SYNTHETIC FIBERS
AP-42 Section 5.19
Reference Number
45

**Pullman Kellogg**
Division of Pullman Incorporated

Industrial Park Ten
Houston Texas 77084
Telephone (713) 492-2500

A-80-7
II-D-36

18 April 1979

Emissions Standards and Engineering Division
(MD-13)
U. S. Environmental Protection Agency
Research Triangle Park
North Carolina 27711

Attention: Mr. David C. Mascone

Re: Contract No. 68-02-2619

Gentlemen:

Transmitted to you for your records is a copy of the non-confidential trip report for the visit to Tennessee Eastman's modacrylic fiber plant in Kingsport, Tennessee. Also enclosed with the EPA material is one copy of the confidential information obtained during that visit. This document has been identified (stamped) as confidential in accordance with procedures specified in our contract.

Very truly yours,

D. O. Moore, Jr.
Sr. Process Development Engineer

DOM:jh
Enclosure

cc: J. C. Edwards w/enclosure
Manager, Clean Environment Program
Tennessee Eastman Company

23.2.4
Mod-Acrylic Fibers

# MEMORANDUM

TO: W. M. Talbert

DATE: 16 October 1978

Tennessee East.
Kingsport, Tenn

FROM: D. O. Moore, Jr.

SUBJECT: Tennessee Eastman - Information to be supplied/ data gaps.

At the conclusion of the meeting with Tennessee Eastman in Kingsport on 12 October it was agreed that they would supply Kellogg the following additional information.

- information booklet covering material requested in Enclosure A. They have prepared the booklet and must clear it through management before releasing it.
- data on monomer conversion and monomer content of polymer.
- block diagram of dope preparation and spinning operation showing emissions of acetone*
- cost of gas chromatograph monitoring system.*
- copy of state permit for VOC from the dissolve and filter process areas.

The following information was not obtained at the meeting. Follow-up steps are indicated (if applicable)

- detailed fugitive emission data including total amount and amounts for specific sources such as pump seals, valves, flanges, equipment cleanout, etc.
- secondary emission data relative to losses from wastewater streams and waste fiber.
- details of dope preparation and spinning. They will prepare block diagrams with emissions and include this information in the booklet.
- cost details relating to acetone recovery (carbon adsorption, stripping, distillation, etc.).

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*to be included in booklet

- detailed information about experimental work regarding attemps to strip monomer from polymer and to obtain increased conversion in the reactors. They said that foaming was a problem with the stripping operation but if it could be overcome, the monomer emissions could be reduced by 90%. They further stated that increased residence time in the reactors may result in increased conversion (unreacted monomers may be reduced by about 50%). They were reluctant to be more specific.

D. O. Moore, Jr.

DOM:sk

cc: David Mascone - EPA
C. N. Click

# TRIP REPORT: TENNESSEE EASTMAN COMPANY
# KINGSPORT, TENNESSEE

October 12, 1978

IN ATTENDANCE:

Tennessee Eastman

| | |
|---|---|
| R. L. Lewis | Clean Environment Program Staff |
| R. C. Yantz | Staff Assistant, Polymers Division |
| S. D. Neely | Department Superintendent, Polymers Division |
| W. Lynn Perry | Filter Products Division |
| H. J. Denton, Jr. | Acetate Yarn Division |

Pullman Kellogg

| | |
|---|---|
| D. O. Moore, Jr. | Chemical Engineering Development |
| Cliff Click | Chemical Engineering Development |

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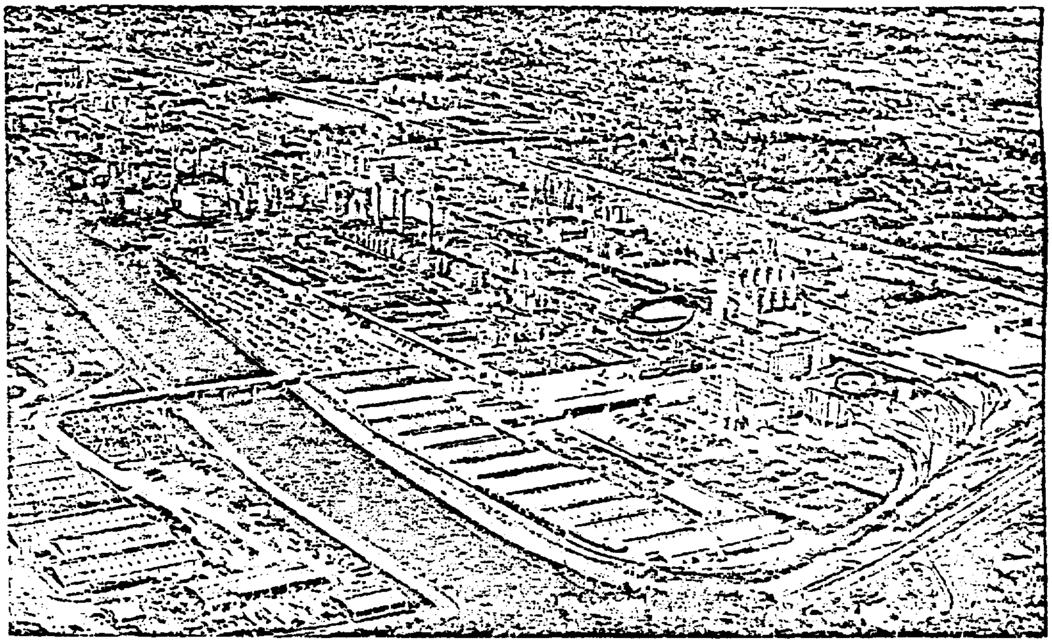
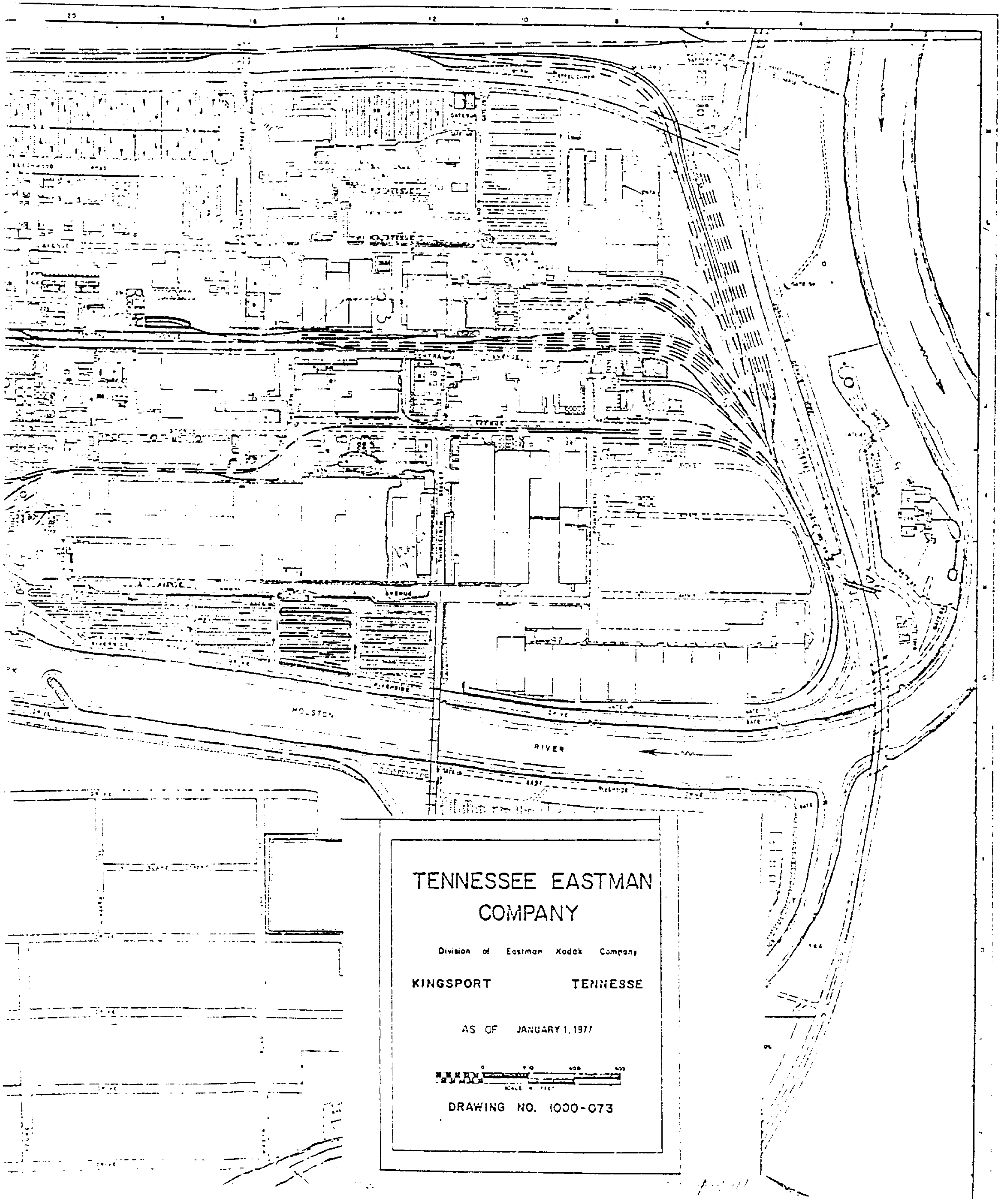


Administration Polymerize storage



# TENNESSEE EASTMAN COMPANY

Division of Eastman Kodak Company

KINGSPORT TENNESSE

AS OF JANUARY 1, 1977

DRAWING NO. 1000-073

## A. Introduction

Tennessee Eastman's(T.E.) Kingsport, Tennessee Modacrylics fibers facilities are contained within the much larger Kingsport, T.E. specialty organic chemicals manufacturing complex. The fiber facilities capacity is 36 MM pounds per year of Modacrylic "VEREL" fibers. The polymer is a mixture of two different polymers, a copolymer of acrylonitrile (AN) and vinylidene chloride ($VC_2$) and a homopolymer of N-isopropylacrylamide. See "Process Description" attached. Major monomers used are AN, $VC_2$ and isoproyl alcohol (IPA) and major solvents are Xylene (XY) and Acetone (AC).

The report that follows is based primarily on the trip notes by Pullman Kellogg personnel and the written booklet submitted by Tennessee Eastman. Pages of the booklet have simply been directly included where appropriate.

## B. Process Description and Flowsheets

### 1. Storage and Transfer

Acrylonitrile (AN) and Vinylidene Chloride ($VC_2$) are stored in low pressure above ground buried tanks. Monomer mix (AN and $VC_2$) and feed tanks are also low pressure tanks and share a common vent. All these pressurized storage tanks are supplied with $N_2$ inert gas and are assumed to have no working and breathing hydrocarbon emissions. The Alcohol (IPA) and AN/alcohol mix feed tanks are vented with conservation vents only. Figure 1 shows the VEREL polymerization process schematically including monomer and reaction solvent (xylene) storage tanks. Also see the T.E. description of "Emissions From Storage Tanks" for additional information.

Acetone (AC) is the process solvent for dope preparation and spinning and although not shown in Figure 1, acetone storage is in above ground buried tanks. Venting is to activated carbon acetone recovery beds and S/T losses are assumed small.

## 2. Polymerization

An unusual feature of VEREL production is the use of Xylene (XY) solvent in the extraction-separation of the N-isopropylacrylamide (NIPAM) monomer from the neutralized mixture in which it is made. After NIPAM monomer production and separation, NIPAM is recovered from Xylene and sent to the second stage of reaction (homopolymerization of NIPAM). The attached "Modacrylic Polymer Process Description" supplied by T.E. describes VEREL polymer production as shown schematically in Figure 1.

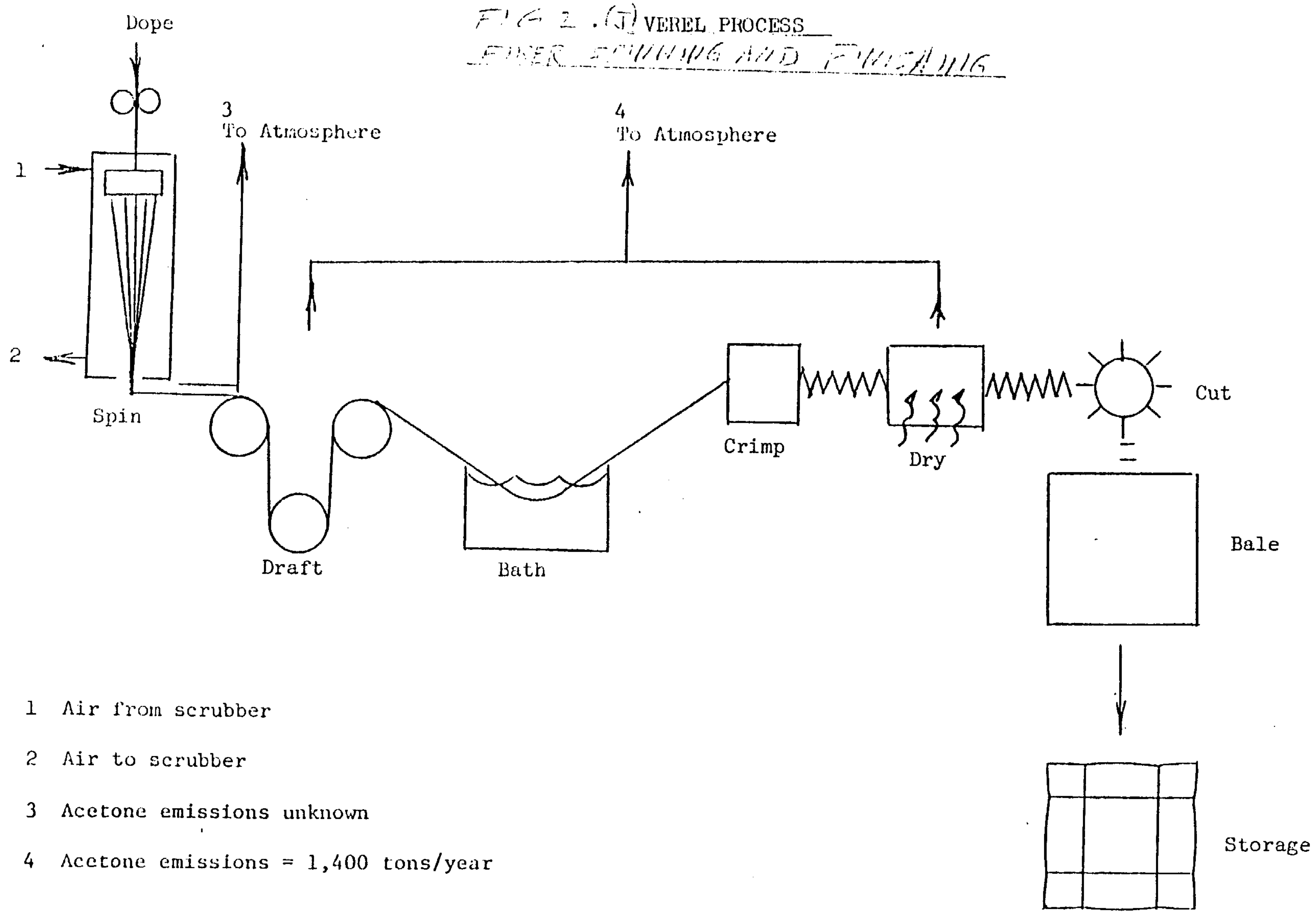
## ✓3. Fiber Spinning and Finishing

Polymer powder is stored in silos prior to fiber production. When needed polymer powder is dissolved in acetone spin solvent, filtered and dry spun. Figure 2 is a schematic showing dry spinning, fiber washing and finishing. Referring to Figure 2, filtered dope is extruded from spinnerets vertically downward into enclosed cabinets. Acetone solvent evaporates into a stream of hot dry air and the resulting fiber "rope" is passed over takeup rolls before washing. After the wash, product fiber is crimped, dried, cut, baled and stored prior to shipping. Acetone evaporated at spinning is recovered from the spinning cabinet air via a water scrubber system. Major acetone losses occur from the rope as it is guided, the bath (wash), and crimping and drying. Activated carbon beds are used to recover acetone from storage tank vents.

[illegible]

FIG 2.(J) VEREL PROCESS

FIBER SPINNING AND FINISHING



1 Air from scrubber

2 Air to scrubber

3 Acetone emissions unknown

4 Acetone emissions = 1,400 tons/year

Precautions are taken to keep below the lower explosive limit (LEL) for acetone in the spinning and finishing areas.

## C. Emissions

In summary, total hydrocarbon emissions for modacrylic fibers production are 1.71 lb AN/1000 lb, 4.24 lb $VC_2$/1000 lb and 125.4 lb AC/1000 lb. Total VOC is 131.4 lb VOC/1000 lb.

### 1. Storage and Transfer

Emissions from S/T of monomers are discussed in the attached T.E. description. Table 1 includes the emissions from S/T of Xylene, the solvent used in polymerization reactions, but not Acetone.

### 2. Polymerization

Table 1 summarizes the AN, $VC_2$ and VOC emissions from polymerization. Figure 3 is a block diagram of the polymerization process with the point source vents indicated in Table 1 shown on the diagram. For AN, the seven most significant point sources in decreasing order are, U, X and I-M. U is the ventilation from the several reaction kill and coagulation tanks. X is a vent discharge from polymer filtration (rotary vacuum) and I through M are the disengaged gases from the filtrate defoaming tanks. Other important AN sources are W and V, two other filter vent discharges and Q and O two polymer dryer line baghouse discharges.

With few exceptions the major AN sources are also major $VC_2$ sources. In decreasing order the top seven $VC_2$ sources are I-M, Q, and U. The next four most important $VC_2$ sources are T, O, X and W. Only T, the polymer transfer and storage baghouse vent, was a significant $VC_2$ source and not also a significant AN source. The parallels in source significance

TE BOOKLET

# MODACRYLIC POLYMER PROCESS

## EMISSIONS FROM STORAGE TANKS

### I. Acrylonitrile Unloading and Storage

There are two buried above ground acrylonitrile storage tanks (see flow sheet). Acrylonitrile is received in rail cars. AN is pumped from the rail cars to either one of the two storage tanks. The vapor space in the storage tank receiving the contents of a rail car is vented to the rail car being unloaded so that no emissions to the atmosphere are encountered on rail car unloading.

The acrylonitrile storage tanks are maintained under 15 psi nitrogen pressure. Each storage tank is equipped with a dual relief device. This device consists of a pressure relief valve set at 25 psi with a rupture disc downstream set at 30 psi. If a relief valve opens or a rupture disc blows, the tank may be switched to the spare relief device.

When the contents of an AN storage tank are transferred to the monomer mix tank, nitrogen pressure replaces the volume displaced.

### II. Vinylidene Chloride Unloading and Storage

This system is identical to the acrylonitrile system in I. above, except only no relief valves are in the system.

### III. AN/VCl2 Monomer Mix and Feed Tanks

The AN/VCl2 monomer mix and feed tanks share a common vent with a spare tank (see flow sheet).

These tanks are operated under a pressure of 5 psi with a pressure relief valve which is common to all three tanks that is set to relieve at 18 psi. Under normal operation the pressure relief valve does not relieve so that no contaminants are discharged to the atmosphere.

### IV. Alcohol and AN/Alc Mix and Feed Tanks

The isopropanol storage tank and the AN/Alc mix and feed tanks are vented through a common header (see flow sheet).

The vent on these three tanks is a conservation vent which relieves at 2" W.C. This vent emitts 0.06 lbs./hr. isopropyl alcohol, 0.26 lbs./hr. acrylonitrile, and 0.32 lbs./hr. VOC; or 0.015 lb./1000 lbs. polymer isopropyl alcohol, .065 lbs./1000 lbs. polymer acrylonitrile, and 0.08 lbs./1000 lbs. polymer VOC.

[illegible] Fiber

are even greater between $VC_2$ and VOC than between AN and $VC_2$. The top 11 polymerization VOC sources in decreasing order are: I-M, U, Q, X, O, W and T.

The seven largest sources for all categories (AN, $VC_2$ and VOC) constitute more than 70 percent of the total emissions and include I-M, the vents from filtrate defoaming, and U, the vents from the kill and coagulation tanks. The seven largest polymerization hydrocarbon emission sources are:

SUMMARY TABLE

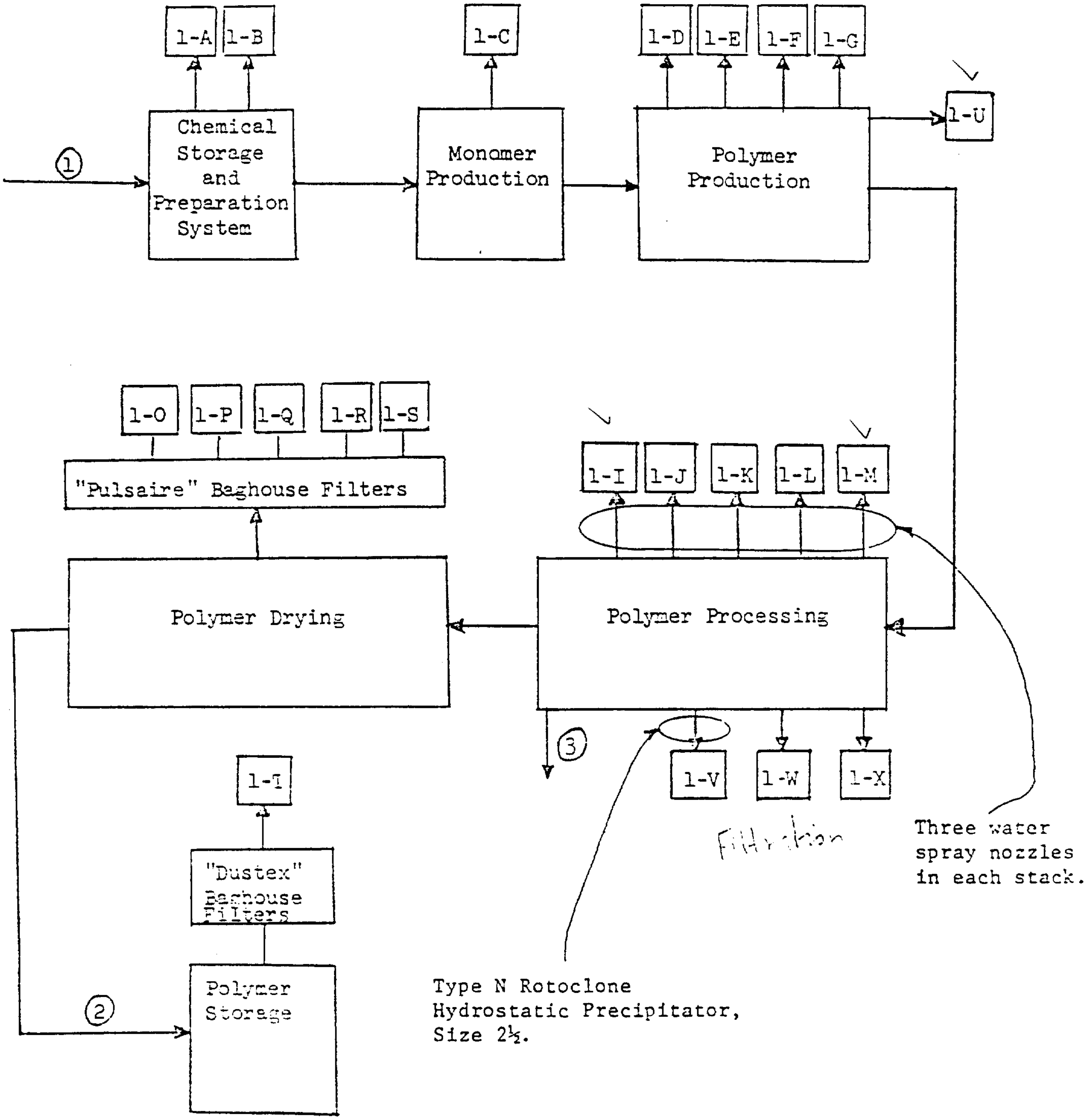
POLYMERIZATION HYDROCARBON EMISSIONS

| ORDER | AN |  | $VC_2$ |  | VOC |  |
|---|---|---|---|---|---|---|
|  | I.D. | Factor | I.D. | Factor | I.D. | Factor |
| 1 | U | 0.22 | I-M(5) | 0.52 | I-M(5) | 0.68 |
| 2 | X | 0.21 | Q | 0.34 | U | 0.56 |
| 3 | I-M(5) | 0.16 | U | 0.33 | Q | 0.43 |
| Totals,<br>lb/1000 lb |  | 1.23 |  | 3.27 |  | 4.39 |
| percent |  | 72 |  | 77 |  | 73 |

3. Dope Preparation, Fiber Spinning and Finishing

Figure 2 is a schematic of dope preparation, spinning and finishing showing the major emission points and Figure 4 is a block flow diagram showing the emissions. Acetone (VOC) emissions total about 1,568 tons per year (tpy) with about 223 tpy from dope preparation (dissolving and filtering) and about 1,345 tpy from spinning and finishing. The total 1,568 tpy represents a factor of 125.4 lb VOC/1000 lb fiber based on an annual production rate of 25 MM lb/yr.

Losses are distributed as follows. Dope preparation loses about 17.87 lb/1000 lb or 14.26 percent of the total and spinning and finishing lose the rest, 107.42 lb/1000 lb or 85.74 percent.



Filtration

Three water spray nozzles in each stack.

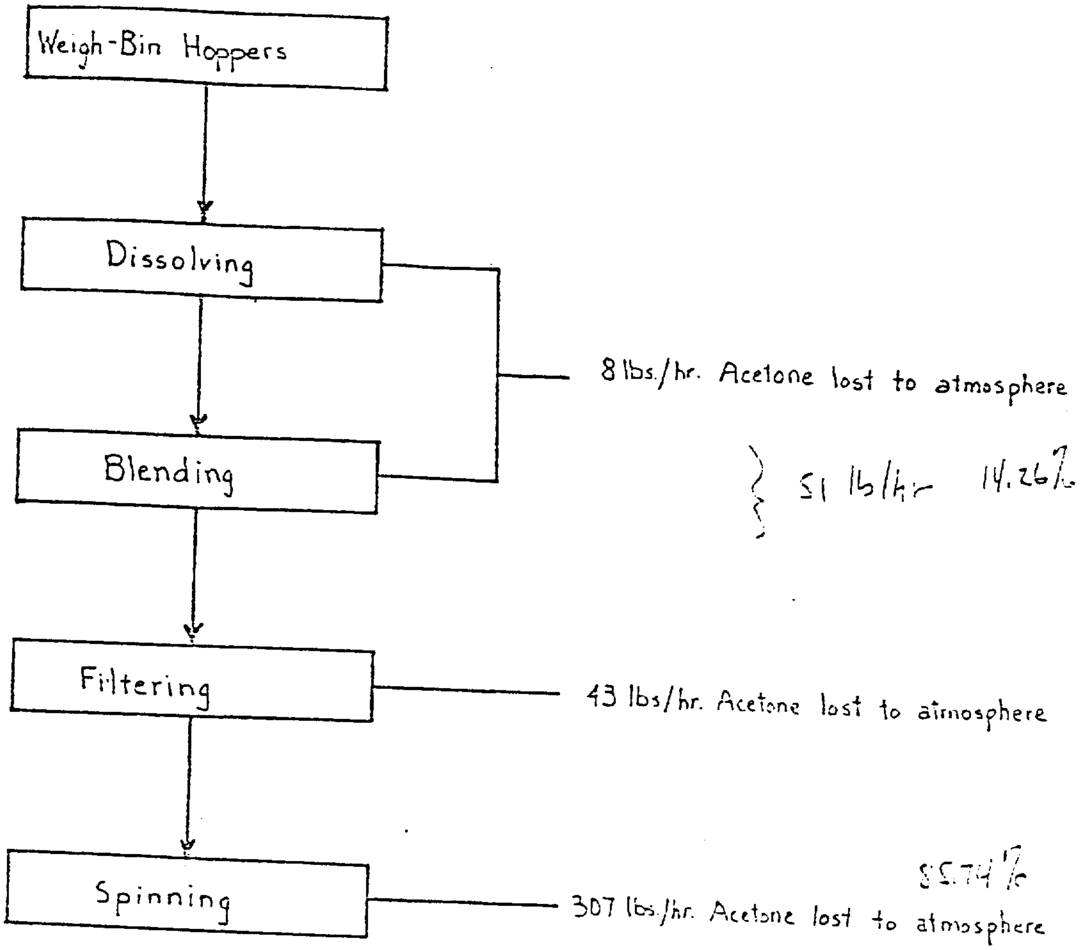
Type N Rotoclone Hydrostatic Precipitator, Size 2½.

FROM LETTER OF JULY 20, 1972

FIG 3

VEREL POLYMERIZATION EMISSIONS

# (J) Acetone Losses For Verel - Determined By Filter Products Division



Total 355 lbs/hr 100.00%

FROM
TE BOOKLET
FIGURE 1.
(J) LOSS FROM DOPE PREPARATION
AND SPINNING

VLP

(VOC) emissions from spinning and finishing are high (125.4 lb/1000 lb)

The low AN and $VC_2$ emissions result from good S/T techniques in the tank farm (including $N_2$-pressure tankage and vapor exchange with incoming railcars) and high conversion in polymerization. Conversion of AN is about 98% overall and although some of this goes into unwanted side reactions, it does not become hydrocarbon emissions. T.E. believes further conversion improvements are possible by means such as increasing residence time and could reduce AN emissions by 50 percent. Presently unconverted monomers are 1.57 lb AN/1000 lb and 0.218 lb $VC_2$/1000 lb. Residual concentrations are 60.4 ppm AN and 147.4 ppm $VC_2$ (weight) in polymer and 14 ppm AN and 12 ppm $VC_2$ (weight) in fiber, See Appendix 2.

Latex stripping was investigated and found to cause foaming problems. If successful, latex stripping could reduce AN emissions by up to 90 percent.

FROM TE BOOKLET

## D. MODACRYLIC POLYMER PROCESS

## CONTROL METHODS

### I. Roto-Clone Hydrostatic Precipitator

Refer to flow sheet FIG 1. Three filter hoods are connected to the Roto-clone. This is a piece of equipment manufactured by American Air Filter that is a type of mechanical spray scrubber. It provides a means of contacting a gas stream with a liquid (water).

### II. Water Spray Nozzles

Refer to flow sheet FIG 1. Water spray nozzles are used to knock down foam.

### III. Pressure Relief Devices

These are explained in Section E for the storage tanks. Other conservation vents are used in the system and indicated in Section C. These vents are in line with accepted engineering practices.

# APPENDIX

FROM
TE BOOKLET
APPENDIX I.

## F. MODACRYLIC POLYMER PROCESS

## FUGITIVE EMISSIONS

The modacrylic polymer process building was extensively monitored for fugitive emissions. As a result of this monitoring, a continuous gas chromatography unit with a flame ionization detector was installed. Ten sample points were located at ten strategic areas throughout the polymer facility. The acrylonitrile and vinylidene chloride concentrations are monitored at each of these locations once each hour.

Attached is a summary of acrylonitrile and vinylidene chloride fugitive emissions from 1976 to the present date of 1978.

# TABLE 1. AN, VCl$_2$ : VOC FROM POLYMERIZATION

MODACRYLIC POLYMER PROCESS
PROCESS EMISSIONS AND AMBIENT AIR DATA

| Vent No. 104-1- | Stack Height Feet | Stack Diameter Feet | Stack Area, Feet$^2$ | Stack Velocity Ft./Sec. | Stack Temperature °F | Stack Flow, Ft$^3$/Sec |  | An Conc. |  |  | VCl$_2$ Conc. |  |  | VOC Conc. |  |  | Control Device |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | At Temperature | At 70°F, 1ATM | PPM Wt. | Lb/Hr | Lb./1000 Lb. Polymer | PPM Wt. | Lb./Hr. | Lb./1000 Lb. Polymer | PPM Wt. | Lb/Hr | Lb./1000 Lb. Polymer |  |
| A | 15 | 0.51 | 0.204 | .74 | 77 | .15 | .15 | 0 | 0 | 0 | 0 | 0 | 0 |  |  |  | None |
| B | 35 | 0.25 | 0.049 | .004 | 77 | .0002 | .0002 |  |  |  |  |  |  | 3.6% | .002 | .0005 (Xylene) | Conservation Vent |
| C | 35 | 0.50 | 0.196 | .0014 | 77 | .0003 | .0003 |  |  |  | 0 | 0 | 0 | 5.0% | .004 | .001 (Xylene) | Conservation Vent |
| D, E, F, G | 35 | 0.50 | 0.196 | .033 | 104 | .006 | .006 | .340 | .024 | .006 | 0 | 0 | 0 | 1.1% | .088 | .072 | None |
| I | 30 | 1.00 | 0.785 | 5.80 | 104 | 4.6 * | 4.32 | 480 | .64 | .16 | 1550 | 2.08 | .52 | 2030 | 2.72 | .68 | Water Spray Nozzles |
| J | 30 | 1.20 | 1.131 | 4.07 | 104 | 4.6* | 4.32 | 480 | .64 | .16 | 1550 | 2.08 | .52 | 2030 | 2.72 | .68 | Water Spray Nozzles |
| K | 30 | 1.20 | 1.131 | 4.07 | 104 | 4.6* | 4.32 | 480 | .64 | .16 | 1550 | 2.08 | .52 | 2030 | 2.72 | .68 | Water Spray Nozzles |
| L | 41 | 1.20 | 1.131 | 4.07 | 104 | 4.6* | 4.32 | 480 | .64 | .16 | 1550 | 2.08 | .52 | 2030 | 2.72 | .68 | Water Spray Nozzles |
| M | 54 | 1.70 | 2.27 | 2.03 | 104 | 4.6* | 4.32 | 480 | .64 | .16 | 1550 | 2.08 | .52 | 2030 | 2.72 | .68 | Water Spray Nozzles |
| O | 41.5 | 1.0 x 2.25 | 2.25 | 182 | 158 | 410 | 352 | 2.8 | .33 | .08 | 7.0 | .83 | .21 | 9.8 | 1.16 | .29 | None |
| P | 41.5 | 2.00 | 3.142 | 118.9 | 158 | 373 | 320 | 1.35 | .14 | .03 | 2.9 | .29 | .07 | 4.25 | .43 | .11 | None |
| Q | 44 | 1.58 x 1.83 | 2.891 | 110.3 | 158 | 324.3 | 278 | 3.9 | .37 | .09 | 14.4 | 1.36 | .34 | 18.3 | 1.73 | .43 | None |
| R | 44 | 1.0 x 2.25 | 2.25 | 152.8 | 158 | 343.7 | 294.8 | .5 | .05 | .01 | 1.4 | .14 | .03 | 1.9 | .19 | .05 | None |
| S | 45 | 1.0 x 2.25 | 2.25 | 152.8 | 158 | 343.7 | 294.8 | .5 | .05 | .01 | 1.4 | .14 | .03 | 1.9 | .19 | .05 | None |
| T | 40 | 1.75 | 2.405 | 44.4 | 77 | 106.9 | 106.9 | 1.85 | .06 | .01 | 29.7 | .93 | .23 | 31.55 | .99 | .25 | Is Particulate Control |
| U | 41 | 0.73 | 0.418 | 6.5 | 104 | 2.7 | 2.5 | 1140 | .9 | .22 | 1690 | 1.33 | .33 | 2830 | 2.23 | .56 | Combined Vents |
| V | 41 | .875 x 1.08 | 0.445 | 65.2 | 130 | 61.9 | 55.6 | 22 | .39 | .1 | 20 | .35 | .09 | 42 | .74 | .18 | Water Scrubber |
| W | 41 | 1.33 | 1.389 | 19.6 | 130 | 27.2 | 24.4 | 71 | .56 | .14 | 77 | .61 | .15 | 148 | 1.17 | .29 | None |
| X | 41 | 1.16 | 1.057 | 25.7 | 130 | 27.2 | 24.4 | 109 | .86 | .21 | 79 | .63 | .16 | 188 | 1.49 | .37 | None |
| Ttl |  |  |  |  |  |  |  |  |  | 1.706 |  |  | 4.24 |  |  | 6.0[illegible] |  |

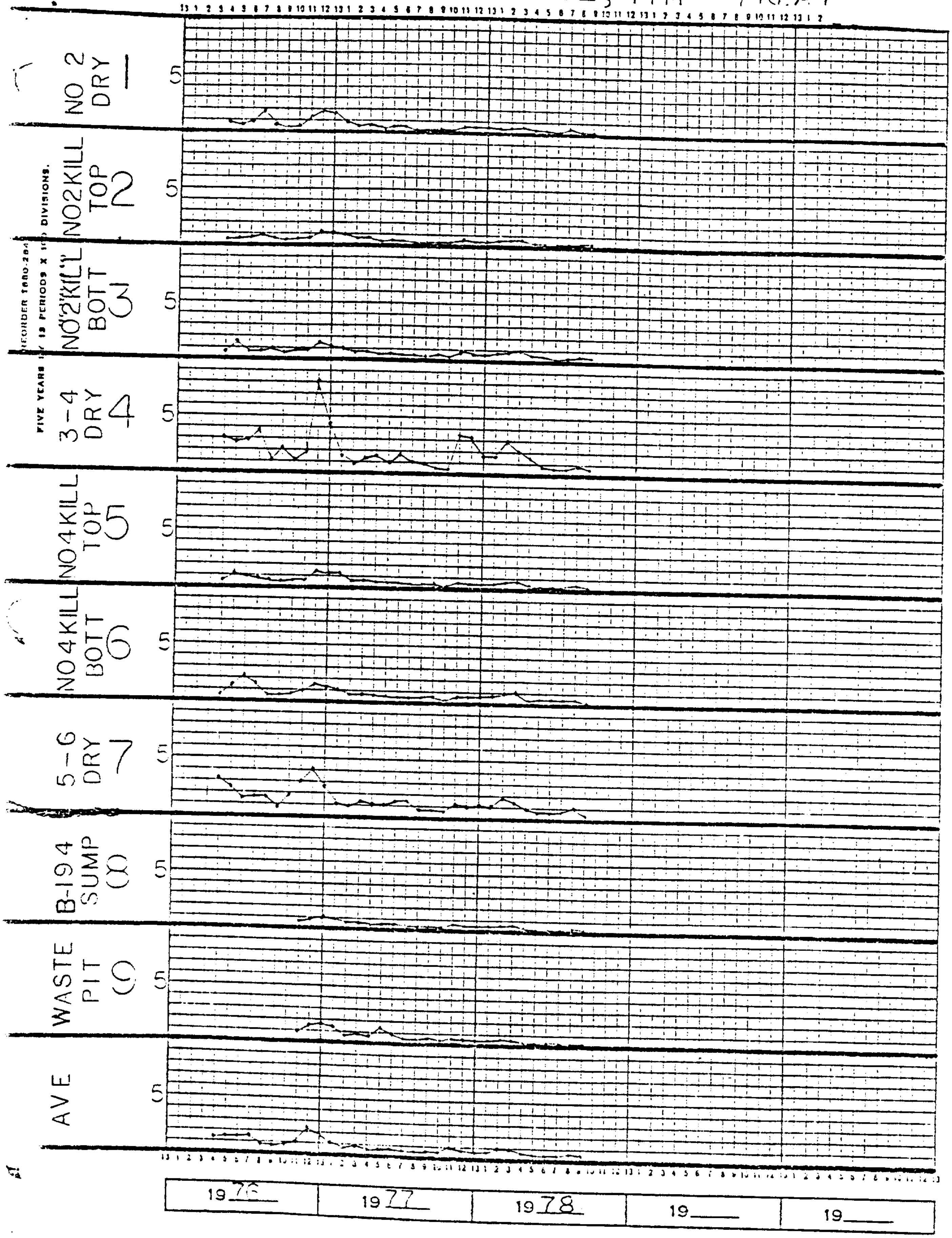
(1) All temperatures, flows, and concentrations were determined by measurement unless marked with asterisk* indicating calculated data.

(2) Assume 4000 lbs fiber/hr production

FROM J E BUCKLEY
PART F

# ACRYLONITRILE, PPM

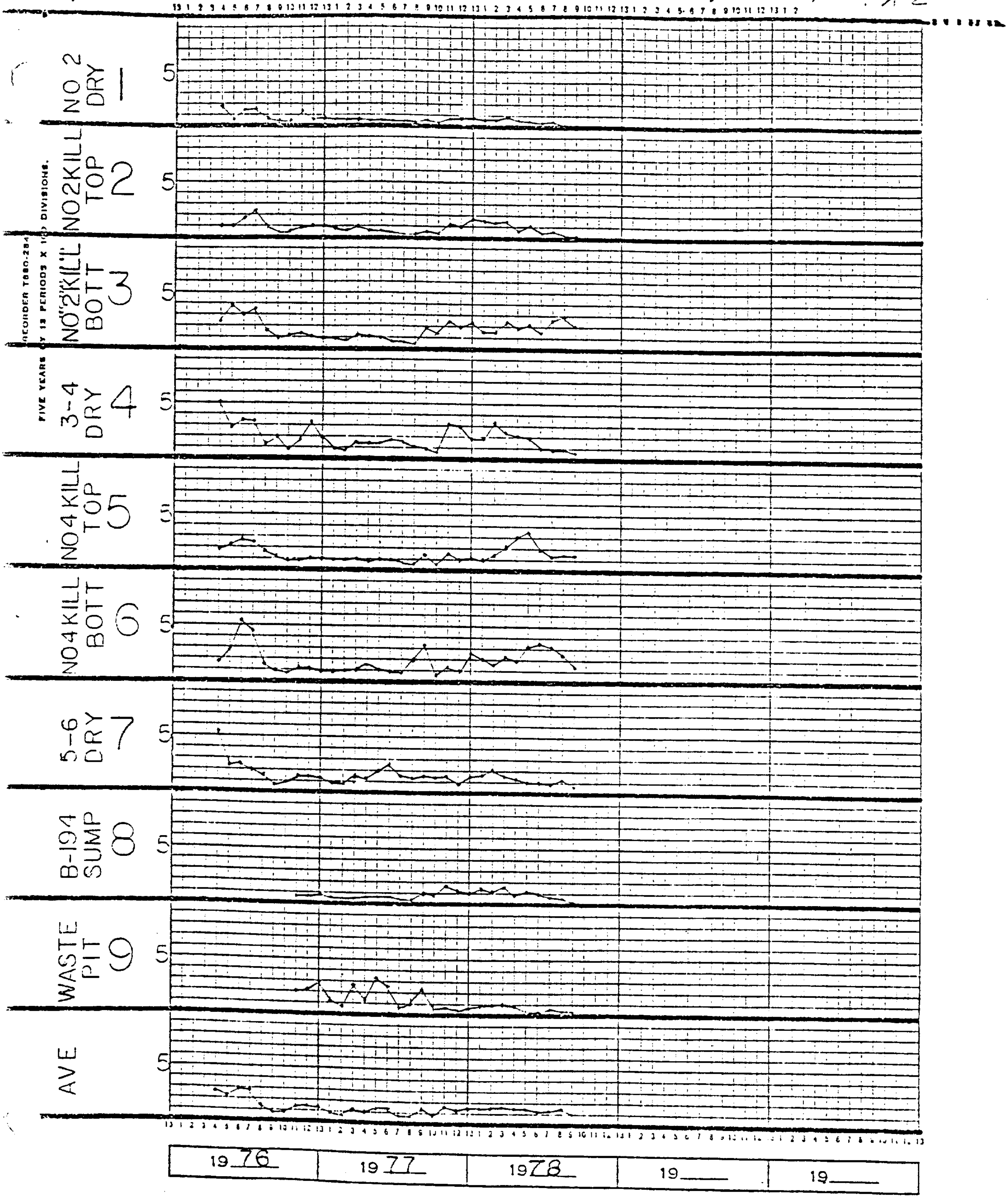
APPENDIX
FIG. A 1



PRAIRIE BARLET
PLANT F

# VINYLIDENE CHLORIDE, PPM

APPENDIX
FIG. A 2



[illegible]

## [illegible] MODACRYLIC POLYMER PROCESS

## APPENDIX 2

The following questions were raised by the people from Pullman Kellogg. Answers to these questions are given as follows:

1. Question: What was the cost of the continuous analyzer installation?

   Answer: $25,000 in 1975.

2. Question: What is the monomer concentration in polymer and fiber?

   Answer: The monomer concentration in polymer is 60.4 ppm by weight acrylonitrile and 147.4 ppm by weight vinylidene chloride. The monomer concentration in fiber is indicated to be 14 ppm by weight acrylonitrile and 12 ppm by weight vinylidene chloride.

3. Question: What is monomer conversion, i.e., what is the quantity of unreacted monomers?

   Answer: 1.57 lbs. acrylonitrile/1000 lbs. modacrylic polymer

   0.218 lbs. vinylidene chloride/1000 lbs. modacrylic polymer