POLYSTYRENE
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Reference Number
3

Pullman Kellogg
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U.S. EPA, OAQPS, ESED, CPB, CAS
Room 730 Mutual Building (MD-13)
Research Triangle Park
North Carolina 27711

Attention: Mr. M. R. Clowers

Dear Mike:

Attached is a trip report containing the non-confidential data supplied by Amoco Chemical regarding VOC emissions from their manufacture of polystyrene and polypropylene. This information has been reviewed for accuracy and non-confidentiality by Mr. H. M. Brennan of Amoco, and its non-confidential status confirmed.

Also attached is the letter from Amoco containing the additional data we had requested during the visit.

Very truly yours,

PULLMAN KELLOGG
a Division of Pullman Incorporated

E. L. Bechstein
Sr. Process Engineer

ELB:jh
Attachments

cc: W. M. Talbert w/attachment
H. M. Brennan "

Trip Report: Amoco Chemicals Corporation, Chicago, Illinois for Polypropylene and Polystyrene VOC Air Emission Data

October 12, 1978

The following personnel were in attendance:

Amoco Chemicals Corporation

Harry M. Brennan	Director, Air & Water Conservation
Richard A. Symuleski	Specialist, Air and Water Conservation

EPA

M. R. Clowers

Pullman Kellogg

E. L. Bechstein

D. K. Webber

Amoco Chemicals manufactures polystyrene and polypropylene resins at several locations. Descriptions of the processes and storage facilities by Amoco including notes by Pullman Kellogg during the visit follows:

I. Slurry Polypropylene Process

A. Process Description (See Figure 1)

This is a continuous,slurry process for the manufacture of polypropylene polymer from propylene and n-hexane. Nominal plant capacity is 250 MM lbs/yr. at the New Castle, Delaware plant and 270 MM lbs/yr. at the Chocolate Bayou, Texas facility. Except for minor differences in the process trains, both plants are identical and all the data presented here is based upon a 520 MM lbs/yr. production basis. The differences between the processes will be identified in the following narrative.

The major raw material, propylene, is stored in pressure vessels, and results in no emissions. Methanol and n-Hexane solvents are stored in vertical floating and fixed roof storate tanks. The New Castle solvent tankage vents are manifolded to a flare system. At the Chocolate Bayou plant the individual tanks are vented to atmosphere. Table 1 shows raw materials requirements, and tankage emissions data for the Chocolate Bayou plant.

In the process, hexane and catalyst are fed to the mix tank from storage on a continuous basis. From the mix tank, the blend is fed to the reactor where it is mixed with propylene, hexane and recycle and polymerized. A portion of the reactor contents is continuously fed to the flash tank where volatile components, mostly propane, are vaporized. The resulting vapor stream is used as make-up fuel at New Castle and sent to the olefins plant for recovery at Chocolate Bayou; hence no emission results from this stream.

Slurry from the flash tank is fed to the decanter where crude product is separated. The heavy methanol-water phase is withdrawn from the decanter and fed to the methanol recovery section. The light hydrocarbon layer, containing solid isotactic polymer and an atactic polymer-hexane solution is fed to a centrifuge where the two phases are separated. The resulting atactic-hexane solution is fed to the hexane recovery section while the isotactic polymer solids are fed to the product drier. The exhaust gas from the drier is flared (Vent 1, Table 2). The flare system is believed to provide 100% combustion of emissions. Dried polypropylene, containing less than 0.5% volatiles by weight, is extruded, pelletized and sent to product storage.

In the methanol recovery section, the crude methanol streams are refined and recycled and the bottoms streams, mostly water and catalyst metals are sewered. The hexane recovery section consists of two towers. Hexane is purified for recycle and atactic solids are recovered at New Castle and landfilled at Chocolate Bayou. Non-condensibles from this section are flared (Vent 2, Table 3) and the water stream, containing small amounts of hexane is sewered at Chocolate Bayou and recycled for cooling water at New Castle.

This hexane results in a secondary emission in an API separator. (Data on this emission has been requested from Amoco Chemicals)

B. VOC Emissions Data

All emissions except those from the API separator downstream of the hexane recovery towers are summarized in Tables 1, 2, and 3. No fugitive emissions data was available. Fugitive emissions were stated to be low.

C. VOC Emission Control Devices

Monomer and solvent storage vents in the Chocolate Bayou plant are uncontrolled. In the New Castle plant storage tank vent vapors are collected and sent to a low pressure flare. All process vent emissions are collected and sent to flare in both palnts. The flare system was stated to have 100% combustion efficiency in both cases. Hexane emissions from the API separator are uncontrolled.

Figure 1

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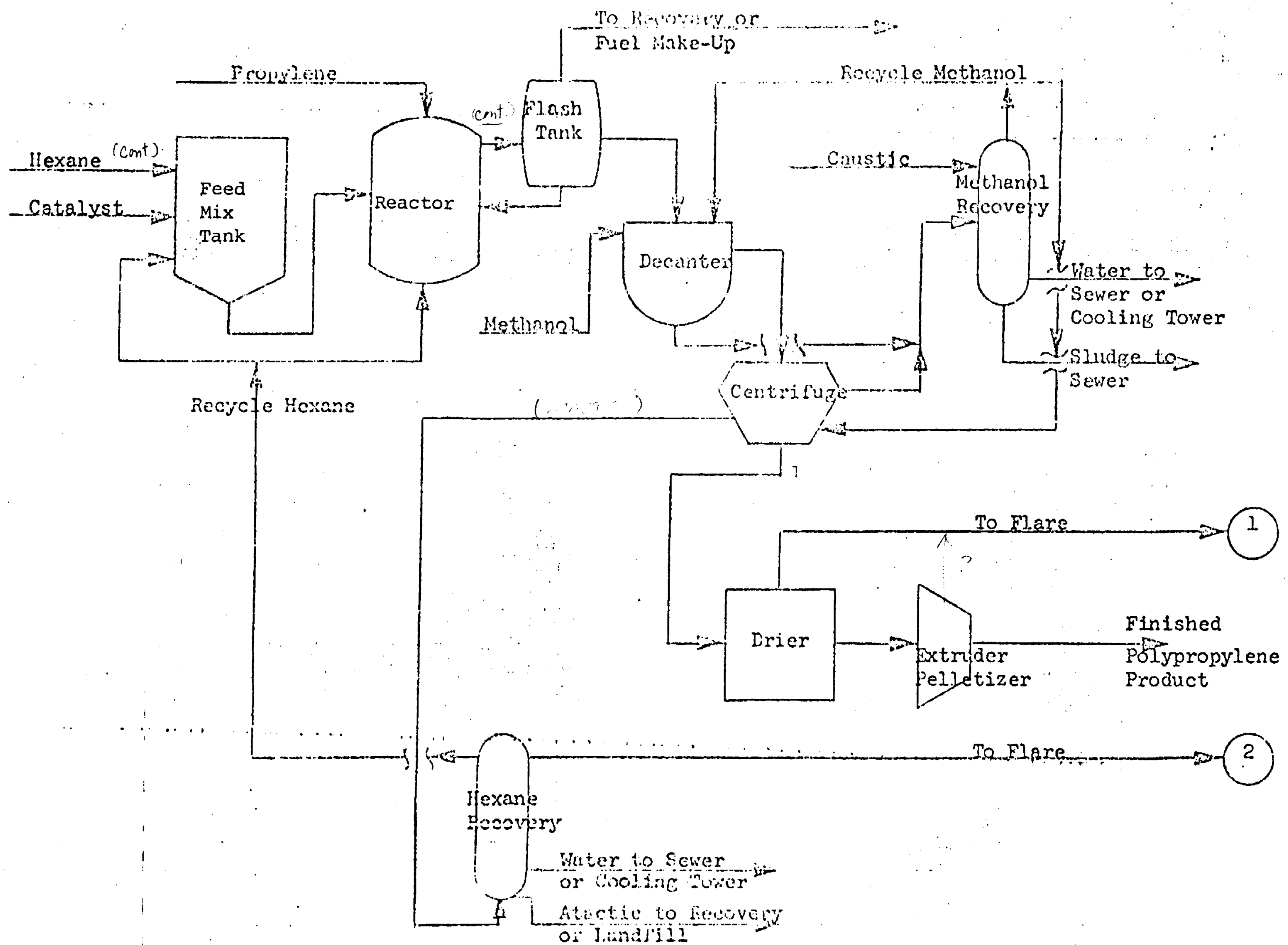
Slurry Polypropylene Process --
New Castle, Delaware & Chocolate Bayou, Texas



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SLURRY POLYPROPYLENE PROCESS

Table I

Typical Reactor Feed Composition

Component	Weight %
propylene	97.-99.
n-hexane	1.- 3.

Basis: Engineering estimates on catalyst-free basis

Monomer Storage Conditions & Emissions*

Propylene Storage

Vapor pressure	170 psia @ 80°F
Temperature	30°F minimum 105°F maximum
Pressure vent valve setting	300 psig
Vent discharge	atmosphere
Emissions	nil

n-Hexane Storage

Vapor pressure	5 psia @ 100°F
Temperature	30°F minimum 105°F maximum
Emissions	29,000 lbs. hexane/yr.

Methanol Storage

Vapor pressure	5.4 psia @ 105°F
Temperature	30°F minimum 105°F maximum
Emissions	21,600 lbs. methanol/yr.

Basis: engineering estimates

*Chocolate Bayou emissions only. New Castle tankage vents to flare.

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SLURRY POLYPROPYLENE PROCESS

Table 2 Vent 1

Product Drier Vent

This stream, resulting from an inert gas drying system contains volatiles removed from isotactic polymer solids. Under normal operation, this stream is flared.

Flare Inlet

Temperature	105°F
Pressure	168 psig
Volumetric Flowrate	11.5 ACFM
Mass Flowrate	865 lbs./hr.

Composition	Weight %
propane	79
propylene	18.3
n-hexane	2.4

Basis: engineering estimates

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SLURRY POLYPROPYLENE PROCESS

Table 3 Vent 2

Hexane Recovery Unit Vent

This stream results from the dehydration of spent hexane purified for recycle. Under normal operation, this stream is flared. Conditions of inlet to the flare are unknown.

Mass Flowrate

n-hexane	10.5 MM lbs./yr.
methanol	1.04 MM lbs/yr.

Basis: Calculated by difference from an overall process mass balance.

II. Continuous Polystyrene Resin Process - Joliet, Illinois

A. Process Description (See Figure 2)

This is a fully continuous, thermal copolymerization process for the manufacture of pelletized polystyrene resin from styrene monomer and polybutadiene. Numerous grades of crystal and impact polystyrene can be produced by three identical process trains having a total nominal capacity of 280 MM lbs/yr. Feed formulations and process operating conditions are adjusted as necessary to meet various desired product specifications. The data presented in the attached relate to the total plant throughput.

Styrene, polybutadiene, mineral oil and minor amounts of recycle polystyrene, antioxidants and other additives are introduced into the feed dissolver tank in proportions that vary according to the grade of resin being produced. Typical feed blend compositions and estimated fugitive emissions from monomer storage facilities are presented in Table 4. Monomer storage tankage is of the fixed roof variety tankage. In-process storage utilizes fixed roof tanks. Styrene tankage is small since stryene is delivered by pipeline.

Blended feed is pumped on a continuous basis to the reactor where the feed is thermally polymerized to polystyrene. The polymer melt, containing some unreacted styrene monomer and by-products is pumped to a vacuum devolatilizer where most of the monomer and by-products are separated, condensed and sent to the styrene recovery unit. Vapors from the styrene condenser are vented through a steam ejector (Vent 1, Table 5).

Molten polystyrene from the bottom of the devolatilizer is pumped through a stranding die-plate into a cold water bath. Vapors from this step, consisting mostly of steam with traces of styrene are vented through a forced-draft hood for housekeeping purposes (Vent 2, Table 6). The cooled strands are pelletized and sent to product storage.

In the styrene recovery unit, crude styrene monomer is separated in a tower. The styrene vapor off the tower is condensed and recycled to the feed dissolver tank. Minor amounts of non-condensibles are vented through a steam ejector (Vent 3, Table 7). Heavies from the tower are used as fuel make-up.

B. VOC Emissions Data

VOC emissions were reported for four sources; storage tankage, devolatilizer condenser, styrene recovery column condenser, and pelletization strand bath. See Tables 4, 5, 6 and 7. No fugitive emissions data was available. VOC emissions from pellet storage are negligible.

C. VOC Emission Control Devices

The only control devices utilized are condensers upstream of steam jets which are also required for process operability. Amoco has not explored alternate pelletization approaches (such as underwater pelletization) which might have lower emissions.

Figure 2

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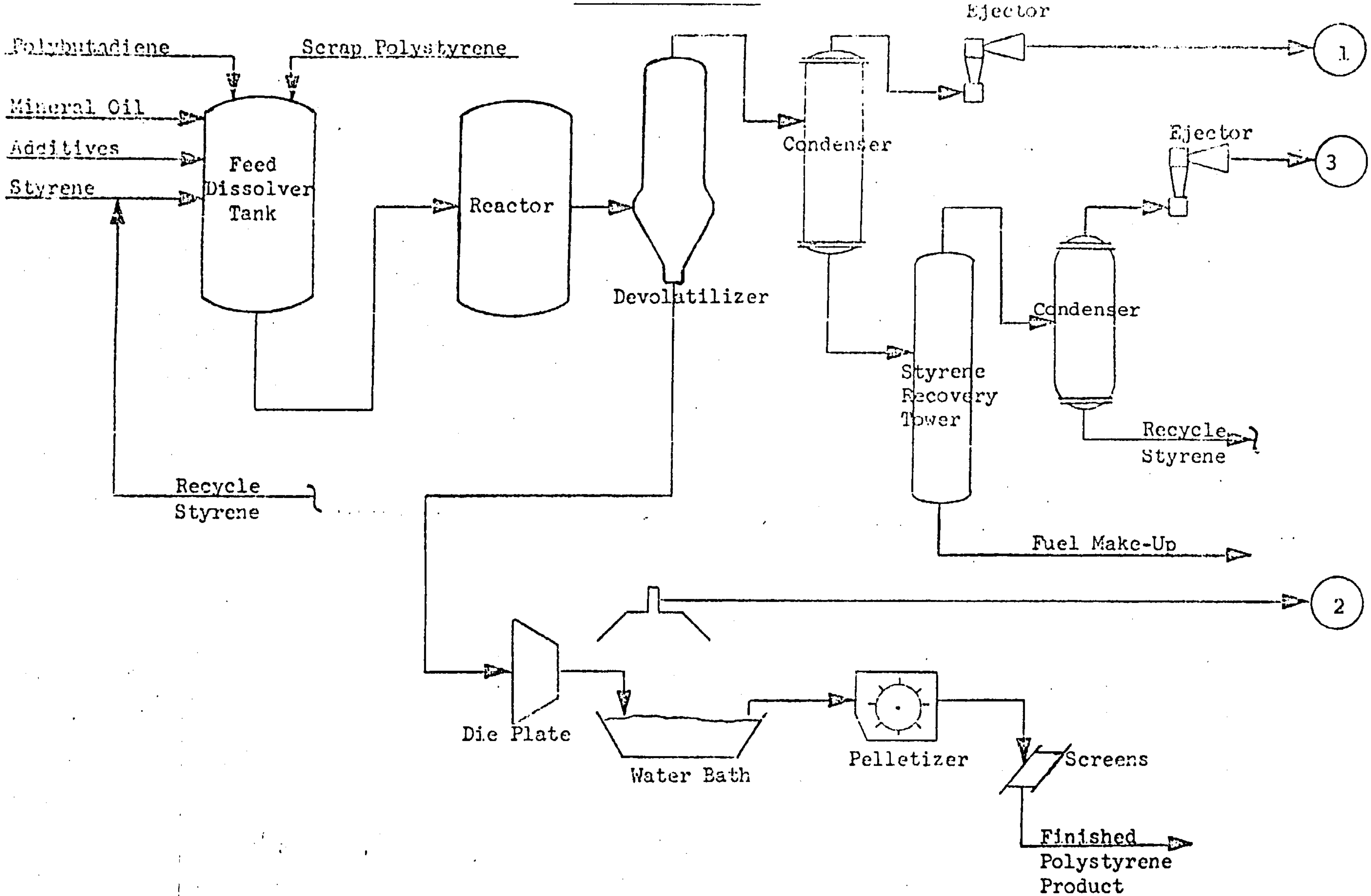
Joliet, Illinois

Continuous Polystyrene
Resin Process



Continuous Polystyrene Resin Process

AMOCO CHEMICALS CORP.

Continuous Polystyrene Resin

Table 4
Typical Reactor Feed Composition --
Continuous Polystyrene Resin Process

Component	Weight %
styrene monomer	81.5 - 100.0
polybutadiene	0 - 15.0
scrap polystyrene	0 - 5.0
mineral oil	0 - 4.0
Antioxidants/additives	0 - 0.5

VOC Emissions from Tankage*

	lbs.styrene/year
styrene monomer storage	25,275
feed dissolver tank	2,580
interim feed storage tank	2,540
styrene tower feed tank	715
recycle styrene storage tank	240
styrene tower bottoms storage tank	125

*Basis: Engineering estimates of breathing and working losses as per USEPA Manual AP-40, 2nd Edition.

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Continuous Polystyrene Resin

Table 5 Vent 1
Styrene Condenser Vent

This stream consists of traces of unreacted styrene and volatile components separated from the polystyrene melt in a vacuum devolatilizer. The stream is vented through a steam ejector.

Volumetric Flowrate	155 ACFM
pressure	atmospheric
temperature	210°F
Mass Flowrates	
steam	2.98 MM lbs/yr
styrene	0.83 MM lbs/yr

Basis: engineering estimates

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Continuous Polystyrene

Table 6, Vent 2
Extruder/Quench Vent

This stream is formed when hot, extruded polystyrene strands emanating from the dieplate contact the cold water in the quenching bath. The resulting steam, containing traces of styrene are exhausted through a forced-draft hood.

Volumetric Flowrate	60,000 ACFM
temperature	70°F
Mass Flowrate	
styrene	42,000 lbs/yr

Basis: Engineering estimate of 5-7 ppm styrene concentration in exhaust gas.

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Continuous Polystyrene

Table 7, Vent 3
Styrene Recovery Unit Condenser Vent

This stream contains the non-condensible components separated in the styrene recovery tower and is vented through a steam ejector.

Volumetric Flowrate	95 ACFM
pressure	atmospheric
temperature	210°F
Mass flowrates	
steam	1.73 MM lbs/yr
styrene	37,230 lbs/yr

Basis: engineering estimates

III. Batch Polystyrene Resin Process - Illinois & Torrance, California

A. Process Description - See Figure 3)

This is a batch, thermal polymerization process for the manufacture of polystyrene resin from styrene monomer. Different grades of polystyrene resin are produced by five identical process trains at Willow Springs, Illinois having a total nominal capacity of approximately 87 MM lbs/yr. and by three identical process trains at Torrance, California having a total nominal capacity of 50 MM lbs/yr. Feed formulations and operating conditions may vary slightly from one batch to another to meet various desired process specifications. The process flowsheet presented in the attached is applicable to all operating process trains and the data relate to emissions based on a total plant capacity of 137 MM lbs/yr. The batch polymerization facilities are utilized mainly for crystal polystyrene manufacture but also produces smaller amounts of impact grades. Polymerization is carried out batch-wise. Devolatilization and pelletization as carried out continuously and in essentially the identical manner as in the continuous polymerization process.

Pure styrene monomer is pumped from storage on a batch-wise basis to the mix feed tank where it is blended with USP mineral oil in various proportions to produce different flow grades of product. Typical feed blend compositions and estimated fugitive emissions from monomer storage facilities are presented in Table 8. All tankage is of fixed roof design.

The blended feed is pumped into either of two batch reactors. During the filling process, which normally requires about one hour, vapors from the reactor are vented through an overflow drum (Vent 1, Table 9). When the reactor is full, the vent is closed and the feed is thermally polymerized to polystyrene. Each line has two reactors which are operated on an alternate basis, once each per 24 hours.

After polymerization is complete, the polymer melt, containing some unreacted styrene monomer and by-products is pumped to a vacuum devolatilizer where most of the monomer and by-products are separated, condensed and sent to storage for off-site use as fuel make-up. Overhead vapors from the condenser are exhausted by the vacuum pump used to operate the devolatilizer. The pump exhaust vents through an oil demister to the atmosphere (Vent 2, Table 10).

Molten polystyrene from the bottom of the devolatilizer is pumped through a stranding die-plate into a cold water bath. Vapors from this step, consisting mostly of steam with traces of styrene are vented through a forced-draft hood, (Vent 3, Table 11). The cooled strands are pelletized and sent to product storage.

B. VOC Emissions Data

VOC emissions were reported for four sources; storage tankage, reactor vent drum vent, styrene condenser vent, and extruder/quench vent. See Tables 8, 9, 10 and 11. No fugitive emissions data were available. VOC emissions from pellet storage are negligible.

C. VOC Emission Control Devices

The only control devices utilized are condensers up-stream of steam jets which are also required for process operability.

Figure 3

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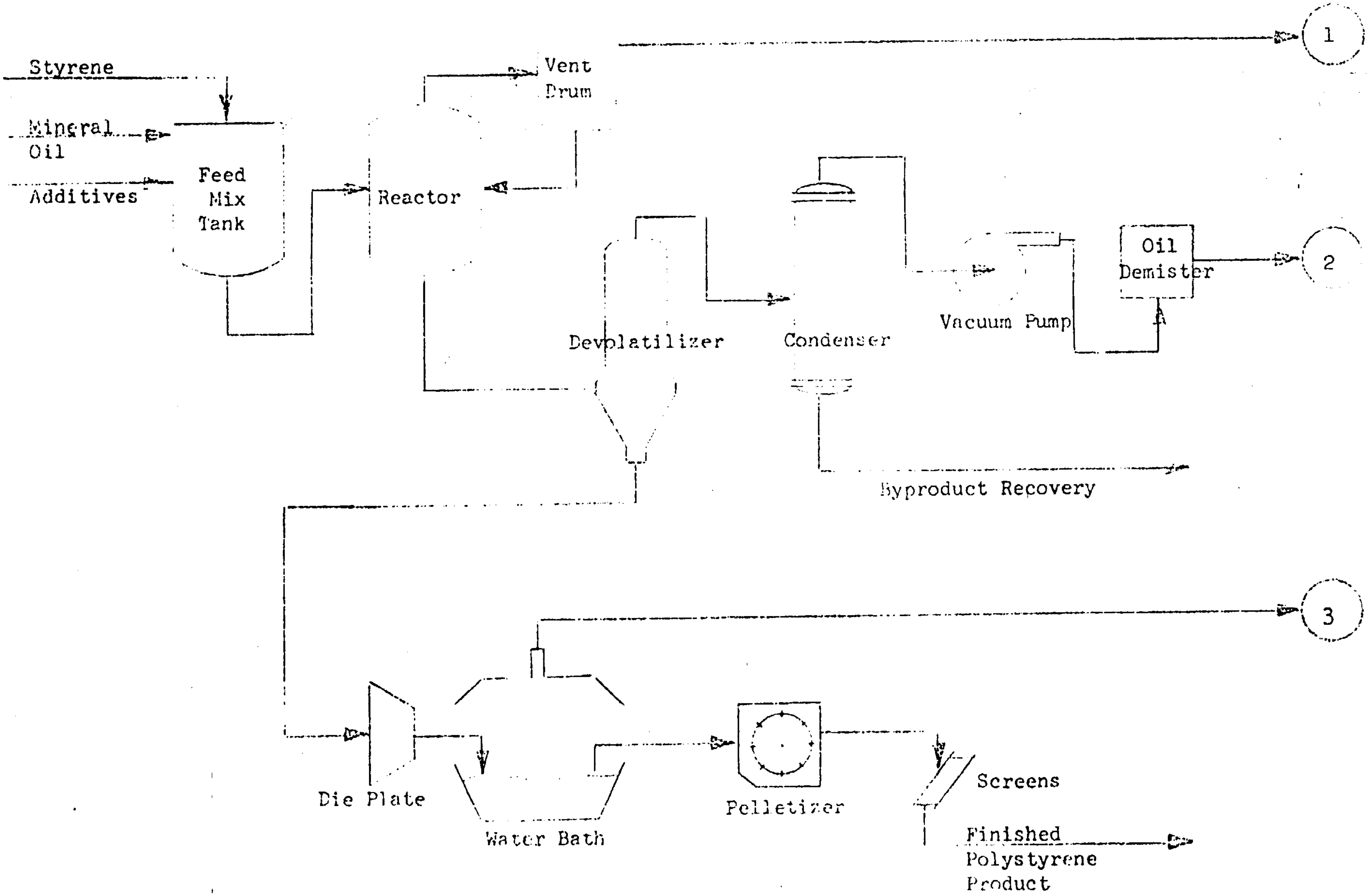
Willow Springs, Illinois & Torrance, California

Batch Polystyrene Resin Process



Batch Polystyrene Resin Process

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Batch Polystyrene Process

Table 8

Typical Feed Blend Compositions

Component	Weight %
styrene	95.0-100.0
mineral oil	0- 5.0

VOC Emissions from Tankage*

	lbs. styrene/year
styrene monomer storage feed dissolver tanks	12,000
devolatilizer condensate tank	270

*Basis: Engineering estimates for breathing and washing losses as per USEPA Manual AP-40, 2nd Edition.

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Batch Polystyrene Process

Table 9 Vent 1

Reactor Vent Drum Vent

This stream consists of vapors that are released from the batch reactor vent drum during the loading cycle. The loading cycle requires approximately one hour and each of two reactors per line is loaded once every twenty-four hours.

Loading temperature	110°F
Vapor pressure of styrene at 110°F	20 mm Hg
Emissions	16,390 lbs. styrene/yr.

Basis: engineering estimates

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Batch Polystyrene Process

Table 10, Vent 2

Styrene Condenser Vent

This stream consists of traces of unreacted styrene and volatile components separated from the polystyrene meet in a vacuum devolatilizer. The stream is exhausted through a vacuum pump which supplies the operating vacuum, followed by an oil demister which vents to the atmosphere.

Volumetric flowrate	50.4 ACFM
pressure	atmospheric
temperature	80°F
Mass flowrate	
styrene	34,164 lbs/yr.

Basis: engineering estimates

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Batch Polystyrene Process

Table 11, Vent 3

Extruder/Quench Vent

This stream is formed when hot, extruded polystyrene strands emanating from the dieplate contact the cold water bath. The resulting steam, containing traces of styrene are exhausted through a forced-draft hood.

Temperature	ambient
Mass Flowrate styrene	20,588 lbs/yr.
Volumetric Flowrate	29,400 ACFM

Basis: Engineering estimate of 5-7 ppm styrene concentration in exhaust gas.