Air Products and Chemicals INC.

ESCAMBIA PLANT

INTEROFFICE MEMORANDUM

To: Mr. J. T. Barr

Date: 14 June 1974

From: Mr. D. H. Francke

Copies: R. E. Jones
A. K. McMillan
E. A. Primeau

Re: E. P. A. Request for VCl and PVC Emission Data

Attached please find a summary of the information requested by Mr. D. R. Goodwin of the E. P. A. regarding the vinyl chloride and polyvinyl chloride emissions from the Escambia PVC Plant in Pace, Florida. This plant has a capacity of about 75 million pounds of PVC resin per year.

Calculations were made using data collected for monthly material balances starting in February, 1974. The data runs through May, 1974. Below is a summary of the products and losses as percentages of the total vinyl chloride charged for the February-May period.

Vinyl Chloride Charged	100%
PVC Resin Sold	94.79
Known PVC Losses to the Air	1.24
Known PVC Losses to the Water	.29
Known PVC Scrap to Dump	.64
Known VCl Losses to the Air	1.18
Known VCl Losses to the Water	.04
Total VCl Accounted For	98.18
Total VCl Unaccounted For	1.82
Total VCl Out	100.00%

D. H. Francke

D. H. Francke

DHF:aw

Attachments

AP00027793

PROCESS AND EMISSION DATA

A) General Process Description

Purchased vinyl chloride monomer is suspension polymerized to produce various types and grades of PVC resin. In the polymerization step, only 83 to 87% of the vinyl chloride is converted to PVC resin. Therefore, it is necessary to vacuum strip at the end of the polymerization cycle to remove the unreacted monomer which is then condensed and recycled to the polymerization step. The recovery and recycle of the monomer is done in a stripping vessel using vacuum recovery equipment, compressors and condensers.

Following the stripping operation, the slurry containing PVC resin and water is stored in blend tanks and then pumped continuously to a centrifuge for dewatering. The water effluent from the centrifuge is treated through a pre-treatment system and flows via an industrial sewer system to the biological system for final polishing prior to discharge to Escambia Bay after approximately 100 days of residence time in the treatment system.

The dewatered wet cake from the centrifuge solids discharge is fed to a dryer where the moisture content of the resin is reduced to 0.2%. From the dryer the resin passes through a screening operation to remove resin particles larger than 40 mesh and is then sent to storage. From storage the resin is bagged or bulk loaded to hopper cars for shipment to customers.

B) Emissions

Vent #	Source Description	Type‡	lb PVC lost / lb Produced	lb VCl lost, / lb. PVC produced	Ave. Wt. % PVC	Ave. Wt. % VCl	#PVC/ hour*	#VCl/ hour*
1a.	Reactor Safety Valves	(I)	NA	.0032	NA	NA	NA	29.2
1b.	Reactor Jet	(I)	NA	.0003	NA	6.0	NA	2.4
2.	Stripper Jets	(I)	NA	.0015	NA	2.2	NA	14.1
3.	Recovery Condenser Vent	(C)	NA	.0015	NA	17.1	NA	13.2
4.	Blend Tank Vent Blower	(C)	NA	.0018	NA	.24	NA	16.5
5.	Dryer Discharges	(C)	.0144	.0020	1.30	.015	117.0	18.2
6.	Purification Condenser	(C)	NA	.0019	NA	80.	NA	17.4
7.	Reactor Exhaust System	(C)	NA	7.45×10^{-6}	NA	.0025	NA	.068
8.	Reactor Purge System	(C)	NA	1.46×10^{-4}	NA	.05	NA	1.33

*Basis: Material Balance Data February 1974 - May 1974 (26, 271, 100 lbs. PVC produced)
‡I = intermittent, C=Continuous
See Drawing Polyvinyl Chloride Plant for location of points 1 thru 6

Calculations:

Items 1 - 6: Pounds Lost (PVC and/or VCl) from a Material Balance Summary through May, 1974. Divided by 26, 271.1M Pounds PVC Produced for the lb/lb value and by 2, 880 hours (Feb.- May) for the lb/hr. values. Average Wt.% based on average analysis from the Material Balances.

Item 7: Blower used is 2,000 CFM. Blower runs continuously but is open to VCl source only during cleaning of reactors (approximately 2.25 hours per reactor and 3 reactors/day). Average reactor VCl level during cleaning is about 25 ppm (from Bendix Analysis).

AP00027795

B)Emissions
Page 2

$$\frac{6.75 \text{ hrs.}}{24 \text{ hrs.}} \times \frac{2,000 \text{ ft}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{.0808 \text{ \#air}}{\text{ft3}} \times \frac{.000025 \text{ \# VCl}}{\text{\#air}} = .068 \text{ Ave \# VCl/hr. on a continuous basis.}$$

Total = .068 VCl/hr x 2880 hrs $\doteq$ 195.8 lbs.

Item 8: Blower = 2,000 CFM, Blower continuous but open to reactors during .25 hr./reactor

25 reactors/day @ .05% VCl ave. plus reactor cleaning of .068 #VCl/hr.

$$\frac{\text{Day}}{24 \text{ hr}} \times \frac{.25 \text{ Hr.}}{\text{Reactor}} \times \frac{25 \text{ reactor}}{\text{day}} \times \frac{.0808\text{\# air}}{\text{ft}^3} \times \frac{2,000 \text{ ft}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{.0005 \text{ \#VCl}}{\text{\# Air}} = 1.26 \text{ \#VCl/hr} + .068 \text{ or } 1.33 \text{ \#/hr.}$$

1.33 #/hr. $\div$ 9122 # PVC/hr. = 1.46×10^{-4}

AP00027796

C) Control Devices

Source 1 A (Reactor Safety Valve) - No control device, no device should be installed since this device is used to prevent over pressuring of a reaction vessel.

Source 1 B (Reactor Jet)- No control device, investigation is currently being made into the use of a Nash Vacuum Pump and Compressor to replace this jet. Reduction ould amount to ~85% of current losses (2 lbs/hr reduction).

Source 2 (Stripper Jet)- No control device, use of a Nash Compressor and/or vacuum pump to replace the jets. Reduction of ~85% of current losses or 12 lbs/hr

Source 3 (Recovery Vent Condenser) - A 3 stage condenser, involving a cooling tower water condenser, refrigerated water condenser and a freon condenser. The flow is 90/10 VCl/H_2O at a rate of about 2010 lb/hour. Inlet vapor enters at 70°F and 80 psig and exits at 40°F and 70 psig. Exit flow is about 8CFM average. Liquid VCl and water are removed prior to vent. Efficiency $\left(\frac{\text{lbs. recovered}}{\text{lbs. entered}}\right) \cong 99\%$.

Source 4 (Blend Tank Vent) - No control device. This is a saturated air stream at 120°F and a 1500 CFM flow and <.5% VCl concentration.

Source 5 (Dryer Discharges) - Current control devices are Dustex Bag Collectors. Inlet flows to the bag collectors average 9,122 lbs/hr. of PVC and 18.2 # VCl/hr. with air flows of 34 MCFM @ 120°F - 150°F. Discharge flows average 34 MCFM @ 120°F - 150°F with 117# PVC/hour and 18.2 # VCl/hr. Particulate efficiency averages 98.7% with major losses due to bag breakages. New collectors have been ordered. These are dust cyclones and will reduce PVC losses to about 10 lb/hr.

AP00027797

Source 6 (Purification Condenser) - This control device consists of an atmospheric condenser which is mounted on top of the purification column. This condenser is cooled with well water. Flows into the condenser are 1,720 lbs/hour of a 99.7/.1/.2 mixture of VCl/H_2O/inerts. Vent losses are estimated at 19.75 lbs/hour of a 85/15 mixture of VCl/inerts. Current plans include a revision of the recovery system to eliminate the need for the purification systems and thereby elimination of this emission.

D) Fugitive Emissions

Total unaccounted losses average 170 pounds/hour. These unaccounted losses include valve stem leaks, pump seal leaks, etc.

E) <u>Emission Control Procedures</u>

1) Process Design Features -

The reactors are tied into the strippers so that the stripper can be used to drop "hot" reactors into to prevent venting to the atmosphere in case of an uncontrolled reaction. In addition to this feature, an overhead recovery header is available to permit venting to a recovery compressor of any hot reactor instead of venting to the atmosphere.

A VCl Recovery System is used on each reactor batch for the recovery of VCl and to lower the VCl released to the atmosphere.

2) Plant Operating Procedures -

Current operating procedures for the control and prevention of emissions are as follows:

a. In the case of an uncontrolled reaction which cannot be dropped for recovery, addition of a short stop agent which stops the reaction, is made. This eliminates the pressure generating reaction and stops any further pressure buildup.

b. During each reactor cleaning, the rupture disc is checked for buildup, deteriation, etc. and if replacment is indicated the disc is replaced.

c. Readings are taken throughout the plant on a 3 day/week basis and high readings are traced to the source. Upon source detection, corrective action is taken. The instrument used is a hydrogen flame analyzer which detects combustable vapors. This instrument is manufactured by the Century Instrument Company.

3) Maintenance Procedures -

In addition to regular maintenance to prevent equipment failure and resulting losses, a yearly inspection and testing program of the safety relief valves on the plant equipment is carried out. This program is designed to assure that the relief valves will not operate prematurely or fail to operate, thereby causing unnecessary vapor losses.

AP0027802

CONTROL AND ECONOMIC DATA

rrent Control Devices

Device	Equipment	Total Cost (M$)	Installation Cost (M$)	Year* Purchased	Operating Cost (M$) Labor	Mat'l.	Utilities	Downtime	Material Recovered lb/yr	lbs/lb PVC	$/yr	$/lbPVC
Recovery Condenser					---	---	---	---	143MM	.19	1.50 MM	.02
	1st Stage Condenser	13	3	1957 (O)	1	---	1.4	---				
	2nd Stage Condenser			1957 (O)	1	---	1.4	---				
	Freon Condenser	4	1	1974 (R)	1	---	1.4	---				
	Freon Compressor	15	5	1964 (A)	4	6	2	---				
	I. R. Compressors	100	25	1957 (O)	10.4	15.6	15	---				
	Nash Compressor	80	26	1973 (A)	2	4	27.5	-0-				
	Storage Tanks	60	25	1957 (O)	2	---	---	---				
yer Discharge		100ǂ	30ǂ		5.5	1.7	---	6.24	This item is also the primary product collector and therefore these numbers are not applicable.			
	Dustex Baghouses			1957 (O)								
	South Line Revision			1964 (A)								
Purification Condenser		10	4		1.0	---	1.4	---	13.5MM	.18	1.42 MM	.019
	Purification Condenser											

Total Cost = Equipment Cost + Installation Cost

ǂ Based on estimated replacement costs

* R=replacement O=original installation A=addition

CONTROL AND ECONOMIC DATA

'anned Control Devices

Device	Equipment	Total Cost	Installation Cost	Year Purchased	Operating Cost (M$)				Additional Material Recovered			
					Labor	Matl.	Utilities	Dntime.	lb/yr	lb/lb PVC	$/yr	$/lb PVC
Ducon Cyclones on Dryers	Duclone Dust Cyclones	$91.8M	$66.8M	1974	2.75	---	---	---	85M	.011	.143M	.0019
Nash Compressors for Stripper and Reactor Evacuation	Nash Compressor and/or Vacuum Pump	$100M	---	1974-1975	1.0	2.0	15.0	---	13.1MM	.0017	.014MM	.00019

AP00027803

Ambient Air Data

Attached is a plot plan of the Escambia PVC Plant showing ambient concentrations of VCl as measured with a Century Combustable Vapor Analyzer. These concentrations are "area" type analysis and are not a specific points. The numbers are averages of about 57 readings taken from 11 Feburary 1974 through 5 June 1974. The Century Instrument used analyzes the air for combustables by way of a hydrogen flame ionization. The readout is in ppm range and is a total combustable analysis. Background levels normally run 3 to 7 ppm with this instrument.

Additional ambient air sampling tests run during the week ending 15 June, 1974 are tabulated below. These data were obtained by gas chromatographic analysis of the samples taken.

Date	Wind	Point	Location	VCl Conc.	Type
10 June 1974	0-3West	Millroom-Lab	1	.2	Carbon Tube
		PVC Office	2	.4	Carbon Tube
11June 1974	0-3 West	PVC Office	2	.4	Carbon Tube
		PVC Lunchroom	3	.7	Carbon Tube
		2 blocks south of PVC Building	4	.1	Carbon Tube
		1 block south of PVC Building	5	.5	Carbon Tube
12 June 1974	0-3 West	PVC Lunchroom	3	.3	Carbon Tube
		1 block north of PVC Building	6	.1	Carbon Tube
		1 block east of PVC Building	7	1.3	Carbon Tube
		Pilot Plant	8	1.4	Carbon Tube
		Maintenance Warehouse	9	.13	Carbon Tube
		Millroom Lab	1	.5	Carbon Tube

13 June 1974	0-3 East	Millroom Lab	1	2.4	Grab
		Lab	10	2.9	Grab
		PVC Office	2	1.5	Grab
		Maintenance Warehouse	9	.5	Carbon Tube
		Fence North	11	.5	Carbon Tube
		Amines Cooling Tower	12	.5	Carbon Tube
		North side of PVC bldg.	13	4.7	Grab
		South side of PVC bldg.	14	.6	Grab
		1 block north of PVC bldg.	6	.3	Grab
		North Fence	11	.6	Grab
		1 block downwind of PVC bldg.	15	4.1	Carbon Tube

Analysis of the water streams from the PVC Plant on June 13 are listed below:

Stream	ppm VCl	*(69.0 ppm is a 3 month average from the Material Balance Analysis
Exit from Reactor Building	21.5	
Exit from the Finishing Building	.9	
Inlet to Foxtrot Pond	15	First PVC Treatment Pond *
Exit from Foxtrot	1.2	
Exit from Echo	0	Intermediate Ponds
Exit from Charlie	0	
Exit from Hotel	0	
Exit from Bravo	0	
Exit from Alpha	0	Discharge to Bay

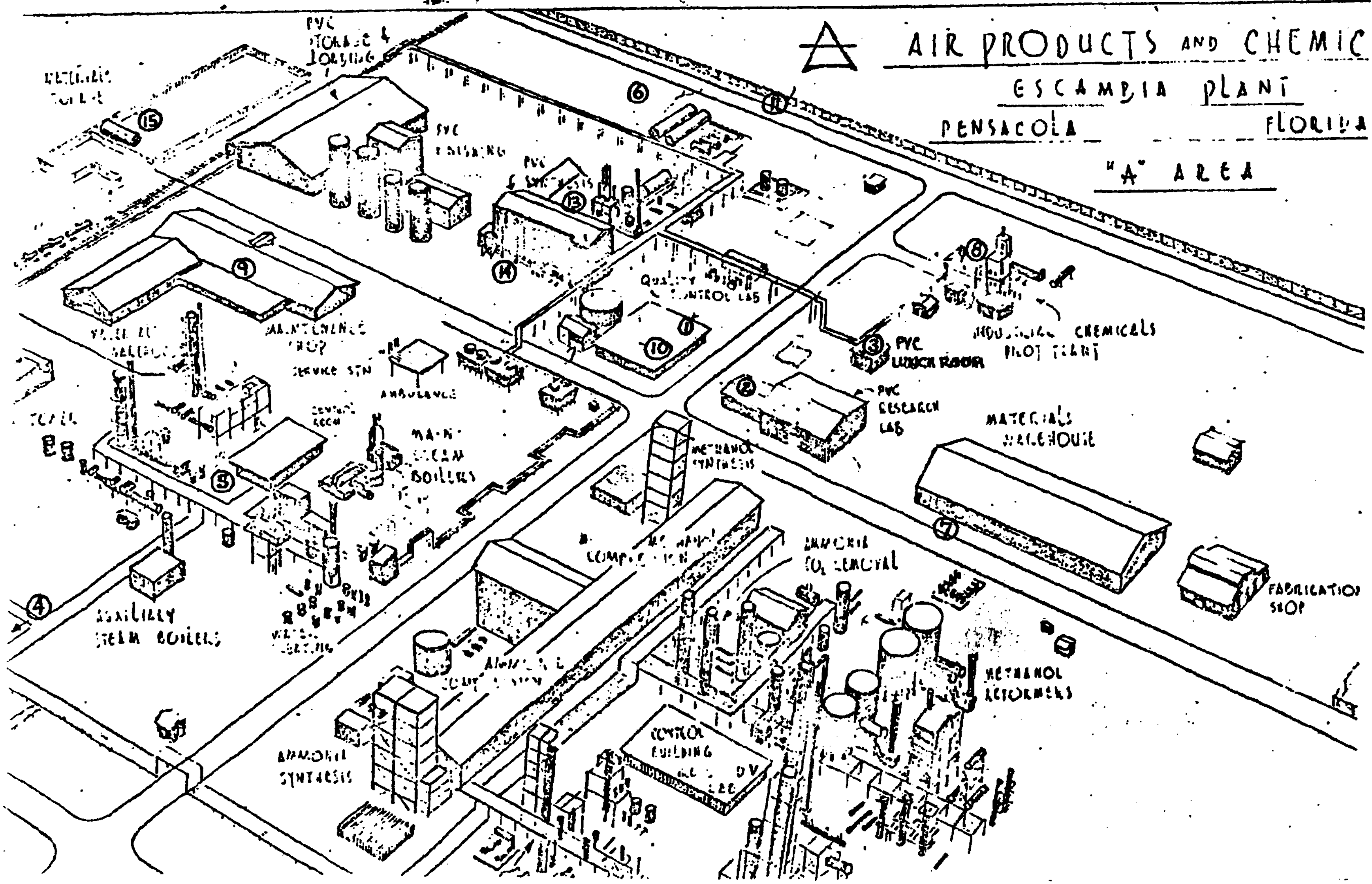
Emission Point Data

Emission point data are as listed below and discharge points are as marked on the plot plan.

Emission Point*	Location	Height (A)	Configuration	Flow	Velocity	Temperature
Vent #1A	Along walls	45	8" dia.	I	NA	~ 140°F
Vent #1B	‡	55	4" dia.	2170CFM**	6200 ft/min	~ 200°F
Vent #2	‡ (2 Jets)	55	4" dia.	2170CFM**	6200 ft/min	~200°F
Vent #3	‡	55	1" dia.	7.78CFM	1430 ft/min	~ 40°F
Vent #4	‡	55	11 3/4" dia.	933 CFM	1250 ft/min	120°F
Vent #5	‡	60	North 20 1/2" dia.	11MCFM	4900 ft/min	150°F
			South 25"x28"	23 MCFM	4900 ft/min	150°F
Vent #6	‡	45	1/2" dia.	.57 CFM	42 ft/min	70°F
Vent #7	‡	45	10" dia.	2000 CFM	3670 ft/min	70°F
Vent #8	‡	45	6"x6"	2000 CFM	8000 ft/min	90°F

* See paragraph B under Process and Emission Data
‡ I = Intermittant
**Based on usage of 870#/hr/jet steam usage (200#steam) plus 140CFM jet capacity

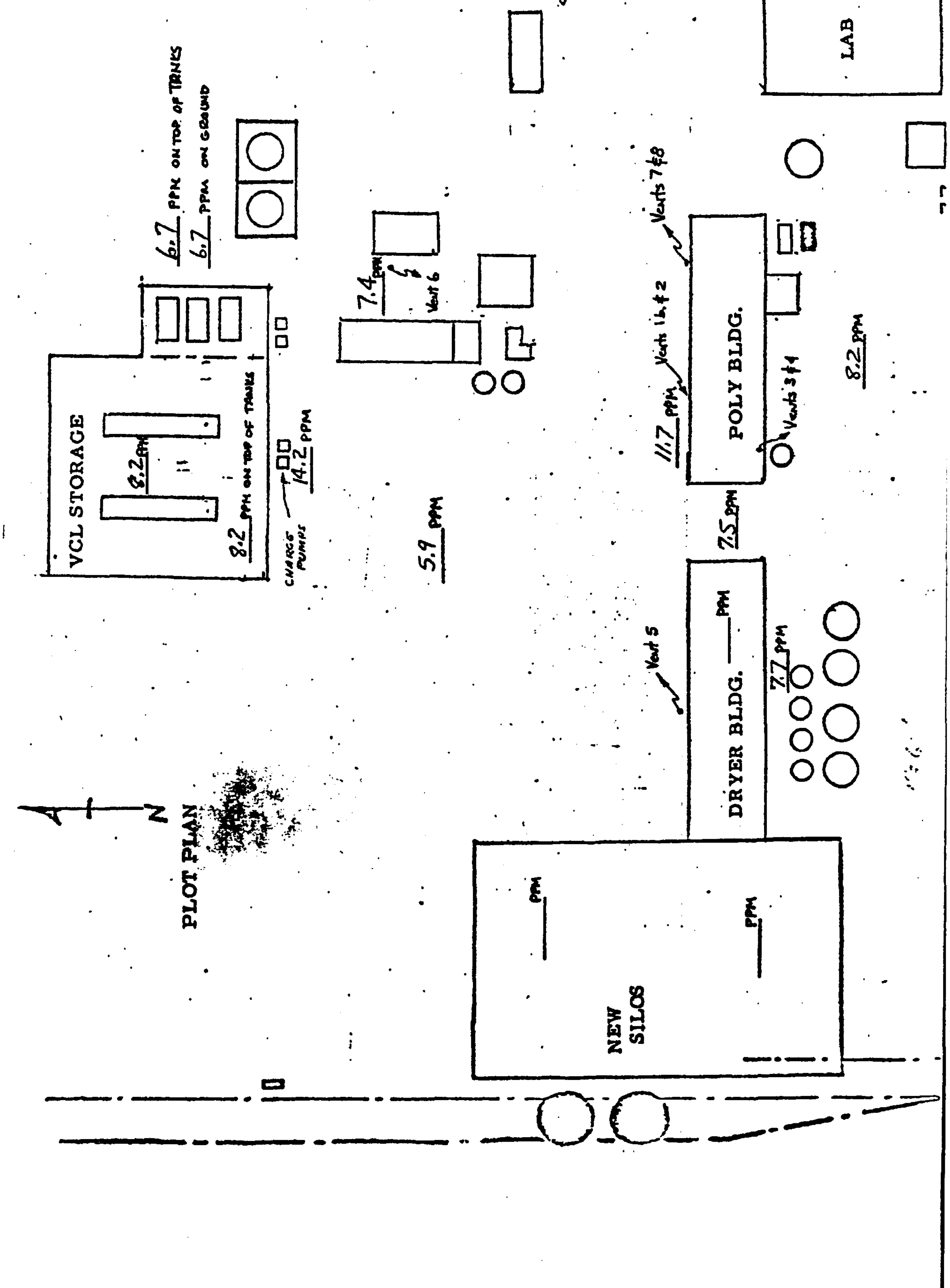
AMBIENT AIR DATA
10-13 JUNE 1974



DATE 2/11/74 → 6/5/74 /C

PVC PLANT PLOT PLAN

57 total readings



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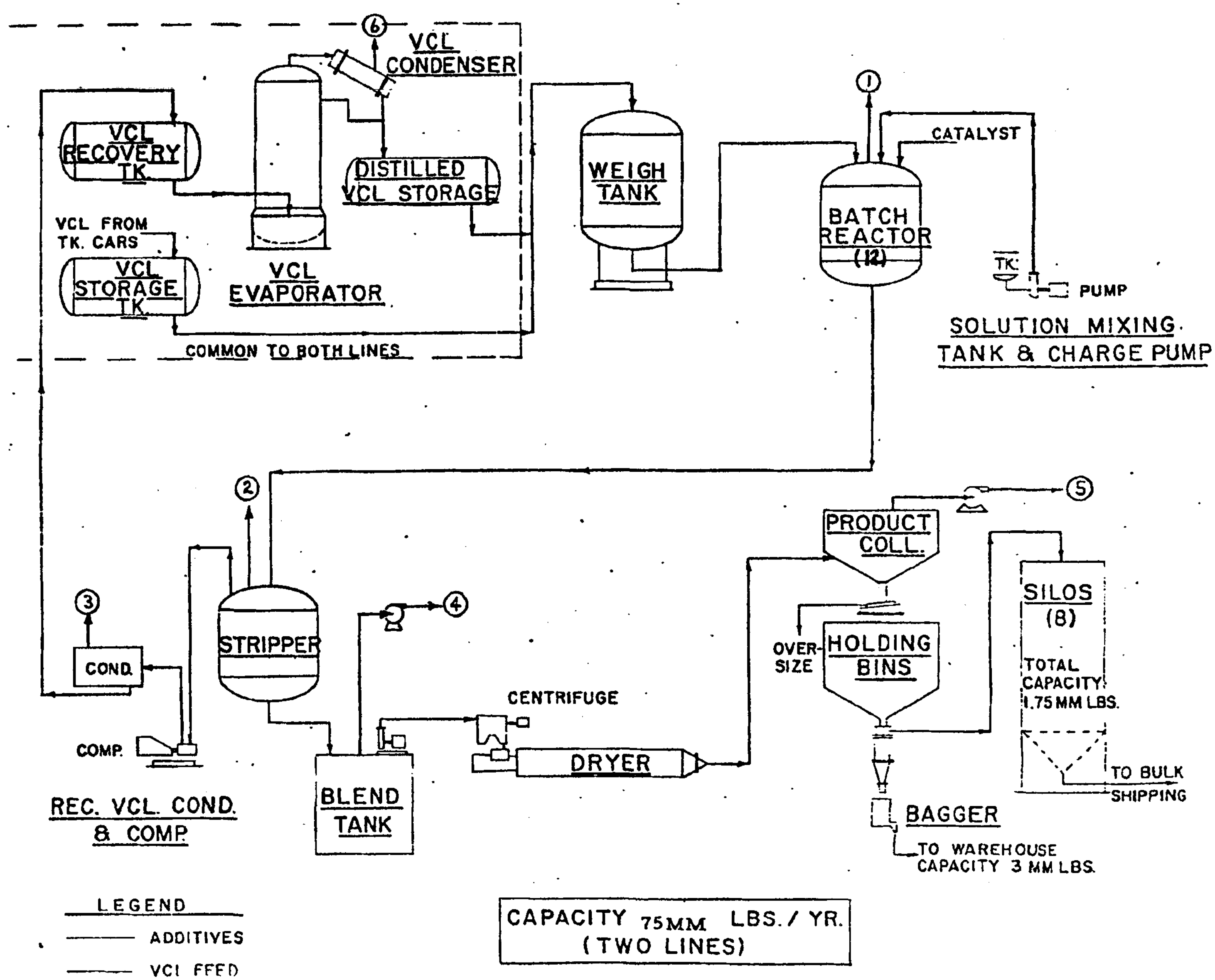
POLYVINYL CHLORIDE PLANT



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OCT 18 1974

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LAW DEPT.

EPA broadens its definition of carcinogen

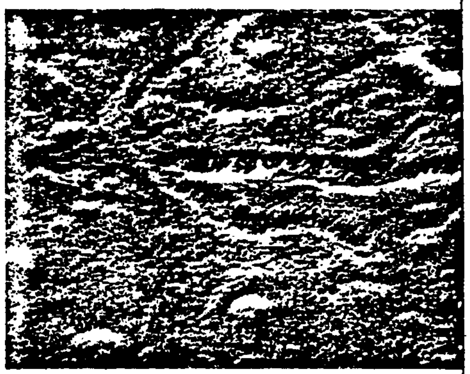
A new and apparently precedent-setting criterion for determining the carcinogenicity of a substance was used in Environmental Protection Agency administrator Russell E. Train's Oct. 1 decision to suspend all major uses of Shell Chemical's aldrin and dieldrin pesticides. Mr. Train is of the opinion that, for purposes of "carcinogenicity testing," tumorogenic substances and carcinogenic substances are "synonymous." This interpretation could have a far-reaching impact on EPA regulation of chemical substances. However, it is in sharp contrast to policies of other agencies, such as the Food and Drug Administration, which define carcinogenic substances as those that actually cause cancerous tumors.

Since laboratory evidence has linked aldrin and dieldrin to liver tumors—benign and malignant—in mice and rats, Mr. Train says that he has concluded that the chemicals also can pose a "high risk of causing cancer in man." According to an EPA enforcement official, this criterion will guide future EPA rulings concerning cancer-causing substances. Indeed, an official in EPA's pesticide division tells C&EN, the words "tumorogenic" and "carcinogenic" won't be in the proposed pesticide regulations that EPA intends to issue next week. In their place, "oncogenic" is used to designate any substance that will produce tumors—cancerous or otherwise—in test objects.

In Mr. Train's suspension order, he explains his criterion and why aldrin and dieldrin are carcinogenic to man. He defines a carcinogenic substance as "one that increases the incidence of benign or malignant tumors in exposed animals, decreases the latency period between exposure and onset of tumor, or results in unusual tumors." To Mr. Train, the distinction between benign and malignant tumors is not a reliable indicator of carcinogenicity, because, "in the thinking of most experimentalists, the induction of a benign tumor is merely a stage in the subsequent occurrence of a malignancy." His opinion is backed by a Health, Education, and Welfare advisory panel that has recommended that a "finding of carcinogenicity" be made when a substance is "judged positive for tumor induction in one or more species."

Although Shell protested during EPA suspension hearings on the pesticides that mice were an inappropriate test species and that there is no correlation between mice and human behavior, Mr. Train points out that not only does Shell use mice in their own cancer experiments, but that mice response is similar "pathologically" to that of man. In addition, Mr. Train refutes arguments that carcinogens are species specific, in that, for instance, aldrin and dieldrin might affect mice but not any other species, including man. He cites research data from organizations such as the International Association for Research on Cancer, which have found species specificity "unsubstantiated."

Further, Mr. Train says it is impossible to establish a "safe level" of exposure of aldrin and dieldrin to man because no one has been able to determine the relationship between the dosage of these two chemicals fed to test animals and the subsequent cancerous response. Nor has anyone come up with a threshold level of carcinogenic effect for the chemicals, Mr. Train points out. He does think that there is a theoretical "no-effect" level although it has not been demonstrated conclusively in laboratory studies. The lowest tested dose of 0.1 p.p.m. aldrin



Cancerous cells show up in this mouse tumor. EPA may now interpret results from such animal studies differently

and dieldrin still produced "significant tumors" in mice.

Anyway, Mr. Train concludes, any substance that will induce cancer in animals "at any dose level, no matter how high or low," should be treated with caution. He admits that high doses of the chemicals were given to the test animals, but points out that, with a limited number of animals, this is necessary to determine gross effects. For instance, Mr. Train says, a chemical that causes one cancer in every thousand men is considered disastrous, but there are very few laboratories that can accommodate 1000 animals and even then, he says, one incidence of cancer "might be disregarded as chance."

Suspension of the major uses and production of an estimated 10 million pounds of aldrin and dieldrin in 1975 will remain in effect during cancellation proceedings, which, when concluded, would ban permanently production of the pesticides. Cancellation hearings on the risk *vs.* benefits of the chemicals have been in progress for a year, and no early end to the hearings seems in sight.

AP00027810