that are described in Section 8.2.2 and shown on the schematic flowsheet.

- [1] Caprolactam monomer storage tanks - This monomer requires a nitrogen blanket on the storage tanks regardless of VOC emission considerations. A pressure equalizing vapor return line to the tank cars or trucks should be used to eliminate working losses from storage tank filling. This represents 58% of the total potential storage losses or emissions. The inert gas blanket system should exhaust tank vapors, on pressure control, to a flare. A minimum reduction of 90% in the remaining VOC emissions from breathing is assumed for either case. Any tank or vessel pressure relief valves utilized for either emission

- control or safety should also be tied into a flare.
- [2] Polymerization reactor - Use a spray condenser to wash emission stream and follow it by bubbling through a seal pot. The result is an extremely low concentration of caprolactam vapor in nitrogen. Route the resulting stream to the flare. (If no flare is available, atmospheric emission would be acceptable because the condenser effectiveness is high and the resulting VOC emission level is low).
- [3] Extrusion/pelletizing sections - All non-direct spinning continuous and batch processes should use the newly demonstrated "underwater pelletization system" to eliminate nearly all VOC fumes. This system also has noise reduction and process economics advantages. For direct spinning, hoods are to be used to collect extrusion emissions and the take-off exhaust from the spinning room air recirculation system. Both should be sent to wet-filter demisters then to flare.

SECTION 9  
NYLON 66 FIBER

9.1 INDUSTRY DESCRIPTION

Nylons (polyamides) are identified by the number of carbon atoms in the monomers from which the particular product is synthesized. Hence nylon 66 is a copolymer of the two six-carbon compounds, adipic acid and hexamethylene diamine. Together nylon 66 and nylon 6 accounted for 98% of the domestic nylon fiber produced in 1976. The primary market for nylon 66 is in fibers, with major applications in carpeting, hoisery, wearing apparel, and tires. A much smaller market exists in thermoplastics applications.

U.S. production of nylon 66 was 1375 MM lbs in 1976. The projected growth rate for U.S. consumption for 1976-1981 is 4.2% per year.

The significant domestic producers of nylon 66 are shown on Table 9-I. Du Pont and Monsanto have 89% (wt) of the total capacity of the six manufacturers listed (18).

9.2 BATCH OR CONTINUOUS POLYCONDENSATION OF NYLON 66

9.2.1 Process Description

The commercial process for manufacturing nylon 66 starts with the production of a water solution of nylon salt

TABLE 9-I.- NYLON 66 FIBERS - PRODUCERS

NYLON 66 - YARN, STAPLE AND TOW  
ANNUAL CAPACITY AS OF SEPTEMBER 1977  
(Millions of Pounds)

PRODUCING COMPANY AND PLANT LOCATION	CONTINUOUS FILAMENT YARN		STAPLE AND TOW		Total
	Textile	Industrial	Textile	Industrial	
CHEVRON CHEMICAL COMPANY OF PUERTO RICO (100% owned subsidiary of Standard Oil of California) Guayama, Puerto Rico	50	21	0	0	71
E.I. DU PONT DE NEMOURS & COMPANY, INC. Textile Fibers Department Camden, South Carolina	X	X			
Chatanooga, Tennessee	X				
Martinsville, Virginia	X		X	X	
Richmond, Virginia	X		X		
Waynesboro, Virginia	X				
	<u>240</u>	<u>344</u>	<u>270</u>	<u>210</u>	<u>1,098</u>
FIBER INDUSTRIES, INC. (62.5% owned by Celanese Corp. and 37.5% owned by ICI, Ltd. (United Kingdom) Greenville, South Carolina Shelby, North Carolina	<u>0</u>	<u>20</u>	<u>0</u>	<u>55</u>	<u>75</u>
KAYSER-ROTH CORPORATION Yarn Processing Division Creedmoor, North Carolina	10	0	0	0	10
MONSANTO COMPANY Monsanto Textiles Company Decatur, Alabama	X	X			
Greenwood, South Carolina	X		X	X	
Pensacola, Florida	X		X		
	<u>94</u>	<u>90</u>	<u>115</u>	<u>175</u>	<u>494</u>
WELLMAN, INC. Wellman Industries, Inc. sub., Man-Made Fiber Division Johnsonville, South Carolina	<u>0</u>	<u>0</u>	<u>0</u>	<u>40</u>	<u>40</u>
TOTAL	394	475	385	480	1,788

(hexamethylenediammonium-adipate). The process described is shown on Figure 9-1. The polymerization reaction takes place in the following three stages:

- o Evaporation of part of the water with some polycondensation.
- o Polycondensation with removal of all but a small quantity of water.
- o Polycondensation to the desired degree and removal of the residual quantity of water. Unlike the nylon 6 reaction, which is of the equilibrium type, this reaction goes to completion.

The nylon 66 process described here can be entirely continuous and make either chips, flakes, or pellets for later spinning. Also it can be combined with direct spinning to produce yarn, staple, or tow. The current trend appears to be toward direct spinning. Continuous nylon salt preparation may be integrated with batch polycondensation, in which case either chips, flakes, or pellets must be made. The diagram depicts all of these operations, but the process as built would have separate trains or items of equipment and control for batch and continuous operations (22), (23).

#### 9.2.1.1 Nylon salt production.-

Adipic acid is dissolved in hot water at 40°C in a jacketed, agitated vessel in a nitrogen atmosphere, and HMD (hexamethylene-diamine) is dissolved in another. The two solutions are brought together in a jacketed, agitated reactor and nylon salt (hexamethylenediammonium adipate) is formed. This aqueous solution of nylon salt is transferred to a surge vessel and stored for later use in the nylon 66 polycondensation reactor.

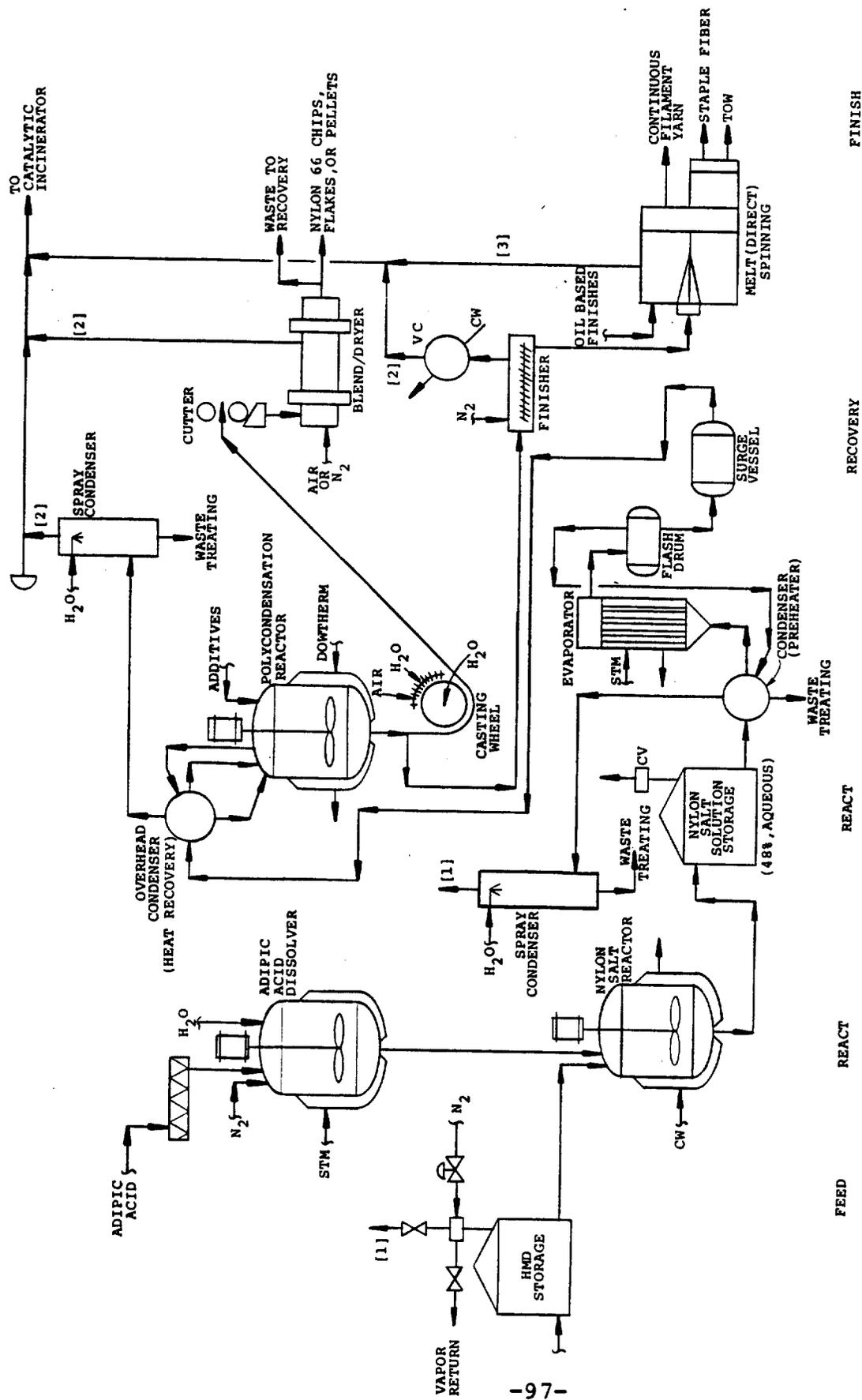


Figure 9-1.- Nylon 66 by batch or continuous polycondensation.

#### 9.2.1.2 Nylon salt purification and concentration.-

The 48% nylon salt solution is concentrated in an evaporator to a concentration of 65%. After passing through a clarifier (typically a cartridge type) to remove the trace of solid, it is ready for polycondensation.

The evaporator can be run for either batch or continuous operation, and generally it will be operated in the same mode as the polycondensation reactor.

#### 9.2.1.3 Polycondensation by a batch process.-

The operation typically requires a cycle of five hours consisting of the following steps:

- A. One and one-half hour charging and heating of the 65% nylon salt solution from the surge or day tank to 230°C; at the same time, the pressure is built up to 250 psig. Viscosity stabilizer is added.
- B. One hour heating, up to 245°C, while the pressure is maintained at 250 psig. During this time, delusterant, stabilizer, and other ingredients are added.
- C. One and one-half hour heating with gradual release of pressure from 250 to 0 psig at 270°C.
- D. One-half hour heating at 270-275°C with pressure still at 0 psig.
- E. One-half hour discharging, with some nitrogen pressure utilized to facilitate discharge.

Two jacketed reactors, each provided with an agitator and nitrogen blanketing are normally used (only one is shown in the diagram).

#### 9.2.1.4 Polycondensation by a continuous tank process.-

Although only one reactor is shown on the schematic, the two stage polycondensation described here is more common than single stage.

The nylon salt solution from the surge or day tank is pressurized to 290 psig, preheated to 530°F, and charged to a first-stage tank reactor, which is regulated at 530°F and 265 psig. Additives, prepared separately in small vessels, are added under nitrogen pressure. In the normally agitated first-stage reactor, the major part of the water is evaporated and a part of the adipate is polycondensed to a low degree. This material is then pumped and sprayed into a second-stage reactor together with a larger quantity of liquor re-circulated from that reactor. A stream of hot nitrogen flows countercurrent to the liquid spray and carries away the water vapor in a manner preventing congelation of the polyamide. Nylon 66 formed in this reactor, still containing some water, is partially recirculated and the remainder is conveyed to a finisher where the residual water is removed and the molecular weight is increased to the desired degree. The mass in the second-stage reactor is viscous and requires agitation.

Typical additives used at this stage are acetic acid as a viscosity stabilizer and titanium dioxide as a delusterant.

Other additives may include phenylphosphonate or kaolinite as a nucleating agents, various substances as stabilizing agents, and glycol as an anti-static agent. The total amount of additives often comes to about 2-3% (wt) of the nylon 66 polymerized. Some additives may be added to the finished nylon 66 after the polycondensation step, but viscosity stabilizer and delusterant should be added only during the polycondensation.

#### 9.2.1.5 Formation of nylon 66 chips.-

Nylon 66 may be used in molten condition (direct spinning process) for processing into fiber, or chips may be formed and later remelted for spinning (chip-remelt, spinning process). Where nylon 66 is produced for plastic use, it must be made in a pellet form.

The process described here, with minor modifications, can be used to produce either nylon 66 chips, flakes, or cylindrical pellets. Molten nylon 66 from the finisher is charged to a casting wheel (chilled with cold water), and solidified and quenched by water sprays, then cooled and dried with a flow of inert gas. The nylon ribbon that forms is loosened from the wheel by a scraper and fed to a cutter which reduces it to small chips or flakes. These fall into the blend/dryer for further drying and an inert gas purge is taken to the catalytic incinerator. The chips or flakes go to storage for shipment or later remelt spinning on site. Heat treatment in the solid state increases the molecular weight and melt viscosity for certain desired blends, such as those for plastic resins.

#### 9.2.1.6 Fiber spinning.-

Fiber spinning is accomplished either directly from the hot melt (direct spinning) or by first remelting chips or pellets made previously and stored. Direct spinning is only practiced in conjunction with continuous polycondensation.

Nylon 66 and nylon 6 are quite similar in their melt spinning and drawing capabilities. However, VOC emissions from direct spinning is less for nylon 66 than for nylon 6 manufacture because no residual monomer remains in nylon 66 at this stage. The absence of residual monomer in nylon 66 reduces fuming at the spinneret. Minor handling differences result between the two because of nylon 66's higher melting point and lower thermal stability.

#### 9.2.2 VOC Emissions

All significant emission rates and sources for this product are shown on Table 9-II. The schematic flowsheet, Figure 9-1, includes the emission streams and their sources.

The plants studied employ a spectrum of technology (improved over 40 years) and make a wide variety of products such that exact defining of (emission) sources and compositions is impossible and arriving at a representative model is difficult. The differences in common source emissions between batch and continuous operations are minor in composition but significant in amount.

TABLE 9-II.- VOC EMISSIONS FROM NYLON 66 FIBER - BATCH OR CONTINUOUS PROCESS

<u>Stream</u>	<u>Uncontrolled #/1000# Resin</u>	<u>Current Practice #/1000# Resin</u>	<u>Well Controlled #/1000# Resin</u>
[1] Nylon salt preparation Section	0.77	0.44	0.12
[2] Polycondensation Section	2.10	0.29	0.01
[3] Fiber Spinning Section	<u>0.76</u>	<u>0.17</u>	<u>0.08</u>
Totals	3.63	0.90	0.21

It is possible that a significant portion of nylon 66 plant emissions also fall into the category of particulates (primarily as aerosols). The extent of such emissions and the affect of particulate controls and regulations in reducing VOC emissions should be given further consideration in a detailed study.

A description of the designated emission streams follows:

- [1] Nylon salt preparation section - The significant VOC emissions come from the evaporators which concentrate the aqueous solution of nylon salt prepared and stored upstream of the evaporators. Evaporation (concentration) can be either batch or continuous. In either case, the stream will be composed largely of water vapor (99+% by wt) with small amounts of hexamethylene diamine, ammonia, and CO<sub>2</sub> and with traces of hexamethylene imine and cyclopentanone. The temperature (before control) will typically be 212°F.

Monomer storage losses which could be included here were reported to be negligible. Adipic acid is supplied as a powdered crystalline solid and is typically dissolved in water in a closed, N<sub>2</sub> blanketed dissolver vessel. The hexamethylene diamine storage tanks are inert gas blanketed and have vapor displacement lines back to the shipping tank car.

- [2] Polycondensation section - The polycondensation VOC emissions are primarily those accompanying the water vapor exhausted overhead from the polycondensation reactors. They can be from either batch or continuous operations. This is potentially the largest nylon 66 VOC emission source. Although the relative quantities

will vary somewhat, the composition of the exhaust stream is similar with either type of operation - typically water vapor (99+% by wt water of solution and of polymerization), hexamethylene diamine, ammonia, and CO<sub>2</sub>, and traces of volatile, water-soluble, ingredient impurities (i.e. hexamethylene imine, and cyclopentanone). Temperature is 212°F or somewhat above depending on the pressure used.

This stream also includes the exhaust from the finisher and the blend/dryer. The finisher completes the water removal by an inert gas purge and the composition is largely nitrogen, typically 95+% (by wt), 4 to 5% by wt water vapor, and small amounts of hexamethylene diamine and cyclopentanone. The blend/dryer (for chip or flake processing) exhaust has a composition similar to that for the finisher (blend/dryer data were commonly included in the fiber spinning exhaust data received and appear to be relatively small).

- [3] Fiber spinning section - This stream, the second largest potential nylon 66 VOC emission source, includes both emissions from direct (melt) spinning of filament yarn and from the casting and blend-drying of nylon 66 made into chips, flakes, or pellets. In the latter case, the fiber spinning is done later in a separate step when the chips are remelted. This step could be done either at the same or at a separate plant location, and the related VOC emissions for this step are not included here. Direct spinning is only used with continuous polymerization, but indirect spinning via chips, flakes, or pellets can use either batch or continuous polymerization.

The VOC exhausted in direct spinning is composed, primarily of small amounts of oil based finishes (mineral/vegetable oils applied to the fiber in the process to provide lubrication and static suppression) and hexamethylene diamine in water vapor.

In the case where chips, flakes, or pellets are made, the composition is small amounts of hexamethylene diamine and cyclopentanone in water vapor and inert gas (air or nitrogen).

### 9.2.3 Applicable Control Systems

The following control technologies are recommended for the emission streams described in Section 9.2.2 and on the schematic flowsheet for this product. The same stream numbering system is followed here. VOC reduction efficiencies given are based on calculated values from reporting producers and on estimates.

- [1] Nylon salt preparation section - Send overhead vapors from the evaporator to a spray condenser using water as a condensing medium. VOC reduction efficiency is approximately 85%. (No credit was given for the condensation occurring in the preheat exchanger, a unit which would be justified on the basis of process economics). The HMD storage tank would have an inert gas blanket system with vapor displacement back to the tank car for unloading.
  
- [2] Polycondensation section - Send overhead vapors from the polycondensation reactor to a spray condenser using water as a condensing medium. VOC reduction efficiency is approximately 95%. (Typically heat

recovery and condensation occur here which involve preheat of the reactor feed stream).

No pollution control credit was given because of the process economics justification. The remaining non-condensibles from the spray condenser would be sent to the catalytic incinerator. VOC reduction efficiency is approximately 90% for this operation.

Pass the finisher exhaust through a vent condenser (95% efficiency) and then to the catalytic incinerator using platinum catalyst. 90% reduction efficiency is assumed for the latter. The blend/dryer exhaust will go to the catalytic incinerator, again with a reduction efficiency of 90%.

- [3] Fiber spinning section - Send this stream to a catalytic oxidizer using a platinum catalyst. VOC reduction efficiency is approximately 90%. (Demisters often will be used for particulate or aerosol control).