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

by

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SECTION 11
POLYESTER FIBERS

11.1 INDUSTRY DESCRIPTION

Polyester fibers (P.F.) are defined as a manufactured fiber in which at least 85% weight of the fiber polymer is an ester of a dihydric alcohol and a substituted aromatic carboxylic acid. In commercial practice essentially all P.F. polymer is produced from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). The fiber polymer is produced using the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer with either of the two processes. DMT is the older and more entrenched process making up about 77% of the existing capacity, but the TPA process is now preferred and most new construction is built for it.

Polyester is the largest of the synthetic fibers. In 1978 polyester fiber production in the United States reached 3,800 million pounds and it continued to show significant market strength through the first quarter of 1979, (2).

Current polyester fiber capacity in the United States is estimated at approximately 5050 million pounds divided almost equally between continuous filament yarn, staple, and tow. In 1976, capacity utilization for textile-grade filament yarn at 62% (based on November 1976 capacity) was particularly depressed, (27). However, low capacity growth

(about 2% actual per year for 1977 and 1978) and good markets have increased utilization to an estimated 80% for 1979. Sufficient capacity exists to satisfy anticipated demand to 1980/1981. Projected demand until 1982 is essentially equivalent to the planned capacity.

Polyester fiber polymer manufactured directly from TPA is preferred since the recovery and purification of byproduct methanol is avoided. However, much existing capacity is based on DMT because polymerization grade TPA has only been available since 1963. Table 11-I lists the domestic polyester fiber manufacturers. Of the 18 manufacturers listed, four - DuPont, Fiber Industries (Celanese), Eastman Kodak, and American Hoechst - have approximately 80% of the total capacity. Most fiber manufacturers purchase either DMT or TPA as well as ethylene glycol. Only American Hoechst, E.I. DuPont, and Eastman Kodak have captive raw material producing facilities, and all three produce DMT, not TPA.

P.F. polymer manufacture is dependent on aromatic feedstock supplies because DMT and TPA produced in the United States are derived from paraxylene.

The DMT process consists of the catalyzed exchange of ethylene glycol groups for methyl alcohol to yield the intermediate, BHET. The liberated methyl alcohol is removed from the system by distillation in order to drive the exchange to completion. Significant VOC emissions can occur from methanol recovery.

The TPA process produces the intermediate BHET by the reaction of ethylene glycol with TPA and, since there is no byproduct methanol, VOC emissions are lower.

TABLE 11-I.- POLYESTER YARN, STAPLE, AND TOW PRODUCING COMPANIES

PRODUCING COMPANY AND PLANT LOCATION	ANNUAL CAPACITY AS OF SEPTEMBER 1977 (Millions of Pounds)		TOTAL
	CONTINUOUS FILAMENT YARN	STAPLE AND TOW	
AKZONA INCORPORATED (owned 64.5% by Akzo N.V. (The Netherlands) American Enka Company, division Central (Clemson), SC Lowland, Tennessee	X X <u>130</u>	X <u>10</u>	140
ALLIED CHEMICAL CORP. Fibers Division Columbia, South Carolina Moncure, North Carolina	X X <u>70</u>	0	70
AMERICAN CYANAMIDE COMPANY Fibers Division IRC Fibers Co., subsidiary Panesville, Ohio	55	0	55
AVTEX FIBERS INC. Front Royal, Virginia Lewistown, Pennsylvania	X <u>70</u>	X <u>45</u>	115
BEAUNIT CORPORATION Elizabethton, Tennessee	40	20	60
DOW BADISCHE COMPANY (jointly owned by Dow Chemical U.S.A. and BASF AG) Anderson, South Carolina	20	0	20
E.I. DU PONT DE NEMOURS & CO., Textile Fibers Department Camden, South Carolina Cape Fear, North Carolina Chattanooga, Tennessee Cooper River, South Carolina Kinston, North Carolina Old Hickory, Tennessee	X X X X X X X <u>765</u>	X X X X X X <u>840</u>	<u>1,605</u>

TABLE 11-1.- POLYESTER YARN, STAPLE, AND TOW PRODUCING COMPANIES (continued)

PRODUCING COMPANY AND PLANT LOCATION	ANNUAL CAPACITY AS OF SEPTEMBER 1977 (Millions of Pounds)		TOTAL
	CONTINUOUS FILAMENT YARN	STAPLE AND TOW	
EASTMAN KODAK COMPANY Eastman Chemicals Division Eastman Chemicals Products, Inc. subsidiary, Carolina Eastman Co. division	X	X	
Columbia, South Carolina Tennessee Eastman Co., division Kingsport, Tennessee	X	X	
FALK FIBERS & FABRICS INC. Universal Polymer Products Co. subsidiary	115	405	520
Fuquay-Varina, North Carolina	10	0	10
FIBER INDUSTRIES INC. (owned 62.5% by Celanese Corp. and 37.5% by Imperial Chemical Industries Limited (UK) Greenville, South Carolina Palmetto (Darlington), SC Salisbury, North Carolina Shelby, North Carolina	X	X X X	
	450	705	1,155
THE FIRESTONE TIRE & RUBBER CO. Firestone Synthetic Fiber Co., div Hopewell, Virginia	30	0	30
THE GOODYEAR TIRE & RUBBER CO. Chemical Division Scottsboro, Alabama	30	0	30
CLARENCE L. MEYERS & CO. Meyers Fibers, Inc. Ansonville, North Carolina	10	0	10
MONSANTO COMPANY Monsanto Textiles Company Decatur, Alabama Sand Mountain (Lake Guntersville), Alabama	X	X	
	140	100	240

TABLE 11-1.- POLYESTER YARN, STAPLE, AND TOW PRODUCING COMPANIES (concluded)

PRODUCING COMPANY AND PLANT LOCATION	ANNUAL CAPACITY AS OF SEPTEMBER 1977 (Millions of Pounds)		TOTAL
	CONTINUOUS FILAMENT YARN	STAPLE AND TOW	
PHILLIPS FIBERS CORP. (Owned 90% by Phillips Petroleum Company and 10% by Phone-Poulenc SA [France]) Rocky Mount, North Carolina	50	0	50
ROHM AND HAAS COMPANY Rohm and Haas Carolina Inc., sub. Fayetteville, North Carolina	140	0	140
TEXFI INDUSTRIES, INC. Texfi Yarn and Fibers Group Asheboro, North Carolina New Bern, North Carolina	X X <u>45</u>	0	45
WELLMAN, INC. Wellman Industries Inc., sub. Man-Made Fiber Division Johnsonville, South Carolina	0	40	40
TOTAL	2295	2445	4,740

11.2 P.F. MANUFACTURE BY DIMETHYL TEREPHTHALATE PROCESS

11.2.1 Process Description

Polyester fiber is manufactured from DMT in either batch or continuous processes. (Only a batch process is described.) The three basic changes required between batch and continuous operations are; 1) Replacing the kettle-reactor in batch operations for a column-type reactor in the ester exchanger, 2) "No-back-mix" reactor designs are required for continuous processes at the polymerizer, and 3) Differing additives and catalysts are required to make a product with proper molecular weight, molecular weight distribution, etc. The batch process described here is a two-reaction-step process which begins with an ester exchange between ethylene glycol and DMT. The products of this reaction are methanol vapor (MeOH) and BHET monomer. The monomer is polymerized to polyethylene terephthalate (PET) in a second reaction step in the presence of heat, catalysts, and vacuum. The major polymerization by-product is ethylene glycol with smaller amounts of methanol. The ethylene glycol and methanol are condensed and transferred to storage tanks for reprocessing by others (28), (29).

Fibers are produced from PET by spinning, either directly from the polymer melt, or indirectly from chips. Staple fiber is wetted, drawn, crimped, dried with indirect heat, and may be cut before baling. Yarn fiber may be dried and heat set before it is tube wound.

Referring directly to Figure 11-1, Polyester fiber manufacture by the DMT/TPA process, molten dimethyl

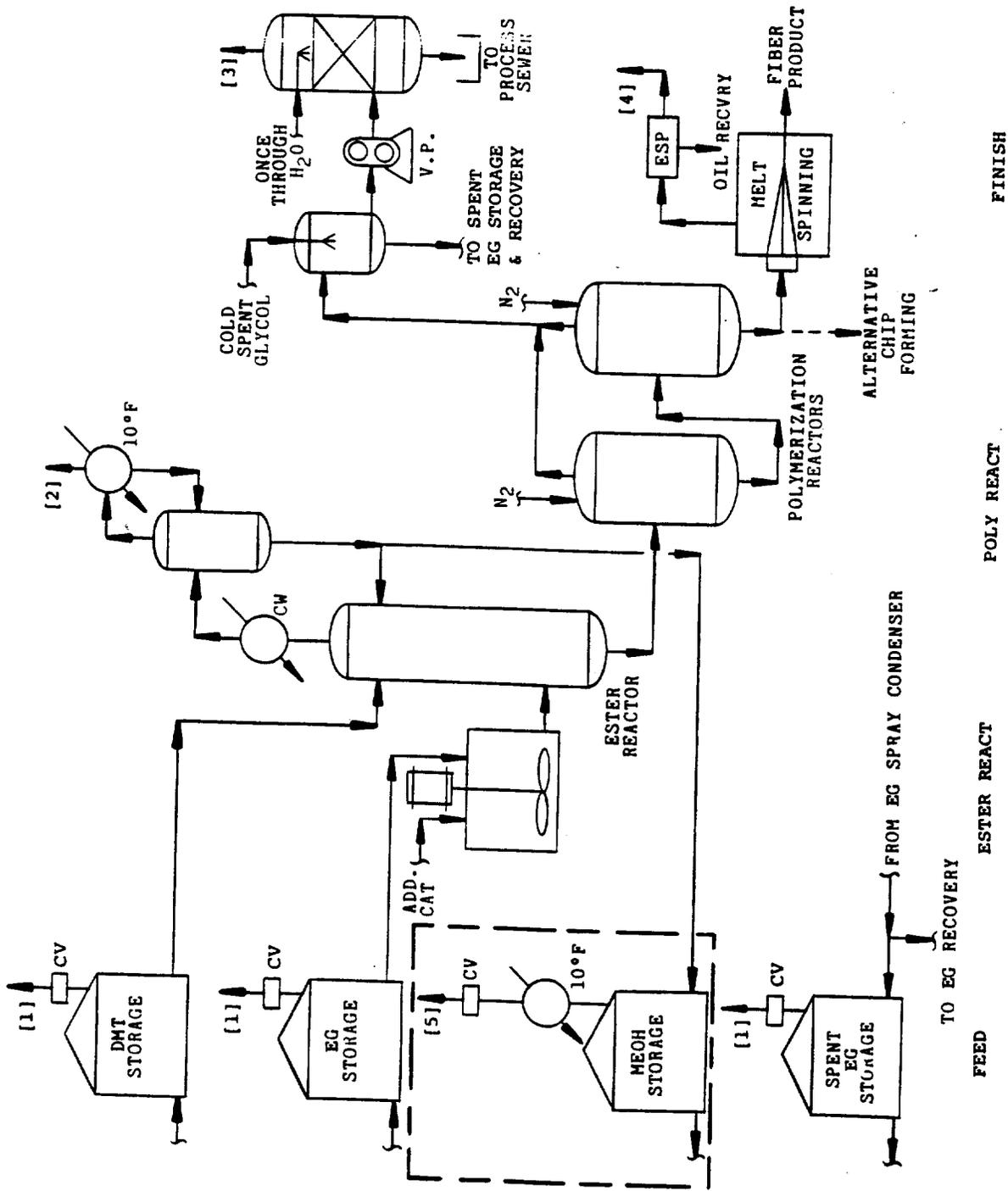


Figure 11-1.- Polyester fibers using DMT/TPA processes.

terephthalate (DMT) and ethylene glycol (EG) are drawn from storage tanks [1] and sent to the first step, or ester exchange, reactor. The EG goes first to a small mix tank where catalysts and additives are stirred in, and then to the reactor. About 0.6 lb EG and 1.0 lb DMT are used for each 1.0 lb PET product. The ester exchange reaction is conducted to start at 170 and end at 230°C with atmospheric pressure, and the major products are BHET monomer and methanol. Methanol has to be removed from the reactor as a vapor to shift the reaction to increase the formation of BHET. Methanol vapor overhead (OHD) from the ester exchange reactor is controlled by cooling water (CW) and refrigerated condensers, and the vent stream [2] is the first major process emission source. Condensed byproduct methanol is sent to methanol storage for export to the DMT supplier for reuse, and the tank vent for this methanol storage tank is another major emission source, [5].

Bottoms from the ester exchange reactor contain the desired BHET intermediate or monomer. They are sent to the second step, the polymerization reactors. In the first polymerization reactor, the pressure is lowered to the range of 1-760 mm Hg absolute and the temperature is increased to 230-285°C to remove residual methanol and the EG forming from BHET polymerization to PET. In the second polymerization reactor, to further reduce methanol and EG residuals, the pressure is lowered below 1 mm Hg, and the temperature is raised to 260-300°C. A metallic catalyst is employed. The vapor streams from the polymerization reactors are combined and controlled by various systems designed to avoid plugging or fouling from PET solids. These systems include EG spray condensers or contactors and the vacuum systems shown in

Figure 11-1. The vent from these vapor systems is the third major process emission point, stream [3]. Systems that use steam jet ejectors for vacuum produce VOC contaminated contact waters, and they will have substantially greater VOC emissions if these waters are cooled with atmospheric cooling towers (atmospheric contact) than if once-through H₂O or mechanical vacuum pumps (non-atmospheric contact) are used.

The two polymerization reactors are operated in series with the (product) bottoms from the second reactor being sent either to melt spinning or to a chip forming machine for later spinning. Chip forming is not discussed in this report. Oil base finishes are applied to the filaments made in melt spinning to provide lubrication and static suppression for fiber processing. The bulk of the oil base (finish) is recovered and recirculated. A small quantity is emitted through the spinning machine vents and constitutes the fourth emission stream, [4]. The oil exits the spinning machine vents in the form of a "smoke".

11.2.2 VOC Emissions (DMT Process)

All significant emissions for this product are shown on Table 11-II. The schematic flowsheet for this product, which includes the emission streams and their sources, is Figure 11-1. The same stream number is used for a given stream throughout, but note that the DMT process has streams [1] through [5] and TPA only has [1] through [4]. The designated streams for the DMT process are:

- [1] Raw and recovered materials storage tanks, except recovered methanol (MEOH) - Fixed roof storage tanks are used throughout in existing facilities.

TABLE 11-II.- VOC EMISSIONS FROM POLYESTER FIBER MANUFACTURE BY DIMETHYL TEREPHTHALATE PROCESS

Stream	Uncontrolled #/1000# Resin	Current Practice #/1000# Resin	Well Controlled #/1000# Resin
[1] Raw and Recovered Material Storage		0.1	
[2] Ester Exchange Reactor	0.15	0.15	0.05
[3] Polymerizers*			
(a) non-atmos contact	0.04	0.04	0.04
(b) atmos contact	3.65	3.65	----
[4] Spinning Machines	3.83	1.28	0.19
[5] MECH Storage - DMT Process Only	0.29	0.09	0.03
Subtotals*			
(a) Non-atmos contact	4.31	1.56	0.31
(b) Atmos contact	7.96	5.21	0.31
Weighted Total - DMT	6.07	3.32	0.31
51.8% (a), 48.2% (b)			

*Emissions subtotals are given assuming polymerizer vents [3] are controlled by (a) non-atmos contact condensers and (b) non-atmos contact + atmos contact (cooling tower) condensers.

Emissions are vapors of EG and DMT and result from vapor displacement (working losses) and tank breathing. The bulk of dimethyl terephthalate (a solid at ambient conditions) is stored in hopper bins until needed. Then it is melted at elevated temperatures in heated, insulated tanks. Fresh and spent ethylene glycol are stored at ambient conditions. Recovered methanol (MEOH) storage is treated as emission stream [5].

- [2] The ester exchange reactor - This stream is one of the larger potential emission sources in this process. The flow rate and stream composition vary as the batch goes through its cycle. The stream carries methanol byproduct vapors primarily and steam, and it is processed through both cooling water and refrigerated condensers.
- [3] The polymerization reactors - This stream carries large quantities of steam and ethylene glycol vapors, small amounts of MEOH vapors, volatile feed impurities, and inert gas. Inert gas is added to the reactor to strip ethylene glycol vapors, residual volatiles, and steam from the polymer and prevent product discoloration from oxygen contamination. The resulting emissions pass through a system that includes glycol and water contact condensers (spray). There are two types of contact condensers; (a) non-atmospheric contact or once-through, and (b) atmospheric-contact. Although type (a) produces a flow of contaminated water, it has low VOC emissions compared to type (b). Type (b) systems use a cooling tower to cool the contaminated water for reuse in the spray condenser, and the cooling tower itself becomes a large potential VOC emission source.

- [4] The spinning machines - A fume or smoke of oil and moisture is emitted from various vents. Usual controls include catalytic incinerators and mist eliminators.
- [5] Recovered methanol storage tank ventilation (DMT process only) - This stream is large due to the volatility of MEOH, and refrigerated condensers are used to control it.

VOC emissions from the DMT process can be summarized as follows:

- o Polymerizer vent gas treatment exhaust, stream [3], is a potentially large emission source, depending on the following process variation. Spray condenser bottoms, largely warm contaminated water, can be handled in either of two ways - Type (a) process, once through or recycle without atmospheric contact and - Type (b), recycle through a cooling tower with atmospheric contact. Type (a) emissions are estimated to be 0.044 lb/1000 whereas Type (b) are estimated to be 3.65 lb/1000.
- o Spinning machine vents, stream [4] are another large emissions source, and they are the largest for the Type (a) variation, second largest for Type (b). Current practice puts stream [4] at 1.28 lb/1000. Thus the total emissions of a non-contact plant [type (a)], with current practice, are estimated to be 1.56 lb/1000 and those for a contact plant [Type (b)] are 5.21 lb/1000. Table 11-II summarizes the emissions for polyester fibers manufacture by the DMT process.

11.2.3 Applicable Controls (DMT Process)

(Section 11.2.3 has been combined with 11.3.3 that follows since the controls are the same for both processes.)

11.3 P.F. MANUFACTURE BY TEREPHTHALIC ACID (TPA) PROCESS

11.3.1 Process Description (TPA)

Polyester fiber is manufactured from TPA in either batch or continuous processes, but only a batch process is described. The process is a two-step process exactly analogous to the DMT process described in Section 11.2. The products of the first, or esterification, reactor are H₂O vapor and BHET. BHET is polymerized in the second step reactors just as in the DMT process. The absence of MEOH vapor as a first step byproduct eliminates the need for the byproduct, MEOH, storage tank, vent [5], and the VOC in major emission stream [2]. For the purposes of this study, these are the only significant differences between the two processes. Figure 11-1, therefore, represents the process flow for the TPA process provided the MEOH storage tank and emission stream [5] are deleted. Of course process conditions for TPA differ from DMT, but the objectives are the same - short reaction time, low polymer ether linkage content, good polymer color and thermal stability.

11.3.2 VOC Emissions (TPA Process)

The emission streams for this process correspond to those for the DMT process except that there are no byproduct methanol emissions. Again, Figure 11-1 can be

used minus stream [5] and the MEOH storage tank. Table 11-III summarizes the emission rates and sources for the TPA process. The major streams are:

- [1] Raw and recovered materials storage tank - Fixed roof storage tanks and bins are used throughout the process and they have conservation vents on the tanks. The emissions are vapors of EG, TPA and TPA dust; and they result from working (vapor displacement) and breathing losses. Terephthalic acid is stored in bins at ambient conditions until needed, and then it is melted and stored in insulated tanks at elevated temperatures until charged. There are no emissions.
- [2] Esterification reactor - This stream consists primarily of steam and EG vapors, with small amounts of feed impurities and volatile side products. For economic reasons (EG recovery) it is controlled with condensers, and exits at about 220°F.
- [3] Polymerization reactors - Like stream [2], this stream consists of steam and EG vapors with small amounts of volatile impurities. It is well controlled by CW condensers exiting at about 120°F.
- [4] Melt spinning - A fume or smoke of oil and water droplets is emitted from various vents. This is the largest single source of hydrocarbon emissions from PET manufacture by TPA. Usual controls include catalytic incinerators and mist eliminators.

The polyester fibers by TPA process is relatively non-polluting because it does not produce byproduct methanol with attendant recovery and storage emissions. Like the Type (a) variation of the DMT process, spinning machine vents, Stream [4], are the largest single emissions source at 1.28 lb/1000 (current practice).

TABLE 11-III.- VOC EMISSIONS FROM POLYESTER FIBER MANUFACTURE BY TEREPHTHALIC ACID PROCESS

<u>Stream</u>	<u>Uncontrolled #/1000# Resin</u>	<u>Current Practice #/1000# Resin</u>	<u>Well Controlled #/1000# Resin</u>
[1] Raw and Recovered Material Storage	Nil	Nil	Nil
[2] Ester Exchange Reactor	0.039	0.039	0.039
[3] Polymerizers	0.042	0.042	0.042
[4] Spinning Machines	<u>3.83</u>	<u>1.28</u>	<u>0.191</u>
Totals	3.91	1.36	0.27

Total emissions are estimated to be 1.36 lb/1000 with current practice. Table 11-III summarizes emissions for polyester fiber manufacture by the TPA process.

11.3.3 Applicable Control Systems (DMT and TPA Processes) (See paragraph 11.2.3)

Because the DMT and TPA processes are similar, differing only in that DMT produces byproduct methanol and has a control option with atmospheric contacting of contaminated cooling water, and TPA produces byproduct water and does not have such an option, the control systems for the two are discussed together. The following controls are recommended for the streams described in Sections 11.2.2 and 11.3.2 and shown on Figure 11-1. The same stream numbering system is used throughout.

[1] Emissions from fresh and recovered materials storage tanks - Fixed roof tanks are satisfactory for ethylene glycol since its vapor pressure is low. Other tanks with more volatile or hazardous vapors should use vapor return lines to loading tank trucks or cars, thereby eliminating working losses or approximately 58% of total (working plus breathing) tank emissions. Conservation vents should be used on all tanks not equipped with more sophisticated vent control and they are almost always economically justified. Inert gas blanketing and flare/incinerator systems may be required for some storage tanks, or CW or refrigerated condensers.

Water scrubbers may be applicable on DMT and TPA tank vents primarily for housekeeping purposes. DMT and TPA are crystalline solids at ambient conditions

and can cause sublimed solids buildup on cool surfaces adjacent to tank vents. High VOC removal efficiencies have been reported when scrubbing phthalic anhydride (12), (13); a material physically similar to DMT. No control efficiency was assumed.

[2] Emissions from the ester exchange or esterification reactors -

- o DMT process - With the DMT process, byproduct methanol vapor must be removed to enhance the reaction and recovered for economic reasons; the reactor vent is a major process emission source. Presently economic controls include a C.W. condenser and provision for refluxing part of the MeOH for continuous or column-type reactors. BDCT will include a refrigerated condenser on the K.O. drum vent. 90% reduction of MeOH vapors was assumed.
- o TPA Process - With the TPA process the main byproduct is H₂O vapor, not MeOH; however, ethylene glycol vapors and volatile feed impurities and side products are all present and the ethylene glycol must be recovered. Present controls are C.W. condensers with the exit vent temperature about 220°F.

[3] For the polymerization reactors -

- o DMT process - The polymerization of BHET is conducted under vacuum to remove EG vapors and shift the reaction toward completion. Temperatures are high (520-560°F) and an N₂ inert gas blanket is used in all equipment

downstream of the polymerization reactor feed tank (not shown in Figure 11-1). For the continuous process a pre-polymerization reactor proceeds polymerization. The major emission point [3] is the vacuum system discharge (at least two separate vents for the continuous version). Cooling water condenser controls are used for EG recovery for economic reasons and the exit temperature is about 100°F. Polymer solids content of the vapor streams is high enough to foul surfaces and plug jet nozzles so some type of prevention is commonly practiced. One method sprays hot EG vapors into the vacuum lines to reduce deposition. The scheme shown in Figure 11-1 shows spray contact condensing the vapors with cold EG liquid to avoid solids clogging the vacuum system nozzles. The contactor bottoms are saponified before EG purification. The well-controlled value assumes discontinuance of atmospheric-contact, cooling water.

- o TPA process - Essentially the same as for the DMT process.

[4] Melt spinning - DMT and TPA processes - Spinning lubricant and water vapor are emitted as an aerosol or smoke from various spinning vents. This stream, [4], is the major emission source for these plants. Common controls include mist eliminators and catalytic incinerators, and expected efficiencies

are 70 and 80%, respectively. Improved control can be obtained by controlling a higher percentage of the total number of spinning machines and by using more efficient control devices such as electrostatic precipitators. An overall (from uncontrolled) control efficiency of 95% was assumed.

- [5] MeOH storage - DMT process only - Byproduct methanol is produced from the DMT process only. Controls include a refrigerated condenser system. An overall efficiency of 90% was assumed.