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HEALTH, SAFETY &
ENVIRONMENTAL AFFAIRS

May 25, 1984

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Subject: Request for Change in Method of Compliance with Part 61, NESHAPS Regulation for Vinyl Chloride Monomer Control, Sources Following Vinyl Chloride Strippers

Gentlemen:

Several years ago a proposal was submitted to the TACB in Austin and the EPA in Dallas for consideration of a statistically-based control system for vinyl chloride monomer (VCM) in our Solution Vinyl Resins production unit at Texas City.[1] This proposal was not acceptable to the EPA because it did not meet the daily monitoring requirements that the EPA considers vital to the degree of control desired for residual VCM under the terms of the regulation. An EPA document [2] was provided which suggested that a daily monitoring of process control parameters that would assure the required residual VCM levels could be attained would be a satisfactory alternative to the stripped sample analyses specified in the present regulation. Such a parameter monitoring program is the subject of this present request.

BACKGROUND INFORMATION

The Solution Vinyl Resins unit at the Texas City Plant of Union Carbide Corporation produces a series of copolymers of vinyl chloride, vinyl acetate and other comonomers by unique solvent-based process technology. Because the major reactant in this copolymerization process is vinyl chloride monomer, the process unit is subject to Federal

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1, 2 See References, page 8

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Government regulation under Part 61, National Emission Standards for Hazardous Air Pollutants (NESHAPS), Subparts A and F and Appendix B, Methods 106 and 107.

Accordingly, since the effective date of this regulation, we have been providing a semiannual report as prescribed by §61.70 of Subpart F. This report includes a record of the VCM content of polyvinyl chloride copolymer resins produced here and analyzed according to Method 107. The analytical data are reported as the daily weighted average VCM content of the dry copolymer resins calculated by the formula §61.70 (c)(2)(ii) and (c)(2)(v). According to §61.64 (e)(1)(ii) which specifies the emission standard for various polyvinyl chloride processes, specifically, for sources following the strippers, the maximum daily weighted average is 400 ppm, dry resin basis, for each type of resin produced.

From information published prior to the promulgation of this regulation for VCM control, we understood that the VCM stripping operation of primary concern involved the removal of unreacted VCM from Suspension, Bulk and Latex products. All three processes are characterized by having small solid resin particles present in dynamic equilibrium with unreacted VCM in the stripping steps of the processes. Because the physical mechanism of removal of VCM from solid particles in these three processes is highly dependent upon VCM diffusion properties and rates in the mixtures, the level of 400 ppm VCM was considered a stringent requirement, calling for considerable care and attention in these production facilities. As a result, the regulation was established with very stringent sampling and analytical procedures and requirements to be sure the processes were adequately controlled to meet the 400 ppm VCM limitation.

However, in the continuous stripping of VCM in the Solution Vinyls Process from the autoclave product solutions, there are no particles of solid resin present. The material is a single phase mixture of copolymers, unreacted monomers and solvents. In this situation, the stripping operation is conducted in a continuous still system by a distillation mechanism which for VCM removal is much more rapid and complete than when a diffusion mechanism is controlling the separation rates, as described above.

As a result of this process characteristic, we are able to consistently remove the VCM to an average level of 10 ppm or less (dry resin, daily average basis). The sampling and analytical procedures and schedules prescribed by the regulation are far more frequent, extensive and costly than necessary to assure ourselves and the regulatory agencies that the 400 ppm limit is being met.

DESCRIPTION OF STRIPPING OPERATION

The production unit has four separate polymerization and product recovery lines, each capable of accommodating the different molecular weight and compositional variations of the copolymers in our production inventory. Each train begins with several polymerization vessels which feed in parallel into a dilution tank for the solvent adjustment of the varnish prior to stripping to provide the optimum specific gravity for the stripping step. The properly diluted varnish then goes to the top of a stripping still column containing sixteen valve trays. All system components in contact with the varnish are of stainless steel construction. The columns vary in diameter from one line to another and have varying capacities as indicated:

Stripper No.	1	2	3	4
Column I.D., inches	48	42	42	36
Average Varnish Feed Rate, Lb/Hr	25,000	18,000	18,000	7,000

Control of the stripping operation[3] to remove the maximum amount of VCM is achieved by the counter-current upward flow of solvent vapors from the base of the stripping column, thereby contacting the down-coming varnish across the valve trays and carrying out the more volatile VCM in the vapor stream from the head of the column

The schematic shown as Figure 1 illustrates a typical stripper configuration with the various streams involved. The description of the designated streams marked in Figure 1 are listed in Table I.

HISTORICAL DATA

As previously stated, this distillation mode of stripping is capable of consistently removing VCM to a much lower level of residual VCM in the resin stream than the 400 ppm weighted daily average required by the regulation. Because of this, we believe that the high frequency of sampling (every eight hours) and the subsequent analytical effort constitute an excessive amount of time, effort and funding for the purposes of the regulation.

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3 The solvent boiling point is 56°C, vinyl chloride monomer (VCM) boils at -14.3°C and the two materials are infinitely soluble in one another.

The Semiannual Report data for the past three years is summarized in Table II, which confirms the previous statements. In reviewing this information, several items should be pointed out. First, there has been only one daily result greater than the 400 ppm upper limit during this three year period. (At that time, there was some question about the validity of the samples which could not be resolved, so the test results were retained.) There is a definite improvement in the mean value for A_{ti} for the six-month periods since September 1982 as well as a significant reduction in the number of days in each period having A_{ti} results of over 10 ppm.

Previous attempts to collect and correlate operating parameter data with residual VCM levels in stripped varnish were unsuccessful because the data taken was within an operating range where the changes made in operating conditions had little or no effect on the VCM levels. Our experience with this stripping operation indicates that conditions must venture well outside the normal operating ranges to see any significant effect on residual VCM.

It has been understood all along that the major controlling variable in the stripping operation is the ratio of the liquid varnish feed down the column trays to the solvent vapor flow up thru the trays (L/V ratio). The solvent vapor passing upward provides the heat and extractive force to essentially remove all the VCM from the varnish.

PROCESS IMPROVEMENTS

During the past two years certain process improvements were made that not only reduced the unreacted monomer left to be stripped from the varnish, but significantly reduced fluctuations in the process that could cause variations in the VCM content. These improvements are described below:

1) "Dynatrol" specific gravity measuring instruments were made fully operational in the first quarter of 1982. This change increased the reliability and accuracy of this process control which permits higher vinyl chloride conversion to polymer in the reaction step. This in turn reduced the amount of unreacted monomer in the varnish feed to the stripping stills. The "Dynatrols" have smoothed out autoclave polymerization operations so that more steady state operations can take place in the stripping step of the process.

2) In the first quarter of 1983, the operation of the gravitometers on the stripping stills was improved by changing from an intermittent to a continuous flow to the instruments, thereby smoothing out the feed to the stripping stills. This helped to improve steady state operation of the stripping stills. We know that it is very important to maintain steady state conditions in the base of the still if the VCM levels are to be consistently low and uniform.

3) Further improved control of the polymerization step of the process that has contributed to better stripping still operation involves an automatic on-stream analyzer coupled with a computer control. An AMSCOR MS IV analyzer has been installed to accurately monitor the quality of the feed streams and other components used to make up the feed streams. This analyzer has been matched with a MOD COMP computer that provides valuable historical data and makes the necessary calculations required to maintain a more uniform autoclave feed consistent with specified product properties desired. This addition was made in the third quarter of 1983.

4) At present, we have just completed a change in autoclave operating procedure that allows for the continuous purging of inerts from the vapor phase in the autoclaves. This improves heat transfer from this exothermic reaction and causes a more reliable temperature control of the polymerization. This improved temperature control in turn permits operating with a greater degree of confidence in the polymerization step, leading to higher conversions of monomer to polymer and thus, less VCM to strip from the varnish to the recovery system.

These changes have effectively improved the stripping operation as shown in Table II with lower daily maximums and a significantly reduced mean value (from around 6 ppm to less than 4 ppm VCM) for the different six-month periods.

STRIPPING CALIBRATION TESTS

In order to show conclusively that the VCM content of the stripped resin could be properly controlled by maintaining the proper L/V ratio on the strippers, we conducted four separate full-scale production tests to determine a quantitative relationship that could be used to achieve the required control for compliance with the regulation.

Three separate tests were run on the largest stripper (No. 1 - 48" diam. column) during the production of VYHH resin, our highest volume product, at high, medium and low varnish rates. VYHH resin is a high

molecular weight, high PVC content copolymer which produces a relatively high viscosity varnish that would be the most difficult to strip of all residual VCM.

The basic controlling factor, as stated previously, is the ratio of stripping still varnish feed rates at the top of the column to solvent vapor feed rates into the base of the stripping column. Accordingly, with steady varnish feed rates at each of the prescribed flows, the vapor feed rates were reduced stepwise (thus increasing the L/V ratio) until the VCM content of the varnish began to increase.

A fourth test was run at low varnish feed rates on VMCC resin (a low molecular weight, low PVC copolymer providing much lower varnish viscosities) in No. 3 stripper (42" diam). This test was selected to see if a VCM breakthrough would occur because of rapid rundown of varnish through the trays without sufficient contact with the solvent vapors.

We would expect in a stripping operation involving equilibrium conditions between a viscous polymer solution and compatible solvent vapors that the higher PVC content, higher molecular weight copolymer varnishes would be more difficult to strip because of the higher varnish viscosity and that the less viscous varnishes would be the easiest. This was clearly demonstrated by the test runs that we made (see Figure 2), although the practical differences were not significant insofar as meeting the NESHAPS requirement for a 400 ppm top limit on VCM content.

The test data for these calibration tests is shown in Table III and the graphs are plotted on Figure 2. It appears quite obvious that as long as the L/V ratio is maintained in the range below 2.5 that the VCM content would be expected to fall below 10 ppm. There are several other variables in this stripping process, but they do not vary appreciably and have far less effect on the VCM remaining in the varnish. The range of operating conditions possible in these stripping stills is shown in Table IV with the corresponding L/V ratios encountered.

PROPOSED DATA COLLECTION AND REPORTING FORMAT, CONTINUOUS VARNISH STRIPPING, CONTROL PARAMETER MONITORING

The production unit is equipped with the necessary instruments to control and record the conditions required to produce the desired varnish VCM stripping quality to meet the regulatory standard. At present, there are control panelboard instruments equipped with strip charts for recording process data, which may or may not all pertain directly to the stripping operations. In cases where critical attention must be given to certain operations to assure proper control is constantly being exercised, we require periodic logging of instrument readings in the operating log to be sure the operators are aware of and respond to the needs of the process.

Accordingly, in this situation, a separate log sheet for the stripper operation could provide the following information on a timely basis:

1) Varnish Feed Rate, MLb/Hr, Recorder = L

2) Solvent Vapor Feed Rate, MLb/Hr Controller/Recorder = V

3) L/V Ratio from 1) and 2) above, range to be always below 2.5

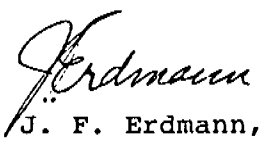
Each stripping system has its own characteristic capacity, with a range of flow rates dictated by the size and design of the system. All systems can be operated within the parameter limits and ranges shown in Table IV to produce the desired stripping effectiveness in accordance with the calibrated stripping curves shown in Figure 1. The objective is to operate all the strippers at steady state conditions with the L/V ratio always less than 2.5.

The log sheets will show the instrument readings at two-hour intervals for the parameters listed above for each production line for a 24-hour day. At the end of each day, a time-weighted mean L/V ratio for all operating strippers could be calculated and reported in place of the A_{ti} value previously reported for each day. As long as the values of L/V remain less than 2.5, the VCM content of the resin in the stripped varnish will be well below the 400 ppm maximum specified by the regulation.

Eventually, this data may be computerized, if this proposal is acceptable, so that the instruments provide continuous readout into a data concentrator which can provide hourly averages of all pertinent parameters, and conclude each shift and each day with the time-weighted average L/V values for all the lines for reporting purposes to establish compliance.

Your approval of this procedure is sought so that we may stop the costly and time consuming daily analytical activities now being performed and use our analytical talents and facilities for more meaningful results. Please direct your questions and comments to my attention. Thank you for your consideration.

Yours very truly,



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REFERENCES

1) Request for Change in Sampling and Analytical Program under part 61, NESHAP Regulation for Vinyl Chloride Monomer Control, letter to Mr. Howard Houston, TACB/Austin from J. F. Erdmann, UCC/Texas City, Jan. 21, 1980.

2) Evaluation of Alternative NESHAP Sampling Procedure for Vinyl Chloride (Method 107) communication to Diana Dutton, EPA/Region VI, Dallas from Don Goodwin, EPA/RTP, Emission Stds and Engring Div, Feb 19, 1981.

TABLE I

DESCRIPTION OF PROCESS STREAMS IN

VARNISH STRIPPING OPERATION

(REFER TO FIGURE 1)

Ⓐ Autoclave varnish to dilution tank.

Ⓑ Fresh acetone to dilution tank.

Ⓒ Fresh acetone to vaporizer to stripping still (also designated vapor feed = "V").

Ⓓ Overhead vapor from dilution tank to vent condenser.

Ⓔ Diluted varnish feed to stripping still (also designated liquid feed = "L").

Ⓕ Stripping still overhead vapor to vent condenser.

Ⓖ VCM and solvent vapor to monomer/solvent recovery system.

Ⓗ Reflux solvent to stripping still.

Ⓙ Stripped varnish to resin recovery system.

MATERIAL BALANCE - TYPICAL FOR NO. 2 or NO. 3 STRIPPING STILLS

Ⓔ	+	Ⓒ	+	Ⓓ	=	Ⓖ	+	Ⓙ	
16,855	+	10,655	+	1575	=	11,675	+	17,410	= 29,085

L/V RATIO = Ⓔ / Ⓒ = 1.58

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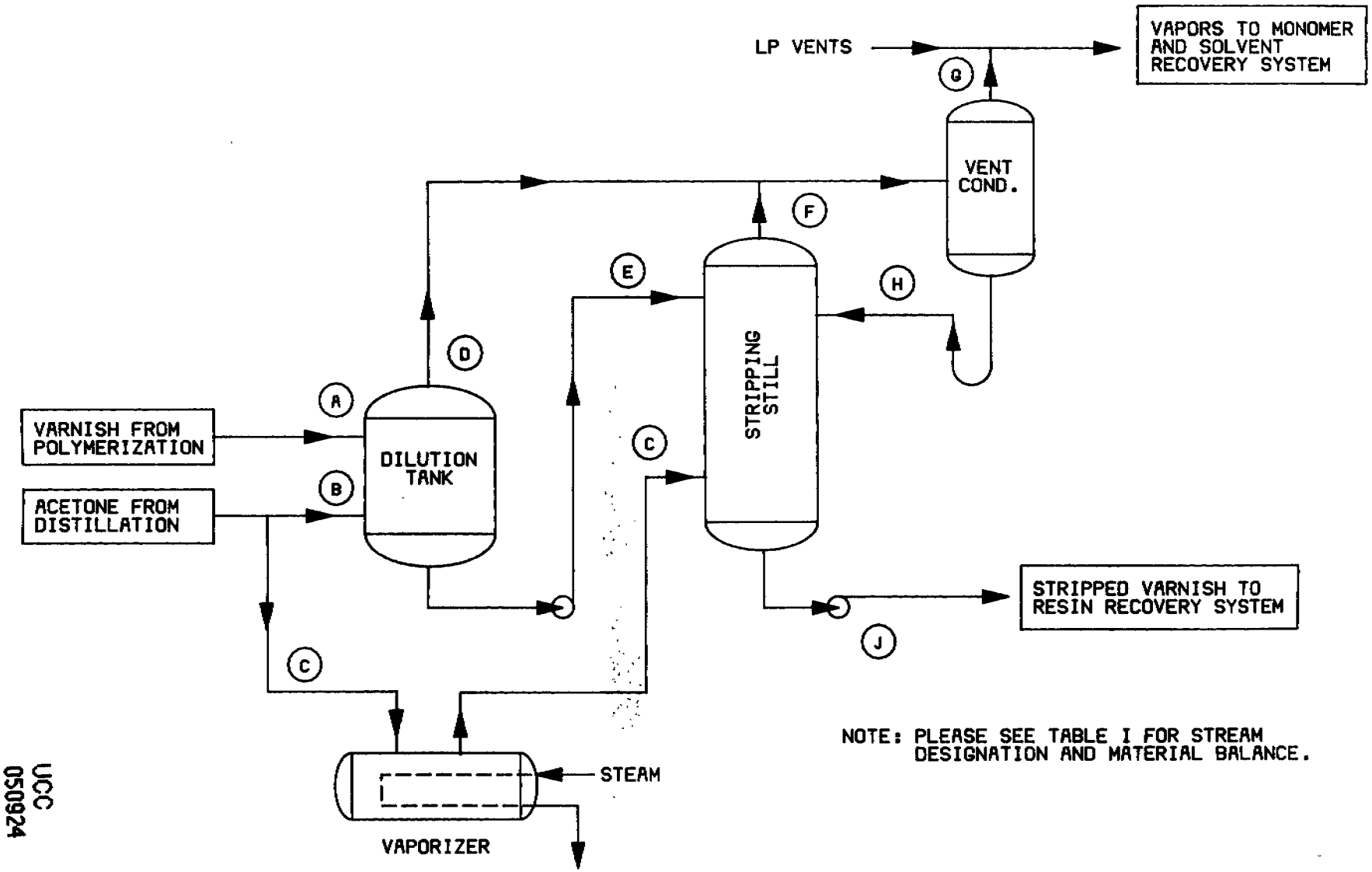
FIGURE 1
SOLUTION VINYL RESINS PROCESS
VARNISH STRIPPING STEP TO REMOVE
UNREACTED VINYL CHLORIDE MONOMER (VCM)



NOTE: PLEASE SEE TABLE I FOR STREAM DESIGNATION AND MATERIAL BALANCE.

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FIGURE 2

A_{t_x} = DAILY MAXIMUM VINYL CHLORIDE CONCENTRATION, 400 ppm

SOLUTION VINYLS STRIPPER OPERATION
CONTROL OF VINYL CHLORIDE MONOMER CONTENT IN STRIPPED RESIN BY L/V RATIO ADJUSTMENT

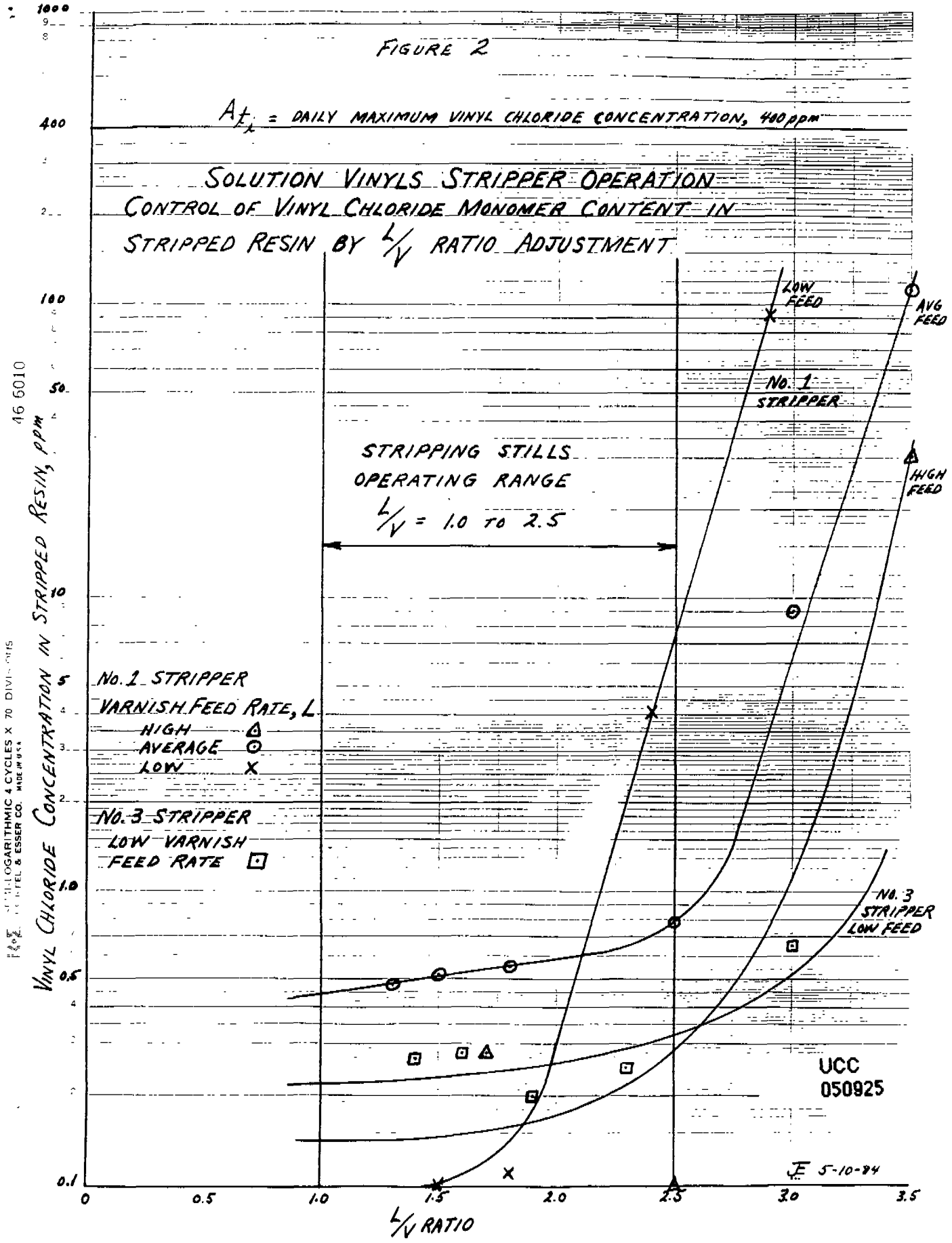

TABLE II

SEMIANNUAL REPORT DATA SUMMARY - MARCH 1981 THRU FEBRUARY 1984

Period	No.of Operating Days	Mean A_{ti} PPM VCM	Highest A_{ti} for Period	Comments
Sept. 83 - Feb 84	117	3.8	87	9 days over 10 ppm
March 83 - Aug 83	172	3.6	104	11 days over 10 ppm
Sept 82 - Feb 83	111	4.4	217	7 days over 10 ppm
Mar 82 - Aug 82	111	6.4	82	19 days over 10 ppm
Sept 81 - Feb 82	122	17.0	795*	34 days over 10 ppm
Mar 81 - Aug 81	180	5.9	62	25 days over 10 ppm

*Only day over 400 ppm, next highest day was 215, all other values for this six-month period were less than 90 ppm.

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TABLE III
VARNISH STRIPPING CALIBRATION TESTS

STRIPPING STILL	TYPE RESIN	VARNISH FEED RATE, L #/HR	VAPOR FEED RATE, V #/HR	L/V RATIO	STRIPPED VARNISH VCM CONC. (1) PPM
No. 1 48" Diam.	VYHH				
		HIGH RATE - △			
Date: 11-21-83	Time				
	7:50 am	27,000	15,500	1.7	0.28
	9:55 am	27,000	10,800	2.5	nil
	10:20 am	27,000	7,700	3.5	30.5
		AVERAGE RATE - ⊙			
Date: 11-16-83	11:55 am	22,000	17,000	1.3	0.48
	12:35 pm	21,700	14,500	1.5	0.52
	1:10 pm	21,700	12,000	1.8	0.55
	1:50 pm	21,700	8,700	2.5	0.79
	2:30 pm	22,100	7,200	3.0	9.00
	3:10 pm	21,000	6,000	3.5	112.00
		LOW RATE - X			
Date: 11-8-83	11:25 am	15,000	10,000	1.5	nil
	12:10 pm	14,500	8,000	1.8	0.11
	12:40 pm	14,500	6,000	2.4	4.12
	1:30 pm	14,500	5,000	2.9	93.40
No. 3 (42" Diam)	VMCC	LOW RATE - ⊡			
Date: 11-8-83	8:20 am	10,500	7,500	1.4	0.27
	12:00 n	10,500	6,500	1.6	0.28
	12:35 pm	10,500	5,500	1.9	0.20
	1:25 pm	10,500	4,500	2.3	0.25
	2:15 pm	10,500	3,500	3.0	0.66

(1) Dry resin basis, same as used to calculate A_{ti} daily weighted average.

TABLE IV
SOLUTION VINYL RESINS PROCESS
TYPICAL OPERATING PARAMETER VALUES

		STRIPPING STILLS			
Stripper No.		1	2	3	4
Stripper Column Diameter, Inches		48	42	42	36
I. Feed Rates					
A. Varnish = Liquid = Ⓔ					
Lb/Hr	Max	32,000	21,000	19,000	10,000
	Avg	25,000	18,000	18,000	7,000
	Min	8,000	8,000	8,000	5,000
B. Solvent Vapor = Ⓒ					
Lb/Hr	Max	21,000	14,000	14,000	8,000
	Avg	18,000	12,000	13,000	7,000
	Min	8,000	6,000	6,000	6,000
C. Ratio L/V = Ⓔ / Ⓒ Most likely operating ranges.					
	Max/Max	1.52	1.50	1.36	1.25
	Max/Avg	1.39	1.50	1.38	1.00
	Avg/Max	1.00	1.33	1.33	0.83
	Avg/Avg	1.78	1.75	1.46	1.43
	Avg/Min	0.44	0.67	0.62	0.71
	Min/Min	1.19	1.28	1.28	0.88

II. Still Columns, average base temperature:
63°C, All Columns, ± 3°C, Solvent boils at 56°C at 1 ATM.

III. Still Columns, average base pressure: 2 psig, All Columns.

IV. Column differential pressures, base to head, inches of H_2O.

Stripper	1	2	3	4
Diff. Press, Inches	30	70	70	40

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