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APR 14 1969

DEPT 5475

A Study of Vinyl Chloride Vapor Concentrations in
Avon Lake Polymerizers

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Summary

The level of vinyl chloride in the atmosphere of a polymerizer after various suction times is quantified. It is concluded that if 500ppm is the allowable maximum when a man enters the poly, there is very little margin of safety in the current plant procedure. In fact, there probably are occasions when the concentration of vinyl chloride exceeds 500 ppm when a man enters a poly.

If the allowable maximum were reduced to the order of 100 ppm, some major changes will be needed. More efficient air changes of poly atmosphere and/or early removal of most of the polymer adhering to the poly surface will be needed.

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Introduction:

During mid-1967, it was agreed between Mr. J.L. Nelson and Mr. W.E. McCormick that studies should be conducted in polymerizers of one or two of the PVC Plants to evaluate personnel exposures to vinyl chloride during poly cleaning operations. Some preliminary studies were subsequently carried out at both the Louisville and Avon Lake Plants, but an analysis of this data indicated a questionable reliability. Therefore, during the last quarter of 1968, a more detailed group of studies was carried out to quantify the effect of some of the variables experienced during poly cleaning operation at the Avon Lake General Chemical Plant. The collection of the samples and the measurements of the poly ventilation rates were performed by Mr. Katzenmeyer. These samples were analyzed by gas chromatographic techniques by Mr. DeCapita and his group. The statistical analyses of the results were performed by Mr. Morgan. The results obtained and the conclusion accruing from them follow.

Results:

148 separate air samples were collected between the period of 9-18-68 to 11-19-68 in 32 different polys. Ten different resins were manufactured in these polys in the Avon Lake Plant. The air samples were collected by a technique developed between Mr. DeCapita and the Department of Industrial Hygiene and Toxicology, involving the use of a small evacuated glass vial placed at a specific location in the poly to extract an instantaneous air sample from the poly. Two sampling locations were chosen: at the level of the bottom agitator, and at 6 ft. above the floor of the polymerizer. Both locations were on the center vertical axis of the poly. The collected samples were transmitted on the same day to Mr. DeCapita for subsequent gas chromatographic analyses. When vinyl chloride concentration exceeds 100,000 ppm, the absolute value of the number becomes questionable, but is thought to be relatively reliable. In order to obtain a reliable estimate of the ambient vinyl chloride concentration in the poly workroom, an air sample was collected 1 ft. above the open manhole of the poly being sampled, during the period of ventilation of the poly.

The results of these studies are presented in Table I. They show that poly concentrations vary from 10 ppm to 300,000 ppm, depending upon; the time at which the sample was taken, the location at which the sample was collected, the type of resin being manufactured, and the rate of ventilation of the poly. The vinyl chloride concentration was not effectively reduced by washing poly walls with water after opening.

The ventilation rate of each poly, in which atmospheric samples were taken, was measured. This was performed by using an Alinor Velometer to determine the inward air velocity through the manhole. The results of these measurements are also shown in Table I. The ventilation rate was found to vary from 23 to 55 lcfm with one hose in use. The rate of ventilation was purposely increased on many of the polys by the insertion of a second hose to determine what effect such increase would have on the atmospheric concentration of vinyl chloride. These comparative results with one versus two hoses are shown in Table I.

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Because of plant schedules and practices data was not obtained on each type of resin in each size polymerizer. However, the following combinations were obtained:

	<u>1100</u>	<u>3300</u>	<u>4000</u>	<u>4300</u>
Paste (121 type)	X			
Pearl (101 type)	X	X		
Pearl (102 and 103 type)	X	X		X
Copolymer (135 type)	X			
Latex (Geon 450X20)			X	

Figure 1 indicates that the rate of vinyl chloride removal is lowest in small poly; and that the small poly will level out at a higher concentration. The real reason for this is thought to be because of one or all of the following facts:

1. Ratio of Surface area to volume is greatest in the 1100 gallon poly.
2. The ambient concentration of VCl in Unit A, which houses the 4300 gallon polys, ranges from 8-30 ppm; while the areas housing the 3300 gallon polys and the 1100 gallon polys have ambient VCl concentrations in the range of 18-90, and 20-140 ppm respectively.
3. The 1100 gallon polys are stainless steel and old, while the 3300 and 4300 gallon polys are glass lined. Perhaps less polymer buildup exists on the glass lined surfaces and hence less effect due to residual vinyl chloride monomer in polymer clinging to the walls.

It was thought that increased ventilation would decrease the vinyl chloride concentration in proportion to the increase in ventilation rate. The decrease in vinyl chloride concentration was less than expected with two hoses. It appears that the air movement within the poly does not sufficiently mix the vinyl chloride rich atmosphere with the incoming air. If this is the case, then the efficiency of ventilation could be improved by the installation of a means to distribute the air throughout the entire cross-sectional area of the poly.

Figures 7 and 8 are essentially the same as Figure 1 except they are drawn for the cfm rates that generally exists at the Avon Lake General Chemical Plant. These two graphs indicate that the present evacuation system and procedure is inadequate to assure that vinyl chloride concentration in the poly is less than 500 ppm.

Conclusions:

1. More efficient ventilation of a poly is obtained by having the ventilation hose 1 ft. off the bottom than at higher levels (See Figure 2).
2. It appears from the data (Figures 4, 5 and 6) that air samples collected within the poly will be strongly influenced by air currents, channeling of the ventilation corridor, etc.

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3. Atmospheric concentrations in polys, when ventilated and entered in accordance with the Plant's routine procedure (hose on the bottom, 30 minutes after opening), were found to vary from 25 ppm to 1539 ppm. This wide variation was observed even with closely controlling the location of the ventilation hose, and indicates further need for better control. It is known that the time of entrance is often less than 30 minutes after opening, and an observation of the Plant's routine procedures clearly demonstrates that the hose is frequently not on the bottom. It can therefore, be assumed that many times, personnel exposures are considerably higher than those obtained under these controlled conditions.
4. The data indicate (See Figure 3) that atmospheric concentrations in polys for low conversion pearl polymer can be expected to exceed 500 ppm after 20 minutes of ventilation.
5. It, of course, is impossible to reduce the atmospheric concentration inside the poly below that existing outside of the poly. There are occasions when this atmospheric concentration exceeds 100 ppm.
6. Serious consideration is being given to reducing to a minimum personnel exposures to vinyl chloride. The data of this study indicate that there are poly vapor concentrations that cannot be further reduced without major changes in manufacturing and operating procedures. These data show that a ventilation rate of 250 cfm, with an evacuation time of 30 minutes, can be expected to produce a poly concentration of 220 ppm for a 1100 gallon poly, 320 ppm for a 3300 gallon poly, and 400 ppm for a 4300 gallon poly (See Figure 1). To obtain lower levels will require considerably greater ventilation rates and/or evacuation times.

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Vinyl Chloride Concentration in Various Polymerizers

Date	Poly No.	Poly Size Gals.	Resin No.	Type Resin	Exhaust				Sample Location 1-Agitator 2-Eye Level	VCl ppm	
					Hose Location 1-Agitator 2-Eye Level	No. of Hoses	Min. on Exhaust Before Sample	Rate CFM		Ambient	In Poly
9-23-68 Bldg. 451	18	1100	135	Co-Polymer Paste	1	2	10 21 22 35	182	1 1 2 1	21	23 103 70 45
9-23-68 Bldg. 451	34	1100	121F4	Paste	1	1	10 20 21 35	125	1 1 2 1	42	333 159 158 121
9-23-68 Bldg. 451	24	1100	135	Co-Polymer	2	1	5 19 20 35	112	2 1 2 2	24	256 116,242 256 195
9-30-68 Bldg. 451	4	1100	110X 127	Paste	1	2	6 21 22 36	174	2 2 1 2	59	482 145 142 114
9-30-68 Bldg. 451	49	1100		Paste	2	1	5 20 21 35	100	1 1 2 1	72	322 1286 181 1224
10-8-68 Bldg. 451	23	1100	135	Paste	2	2	5 20 20 35	273	1 1 2 1	28	152,590 1185 754 235
10-8-68 Bldg. 451	13	1100	135	Paste	1	1	5 20 20 35	129	2 2 1 2	133	842 209 316 158
9-18-68 Bldg. 461	147	3300	102EP FI	Low Conv. Pearl	1	2	12 23 24 25 25 36	234	1 1 2 1 2 1	21	334 41 109 06 12 74

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Date	Poly No.	Poly Size Gals.	Resin No.	Type Resin	Exhaust				Sample Location 1-Agitator	VCl ppm	
					Hose Location 1-Agitator	No. of Hoses	Min. on Exhaust Before Sample	Rate CFM		2-Eye Level	Abient
					2-Eye Level						
9-18-68 Bldg. 461	152	3300	102EP F5	Low Conv. Pearl	2	1	15 20 21 22 24 35	151	2 1 1 2 2 2	47	981 60,000 193,000 382 312 87
9-18-68 Bldg. 461	135	1100	121F4	Paste	2	2	7 21 22 22 24 36	424	2 1 1 2 2 2	49	1032 219 173 101 113 48
9-18-68 Bldg. 461	143	3300	101F21	High Conv. Pearl	1	1	11 20 20 35	119	1 1 2 1	30	1032 543 624 46
9-23-68 Bldg. 461	108	1100	102EP F5	Low Conv. Pearl	2	1	10 20 21 35	172	1 1 2 1	47	141,387 165,056 774 147,029
9-30-68 Bldg. 461	103	1100	102EP F5	Low Conv. Pearl	1	1	5 21 22 35	87	1 1 2 1	68	2402 741 241 167
9-30-68 Bldg. 461	139	3300	103EP F76	Low Conv. Pearl	1	1	5 20 21 34	96	2 2 1 2	88	1349 1963 1353 86
9-30-68 Bldg. 461	137	3300	102EP F5	Low Conv. Pearl	2	2	4 23 24 35	302	1 1 2 1	65	2253 2244 1269 777
9-30-68 Bldg. 461	102	1100	102EP F5	Low Conv. Pearl	1	2	5 20 21 35	277	2 2 1 2	76	986 388 367 230
10-30-68 Bldg. 461	140	3300	102EP F5	Low Conv. Pearl	1	1	1 30 31 61 91 121	117	2 1 2 1 2 1	24	8,471 321 220 143 115 66

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Date	Poly No.	Poly Size Gals.	Resin No.	Type Resin	Hose Location 1-Agitator	No. of Hoses	Min. on Exhaust	Rate CFM	Sample Location 1-Agitator	VCl ppm	
					2-Eye Level		Before Sample		2-Eye Level	Abient	In Poly
11-12-68 Bldg. 461	148	3300	103EP F76	Low Conv. Pearl	1	1	1 31 32 61 90 122	85	1 1 2 2 1 2	18	309,013 1,539 1,486 941 233 137
11-12-68 Bldg. 461	116	1100 washed	101EP F21	High Conv. Pearl	1	1	5 38 39 65 95 125	23	1 1 2 2 1 2	62	266,706 302 320 242 163 148
11-12-68 Bldg. 461	107	1100	101EP F21	High Conv. Pearl	1	1	1 30 31 60 90 121	126	2 1 2 1 2 1	21	8,038 323 87 169 95 87
11-12-68 Bldg. 461	143	3300 washed	102EP F5	Low Conv. Pearl	1	2	2 31 32 62 91 120	279	1 1 2 2 1 2	63	187,313 120 97 60 66 41
11-19-68 Bldg. 461	116	1100	101EP F21	High Conv. Pearl	1	2	2 30 31 60 90 120	233	2 1 2 1 2 1	29	1,882 200 161 58 98 139
11-19-68 Bldg. 461	112	1100	102EP F5	Low Conv. Pearl	1	1	1 31 32 61 91 119	173	2 1 2 1 2 1	73	15,695 98 88 68 88 104
11-13-68 Bldg. 464	201	4300 washed	103EP F5	Low Conv. Pearl	1	2	3 30 31 60 91 121	720	1 1 2 2 1 2	14	7,721 24 18 18 1 14
11-13-68 Bldg. 464	205	4300 washed	103EP F5	Low	1	1	4 32 33 63 93 127	396	2 1 2 1 2 1	27	6,67 11 14 46 14 20

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Date	Poly No.	Poly Size Gals.	Resin No.	Type Resin	Exhaust				Sample Location 1-Agitator 2-Eye Level	VCl ppm	
					Hose Location 1-Agitator 2-Eye Level	No. of Hoses	Min. on Exhaust Before Sample	Rate CFM		Abient	In Poly
11-13-68 Bldg. 464	215	4300	104EP	Low Conv. Pearl	1	2	3	690	1	15	2,437
							30		1		43
							31		2		39
							60		2		35
							92		1		20
							122		2		19
11-13-68 Bldg. 464	204	4300 washed	103EP F5	Low Conv. Pearl	1	1	2	398	2	7	11,374
							31		1		25
							32		2		21
							66		1		19
							92		2		21
							118		1		10
19-68 Bldg. 464	203	4300	103EP F71	Low Conv. Pearl	1	1	2	551	2	13	6,502
							32		1		97
							33		2		90
							60		1		63
							91		2		25
							119		1		39
9-23-68 Bldg. 463	5	4400	450X3	Latex	1	1	6	145	2	22	75,134
							11		1		11,928
							20		1		4,310
							21		2		4,822
							36		1		3,433
							37		2		1,994

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VINYL CHLORIDE (ppm)

100000
10000
1000
100
10

SHOWS RELATIVE DIFFICULTY
PRESENTED BY POLY SIZE
IN ACHIEVING A GIVEN
VCI CONC.

4300 GAL. POLY

3300 GAL. POLY

1100 GAL. POLY

HOSE @ AGITATOR
No. HOSES = 1
CFM = 250
TYPE RESIN = LO CONV. PEARL
SAMPLED @ AGITATOR

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25190010

4 100 10 1



VINYL CHLORIDE (ppm)

100000

10000

1000

100

10

ILLUSTRATES

IMPORTANCE OF PLACING
SUCTION HOSE NEAR
BOTTOM OF POLY.

HOSE LOCATION X FEET

HOSE @ MIDDLE

HOSE @ AGITATOR

No. Hoses = 1

CFM = 250

POLY SIZE = 3300

TYPE RESIN = LO CONV. PEARL

SAMPLED @ AGITATOR

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100

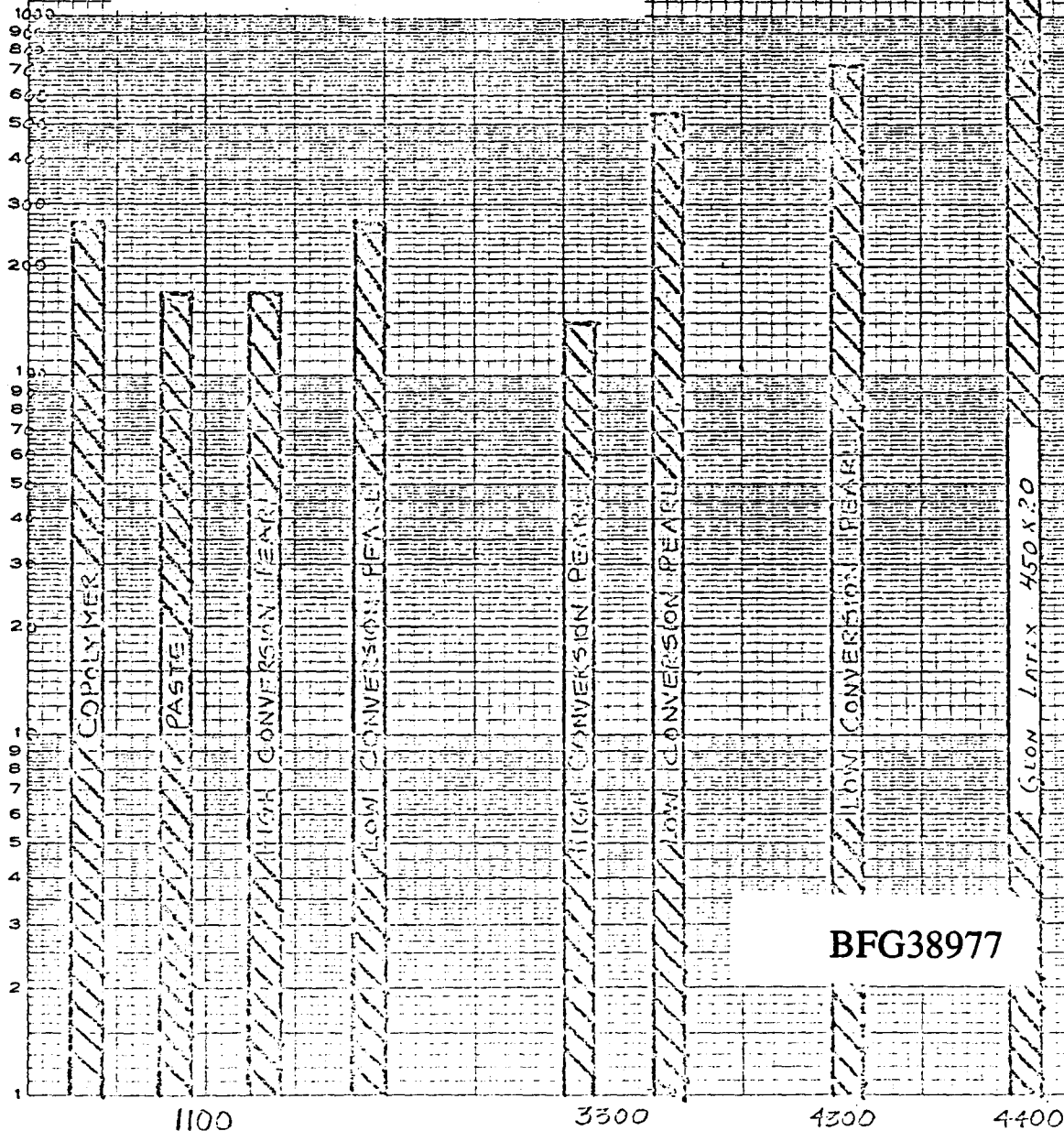
10

25190011

Hose @ AGITATOR
 No. of Hoses = 1
 Time = 20 MIN.
 CFM = 250
 SAMPLED @ AGITATOR

SHOWS RELATIVE DIFFICULTY
 PRESENTED BY RESIN TYPES
 IN ACHIEVING A GIVEN
 VCI CONC.

VINYL CHLORIDE (PPM)



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Poly Size

POLY SIZE = 1100.

TIME = 20 MINUTES

TYPE RESIN = LO CONV. PEARL

HOSE @ AGITATOR

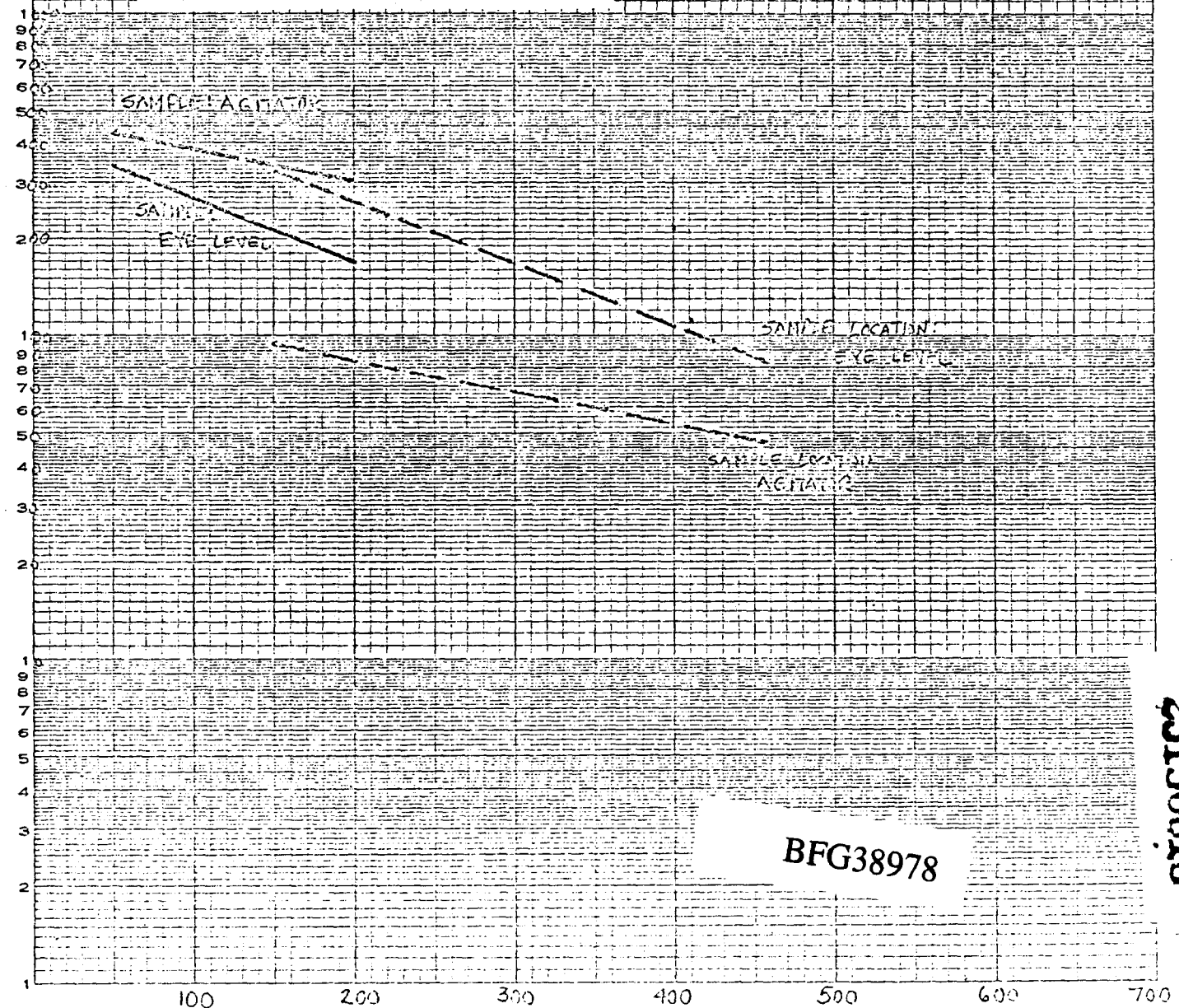
———— = 1. HOSE
 - - - - - = 2. HOSES

1. DOWELING AIR TURNOVER
 • RATE DOES NOT REDUCE
 VCI CONC. AS MUCH AS
 EXPECTED.

2. ILLUSTRATES NON-HOMOGENEITY
 OF VCI CONC. IN THE
 POLY ATMOSPHERE.

(Same applies to figs. 5f'6)

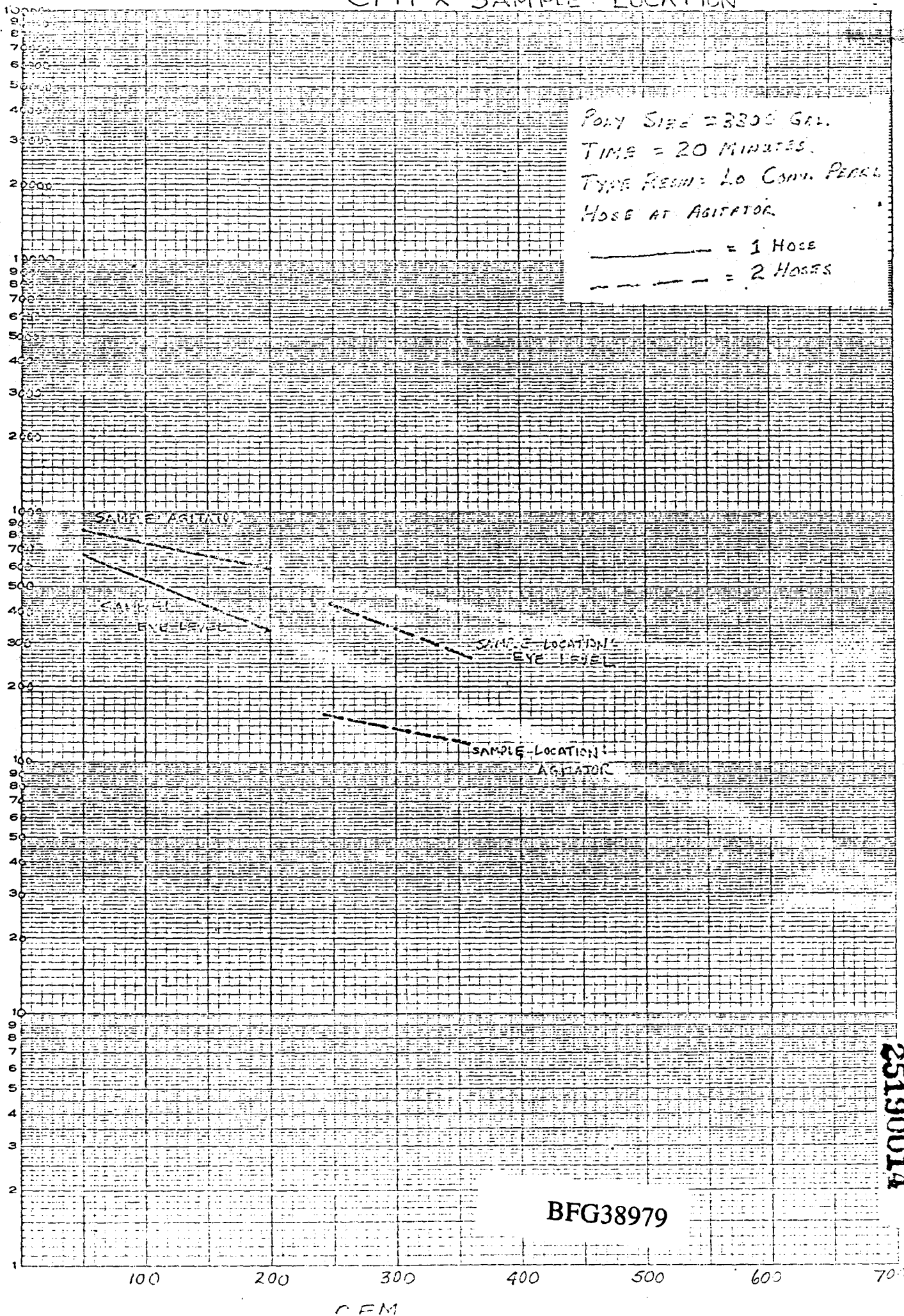
VINYL CHLORIDE (ppm)



NO. 340-LS12 DIETZEN GRAPH PAPER
SEMI-LOGARITHMIC
5 CYCLES X 12 DIVISIONS PER INCH

EUGENE DIETZEN CO.
MADE IN U. S. A.

VINYL CHLORIDE (ppm)



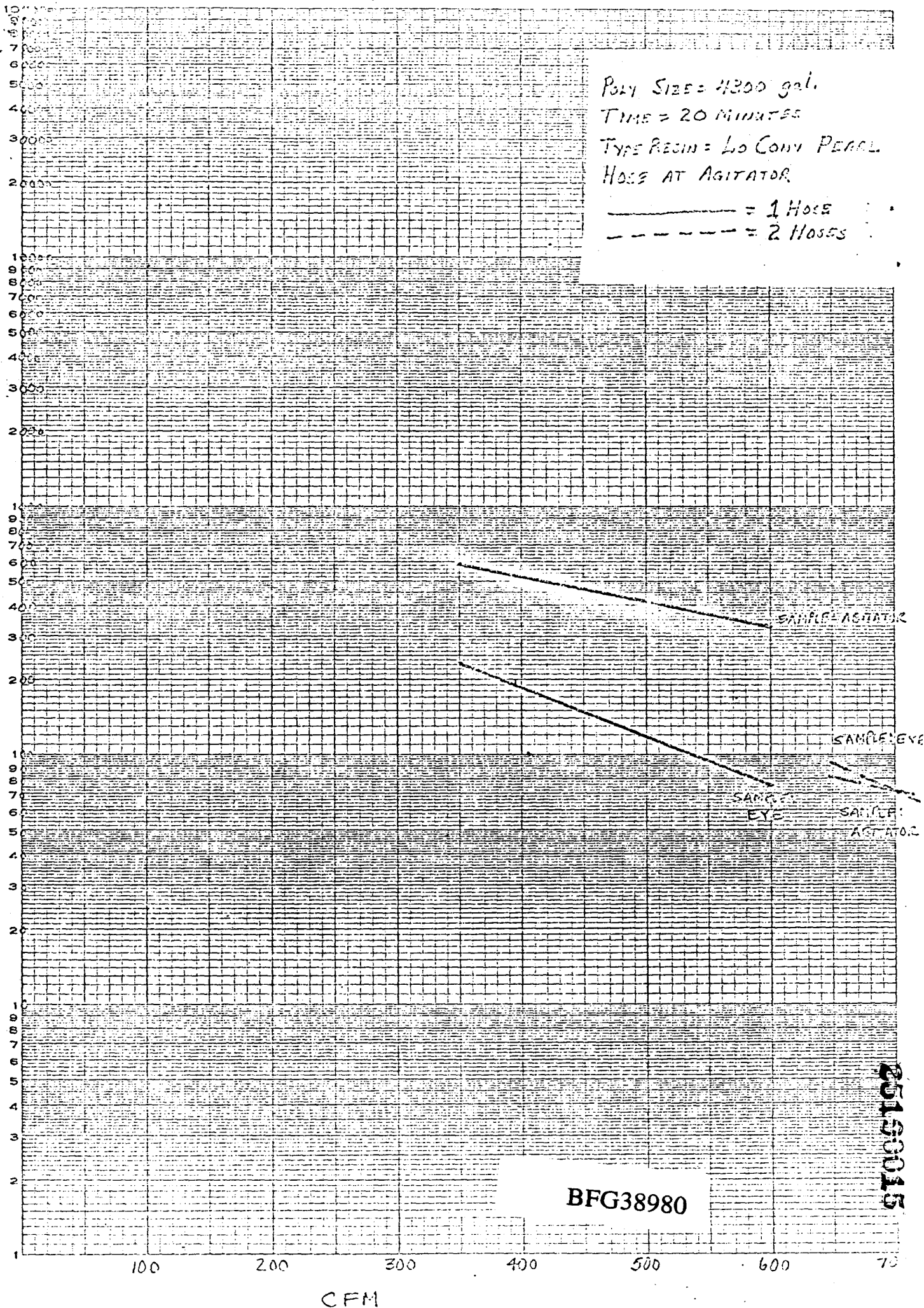
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EUGENE DIETZGEN CO.
MADE IN U. S. A.

NO. 340-LS10 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
5 CYCLES X 10 DIVISIONS PER INCH

VINYL CHLORIDE (PPM)



NO. 31.156. LOGARITHMIC 5 BY 3 2-INCH CYCLES (BASE LONG WAY).



CODEx BOOK COMPANY, INC. NORWOOD, MASSACHUSETTS.
PRINTED IN U.S.A.

VINYL CHLORIDE (PPM)

10

100

1000

10000

EVACUATION TIME (MIN)

10

100

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91065152

PEARL
RESIN-LOW CONVE

CFM = 125

SAMPLE LOC - AGTATD

NO. HOSES = 1

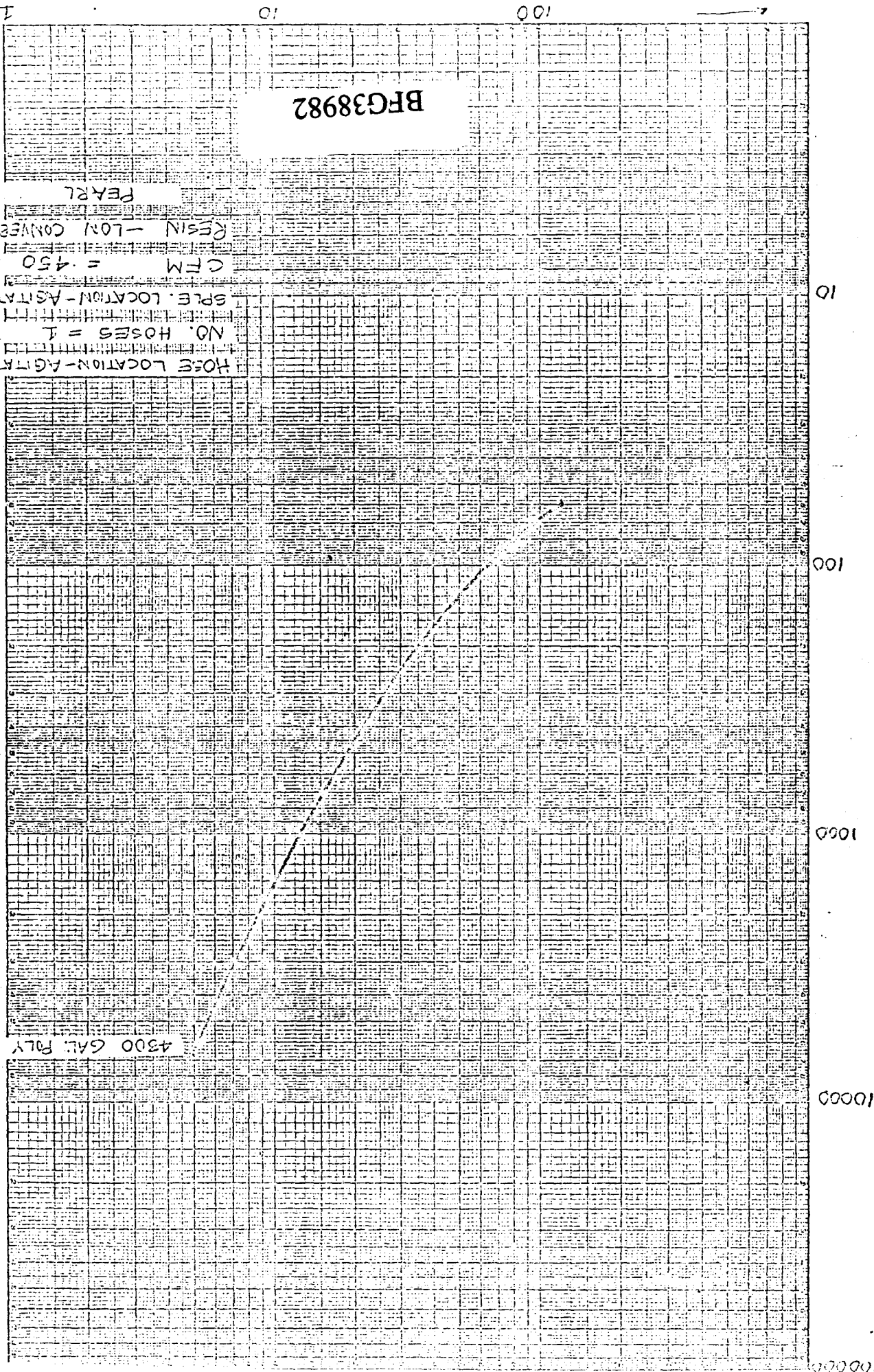
HOSE LOCATION - AGTATD

1100 GAL. POL

3500 GAL. POL



VINYL CHLORIDE (ppm)



25190017

B. F. Goodrich Chemical Company

Inter-Organization Correspondence

To E.B. Katzenmeyer

Date September 3, 1968

Location Akron

From E.G. DeCapita

EGD-55-68

Subject Analysis of Room and Poly Atmospheres From the ALGCP

Your samples of room and poly atmospheres taken at the Avon Lake General Chemical Plant have been analysed by gas chromatography. Quantitative results are tabulated below.

The amount of vinyl chloride in samples No. 1 and 2 taken 8/1/68 and sample No. 1 taken 8/8/68 is grossly out of the calibration range of the standard gas sample used for this analysis. My estimate of the amount of vinyl chloride in these samples is 18-20% for sample No. 1 and 5-7% for sample No. 2 of 8/1/68. Sample No. 1 of 8/8/68 is in the 8-10% range.

<u>Date Sampled</u>	<u>Sample No.</u>	<u>Sample Location</u>	<u>ppm VC1</u>
8/1/68	1	Poly opened	
	2	5 min. after vent bore	
	3	15 min. after vent bore	70
	4	Man enters	40
	5	10 min. after man enters	27
	6	30 min. after man in	24
	7	Atmospheric sample 10 min. after man in	13
	8	Atmospheric sample 30 min. after man in	10
8/8/68	1	Poly opened	
	2	5 min. after 2 vent bores	122
	3	15 min. after 2 vent bores	58
	4	Man enters	29
	5	10 min. after man in	18
	6	Atmospheric sample 10 min. after man in	10

E.G. DeCapita

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