D. R. Montgomery

February 23, 1976

Dr. W. R. Manning
Union Carbide Corporation
Chemicals and Plastics
P. O. Box 8361
S. Charleston, WV 25303

Dear Dr. Manning:

Enclosed is a copy of the report compiled by our Research Center on the recent tests of three Union Carbide PVC resin slurries.

As you will notice in the report, the only problem was in stripping the vinyl acetate copolymer. As I indicated on the phone to you last week, we would be willing to run another sample of copolymer adding defoamer to the slurry at the top of the column rather than in the feed tank. Recent experience has shown that addition of the defoamer at the top of the column works much better than when adding it to the slurry in the feed tank.

Please let me know if you wish to send another sample of slurry for evaluation. I am also enclosing a copy of this report to Mr. Peterson at your Texas City installation.

Thank you for your interest in this process, and we hope to hear from you soon regarding further tests or any other questions you may have.

Sincerely yours,

Arthur L. Hastings

ALH:gat
Enclosure
cc: Mr. A. Peterson

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Project 7716-75
December 28, 1975

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TECHNICAL SERVICE REPORT

STRIPPING TESTS ON UNION CARBIDE'S PVC RESIN SLURRIES IN THE 6-INCH DEVELOPMENT COLUMN

by

G. R. Huddleston and E. J. O'Connor

B. F. GOODRICH
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SUMMARY

Union Carbide, a potential licensee of B. F. Goodrich stripping technology, requested tests with three of their resin slurries to establish capability of the method and to provide stripped resin for their evaluation. One resin was a vinyl chloride homopolymer, one an ethylene-modified PVC and the third a vinyl acetate-vinyl chloride copolymer.

Both the homopolymer and the ethylene-modified resin were stripped in the 6-inch countercurrent steam stripping column at Brecksville under various operating conditions. Five-gallon samples from each run were sent to Union Carbide for their evaluation. The two resins were handled satisfactorily in the column at atmospheric pressure and at 8 psig. The homopolymer was reduced from 5,294 ppm in the cold feed to less than 3 ppm at 8 psig and to 11 ppm at 1.5 psig. The ethylene-modified resin was reduced from 4,475 ppm in the cold feed to about 10 ppm at 8 psig and to 54 ppm at 1.25 psig.

Two attempts were made to strip the vinyl acetate copolymer under vacuum at 170°F. When the slurry entered the column it formed a stable froth that did not flow through the downcomers but instead went overhead. One attempt was made with addition of a defoamer which helped the flow of slurry, but the particular defoamer used appeared to be antagonistic to the dispersant system and caused separation of the resin into agglomerates which stuck to column surfaces, leaving only clear serum to travel through the downcomers. The vinyl acetate resin and serum were severely discolored even at the low temperature of the feed tank (100-110°F) and the color increased in the column at 170°F.

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OBJECTIVE

To demonstrate capability of countercurrent column steam stripping of vinyl chloride from Union Carbide's PVC resin slurries in the 6-inch development column to assist in sale of Goodrich stripping technology.

CONCLUSIONS

Union Carbide's homopolymer and ethylene-modified PVC resin slurries can be readily stripped in a countercurrent steam stripping column at atmospheric pressure or higher. In a column with tray stripping rates equivalent to that of the development column, vinyl chloride could be reduced from 10,000 to 1 ppm in the homopolymer in about 11 trays at 8 psig and 16 trays at 1.5 psig. The ethylene-modified PVC is a little more difficult to strip and would require 16 and 21 trays respectively to reduce vinyl chloride from 10,000 to 1 ppm.

Union Carbide's vinyl acetate copolymer slurry forms a very stable froth under the vacuum conditions necessary to protect the resin from agglomeration. The stable froth did not flow through the column. A defoamer that is compatible with the dispersant system should allow column stripping.

INTRODUCTION

In 1974, B. F. Goodrich Chemical developed stripping technology for removal of vinyl chloride from PVC resin slurries by countercurrent steam in perforated tray columns. This development work was done in the 6-inch, 8-tray column at Brecksville and in the 30-inch, 17-tray column at Avon Lake Geon East. Results from the development were used for design of 54-inch, 20-tray columns which are now being installed at 5 BFG plants in the USA. Goodrich has offered the stripping technology for sale to the industry and several potential purchasers have visited Geon East to observe the 30-inch column in operation.

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Most of them have expressed an interest in having samples of their product stripped in the 6-inch column to demonstrate stripping capability and to provide stripped samples of their products for evaluation.

Union Carbide sent three 55-gallon drum samples, one each of a homopolymer, an ethylene-modified resin and a vinyl acetate copolymer. This report describes the tests and presents results.

RESULTS AND DISCUSSION

I. Equipment

The 6-inch column is made up of stainless steel, in line "bull's eye" sight glass sections obtained from the Ernst Gage Company. Perforated plate trays are installed between sections. The trays are stainless steel and are fitted with a 1-inch stainless steel tube to serve as a downcomer and a wier to hold 1-1/2" depth on the tray. This represents a holdup volume about .1734 gallons per tray and 1.3872 gallons total. Each tray has 17 holes 1/4" diameter on a 1-1/4" equilateral triangular spacing. Open area in the tray is about 3%. About 50 pounds per hour of steam is required to support the slurry on the trays without allowing excessive weeping. With the limited downcomer capacity, this results in a higher steam to resin requirement than needed for adequate stripping. In production equipment, 0.5 pound steam per pound of resin or less has been adequate.

Steam is added below the bottom tray at a rate controlled by manual setting of the valve and pressure control. Effluent from the bottom tray collects in a sump and is discharged on level control. Steam from the column is condensed and pressure in the column is controlled by manual setting of the discharge valve ahead of the condenser.

Feed slurry is heated in an agitated, closed slurry tank which is fitted with a circulating loop. Pressure in this tank is maintained several pounds higher than the column pressure. Feed to the column is provided by a flush mounted valve in the circulating loop. The valve is activated by a pulse timer to control feed rate. For smoothest operation, the feed slurry is heated to near the same temperature as the column operating point. Feed significantly lower in temperature causes some steam condensation and a temporary upset with each pulse.. As feed enters the column, there is a flash above the top tray so this tray does not receive the full

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vinyl chloride load as measured in the cold slurry. A more realistic value is the vinyl chloride level measured in a hot feed sample that is flashed to the atmosphere. This technique was used and both hot and cold feed values are reported.

Samples were also taken from trays 3, 6 and 8 and from the column discharge. Sample taps are flush with the tray surface.

After some evidence of resin discoloration from heat aging in the feed tank at column temperature, the procedure has been modified to reduce temperature in the feed tank to about 150°F. This procedure was used for all Union Carbide resins. To compensate for the condensation of steam by the cooler feed, somewhat higher steam rates were used. Steam rate for calculating steam/resin ratios was considered as that amount which the condenser received.

II. Analytical

A. Vinyl Chloride Measurement

Vinyl chloride content of the samples was determined at Avon Lake Plant Services Laboratory by Dot Lewis and John Whitney. Samples were sent to this lab in tightly sealed, 4-ounce glass bottles with electrical tape wrapped around the cap. Bottle contents were quickly reslurried and filtered in a Buchner funnel to remove most of the water. Samples of the wet cake were checked for total solids content and for vinyl chloride content by the head space method gas chromatography unit. Values were reported as ppm vinyl chloride in dry PVC resin by weight.

B. Resin Properties

Samples of each slurry were analyzed at Avon Lake Technical Center to determine average particle size, particle size distribution, inherent viscosity, porosity, average pore size and pore size distribution. These data are summarized in Table IV.

III. Column Operation

The sample drum contents are reslurried and transferred into the feed tank. Heat is then applied to the jacket to control slurry temperature near 150°F. Just before the run is started, circulation of slurry in the feed loop is started. Pressure in the feed tank is maintained several pounds higher than column pressure.

For each run the column is calibrated to establish condensate rate from heat loss to the atmosphere and steam rate for the two operating conditions chosen. About two hours are required for the column to reach steady conditions of condensate and steam flow. Steam pressure to the column is controlled at 70 psig by regulator. When the column conditions are steady, condensate from the bottom of the column is weighed to establish a rate and steam condensate from the condenser is weighed to establish a rate.

Feed is then started to the column by turning on the pulse timer. For control of feed rate the timer opens the valve for 1 second, then keeps it closed for 29, 44 or 59 seconds depending on the feed rate desired. Feed flashes as it enters the column and froths for a few seconds on the top tray and to a lesser extent on the second tray. Levels on the top two trays are high following the pulse, then the feed slowly works its way down the column. The effect of the pulse is dampened out by the two top trays and flow through the remainder of the column is quite smooth. Discharge from the column is steady with no evidence of the pulse.

After allowing time for about two passes through the column, collection of a 5-gallon sample of stripped slurry is started. This collection is made into an open pail directly from the column discharge. During this sample collection, the column effluent rate is determined by weighing the output for a specific time. Condensed steam is also weighed to determine a rate. By comparing these rates with the calibrated rates, a slurry feed rate is determined and the amount of steam condensed by the feed is also determined. After calibrations are established, samples are taken from the feed tank, trays 3, 6 and 8 and from the column discharge. Samples are taken into an open sample bottle, bottles are capped, then the cap is wrapped with electrical tape and sent to the laboratory for analysis.

When the 5-gallon sample collection is complete, the feed rate and/or column pressure are changed for the next run. After steady state is established, the above sampling procedures are repeated.

A theoretical residence time is calculated for each run. This calculation is made on a tray-to-tray basis considering that the tray receives all the slurry plus the steam condensed by the feed and that the condensate from heat loss to the atmosphere occurs equally on each tray. Volumes to the tray are corrected for composition and density. These residence times are theoretical and real values are somewhat less because the slurry is expanded by the passage of steam. In some calibration tests it has been estimated that the actual holdup volume is about 0.7 times

theoretical at the steam rates used. This factor will no doubt vary with type of dispersant, total solids and other conditions. The theoretical residence times should be adequate for relative comparisons. Accurat measurement of differential pressure between top and bottom of the column could be used to calculate a more accurate column holdup, but this has not been applied to the 6-inch column. It was used for estimates in the 30-inch column.

IV. Operating Data and Analytical Results

A. Homopolymer Resin QSAN

Contents of the drum were reslurried and loaded to the feed tank on November 4, 1975. Solids content of the slurry was 33.7%. Runs were made at 8 psig, 236°F using two feed rates and at 1.5 psig, 216°F. At 236°F vinyl chloride content was reduced from 5,294 ppm in the cold feed to less than 2 ppm. At 216°F vinyl chloride content was reduced to 11 ppm and it is projected that another three trays would have reduced the level to 2 ppm. Data from these runs are shown in Table I. Figure 1 shows a log plot of vinyl chloride content against tray number. Figure 1A shows a similar plot against residence time in minutes. In both plots the effluent values were considered as having occurred after one additional tray.

B. Ethylene-modified Resin QSQH

A first attempt was made to strip this sample on November 6, 1975. Shortly after feed was opened to the column, the feed pump motor threw the breaker and the circulating loop plugged. The slurry was cooled and returned to the drum. The column and lines were cleaned and other stripping tests were carried out.

Another attempt was made on November 20, 1975 but again the pump failed to handle the slurry and the lines plugged before feed was established to the column. The slurry was cooled and left in the feed tank while the lines were cleaned.

A third attempt was made November 21, 1975 and it was successful. Before opening the feed tank to the pump, the circulating loop was filled with water to establish a good flow, then when feed was opened to the pump, it was able to handle the slurry. Slurry as loaded to the feed tank had a solids content of 23.8%.

Runs were made at 8 psig, 236°F using two feed rates and at 1.25 psig, 214°F. At 236°F, vinyl chloride was reduced from 4,475 ppm

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in the cold feed to 10-25 ppm. At 214°F, vinyl chloride content was reduced to 54 ppm, and it is projected that five more trays would have been needed to reach 10 ppm. Data from these runs are shown in Table II, Figure 2 and Figure 2A.

C. Vinyl Acetate Copolymer VSJE

This slurry was loaded to feed tank on November 13, 1975. As loaded, the slurry and serum were colorless but after heating to about 105°F, the serum was yellow to orange and after feeding to the column at 170°F, the color of the resin and serum became deep orange colored.

A run was attempted at a 17-inch Hg vacuum. When the slurry entered the column it formed a stable froth which did not flow down the column properly. The froth stayed on the trays and there was some agglomeration which plugged downcomers. Feed was discontinued and the column was cleaned.

Another attempt was made on November 14, 1975, and the same results were observed. The heavy froth built up on the top tray and carried over to the condenser as feed was continued. A defoamer was added to the feed tank and appeared to help break the froth to some extent. More was added and flow started through the column, but the resin agglomerated and separated from the serum, leaving clear serum flowing through the column and resin clinging to the column surfaces. It appeared that the defoamer was antagonistic to the dispersant system. Another possible explanation was that the cloud point of the dispersant had been exceeded but contact with Union Carbide revealed that the cloud point was well above 212°F.

Union Carbide suggested one of their specific defoamers but none was available in the area.

About 15 gallons of the vinyl acetate slurry is retained at Brecksville. This is enough to make a run with Union Carbide's defoamer added if further tests are desired.

V. Discussion of Results

From Figures 1 and 2, equations of the type $C = C_o e^{-AN}$ were derived. C represents the predicted vinyl chloride content in ppm at tray N when starting with a feed containing C_o ppm. The slope of the line is -A, and this value can be considered a rate of stripping factor. Similarly, from Figures 1A and 2A, equations of the type $C = C_o e^{-Bt}$ were

derived. In these equations -B is the slope of the line and t is the residence time in minutes. A and B are related by equations of the type:

$$B = \frac{A(8)}{t(\text{for 8 trays})} .$$

By using these equations, the number of trays or time required t strip slurry from one level of vinyl chloride to any other level can be estimated. In using these equations, C_o should be taken as the vinyl chloride content actually received by the top tray. In the absence of an actual sample measurement from this tray, it is necessary to make an estimate. When feed enters the column, there is a significant flash of vinyl chloride as the slurry falls to the top tray. The degree of this flash is dependent on the temperature of the feed and the vinyl chloride content. For all these tests the C_o or hot feed value was determined by allowing a sample of the heated feed slurry to flash to the atmosphere. In most cases these values fit the plot quite well. Another way to estimate the C_o is by backward extrapolation of the lower tray results. From the figures it can be noted that there is appreciable scatter of the data. There was some loss of vinyl chloride from small leaks in the system. To minimize the effect of this on the data, a hot feed sample was taken at the same time that other samples were taken from the column.

When two feed rates are used under the same operating conditions, data from the two runs in most cases yield a line with essentially the same slope when plotted against tray number. When plotted against time, the fast feed rate data usually has a steeper slope indicating faster stripping at faster feed rates. These factors indicate that the number of trays is the controlling factor and not the residence time. Similar data were obtained during development work with the 30-inch, 17-tray column. Obviously some minimum residence time is required for diffusion of the vinyl chloride from the particles and this time is quite short at temperatures over 200°F. Once the minimum time is exceeded, allowing more time has little effect on increased vinyl chloride removal.

Analytical data from samples taken on tray 3 tend to fall below the line. This can probably be explained by considering the operating characteristics of the development column. Feed is added by a pulse value which is open for 1 second, then closed for 29, 44 or 59 seconds depending on the feed rate desired. The size of the slug of feed depends on pressure differential across the valve from feed pump to the column. The slug of feed enters the column, flashes and falls to the top tray where it is heated to column temperature. This tray is flooded at this time and the level gradually decreases until the next slug enters. Tray 2 is also

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flooded as the top tray dumps but from this point down the column the levels are steady. The pulse effect is dampened out by the first two trays and flow discharge further down the column is steady with no indication of a pulse in tne effluent discharge from the bottom tray. Because of higher levels and longer time on the two top trays plus heat up of th feed the results as analyzed on tray 3 samples are lower than would be achieved if feed were steady.

Ideally, a steady feed should be provided for the development column, but it is quite difficult to handle low volumes of fast settling slurry. The pulse feed was chosen as a compromise and since data from the small column correlate very well with those from the 30-inch column, the pulse feed method is considered adequate for development tests.

Rate factors obtained from the figures are listed in Table IV. From these rate factors, the number of trays needed to accomplish reduction of vinyl chloride from C_o to C can be estimated by:

$$N = \frac{-\ln C/C_o}{A}$$

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Column Operating Data

Resin	Table I Homopolymer QSAN			Table II Ethylene-modified PVC QSQH			Table III Vinyl Acetate Copolymer VSJE
Identification Number	1104A	1104B	1104C	1120A	1120B	1120C	1113
Run Number	8	8	1.5	8.5	8.25	1.25	17-inch Hg vacuum
Column Pressure, psig	236	236	216	236	235	214	170
Bottom Temperature, °F	45	60	60	45	60	60	run unsuccessful
Seconds between Pulses	108.1	91.9	105.5	99.5	78.7	87.0	
Feed, #/hr.	---------33.7---------			--------- 23.8 ---------			
Slurry, % Solids	36.43	30.97	35.55	23.68	18.73	20.71	
Resin, #/hr.	51.9	53.1	57.8	50.3	51.3	57.3	
Steam, #/hr.	1.42	1.71	1.63	2.12	2.74	2.77	
Steam/Resin Ratio	151	153	154	136	144	145	
Feed Temperature, °F							
RVCM, ppm, Cold Feed	---------5294----------			--------- 4475 ---------			
RVCM, ppm Hot Feed*	3119	3593	2250	2911	2483	2187	
RVCM, tray 3	69	174	445	452	381	402	
tray 6	14	9	67	64	53	132	
tray 8	3	1.4	11	31	14	64	
effluent	2.6	1.5	11	27	9	54	
Residence Time, minutes							
tray 3	2.26	2.64	2.40	2.02	2.43	2.39	
tray 6	4.39	5.10	4.68	3.94	4.70	4.67	
tray 8	5.74	6.66	6.14	5.16	6.14	6.12	
effluent**	6.41	7.43	6.86	5.77	6.86	6.84	
Condensate Calibration, #/hr.	17.7	17.7	14.9	17.9	17.9	14.8	
Steam Condensed by Feed, #/hr.	7.4	6.2	4.7	7.2	6.2	4.6	

*The hot feed sample was flashed to the atmosphere.

**Residence time for effluent is considered as one more tray than tray 8.

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TABLE IV

Summary of Union Carbide's Resin Properties and Stripping Rates

Resin Identification Number	Homopolymer QSAN			Ethylene-modified PVC QSQH			Vinyl Acetate Copolymer VSJE
				7.2 % ethylene			17.2% vinyl acetate
Inherent Viscosity	0.957			0.715			0.466
Porosity	0.259			0.161			0.030
Average Particle Size, μ	184			200			131
Particle Size Distribution, %	30.52			42.53			44.08
Average Pore Size, μ	0.71			0.82			0.706
Pore Size Distribution, %	5.18			9.38			87.53
Run Number	1104A	1104B	1104C	1120A	1120B	1120C	1113
Stripping Temperature, °F	236	236	216	236	235	214	170°F
Feed Rate, #/hour	108.1	91.9	105.5	99.5	78.7	87.0	run unsuccessful
Rate Factor, A	.869	.973	.595	.562	.626	.435	
Rate Factor, B	1.193	1.155	.780	.868	.820	.554	

Dec mber 28, 1975

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Figure 1

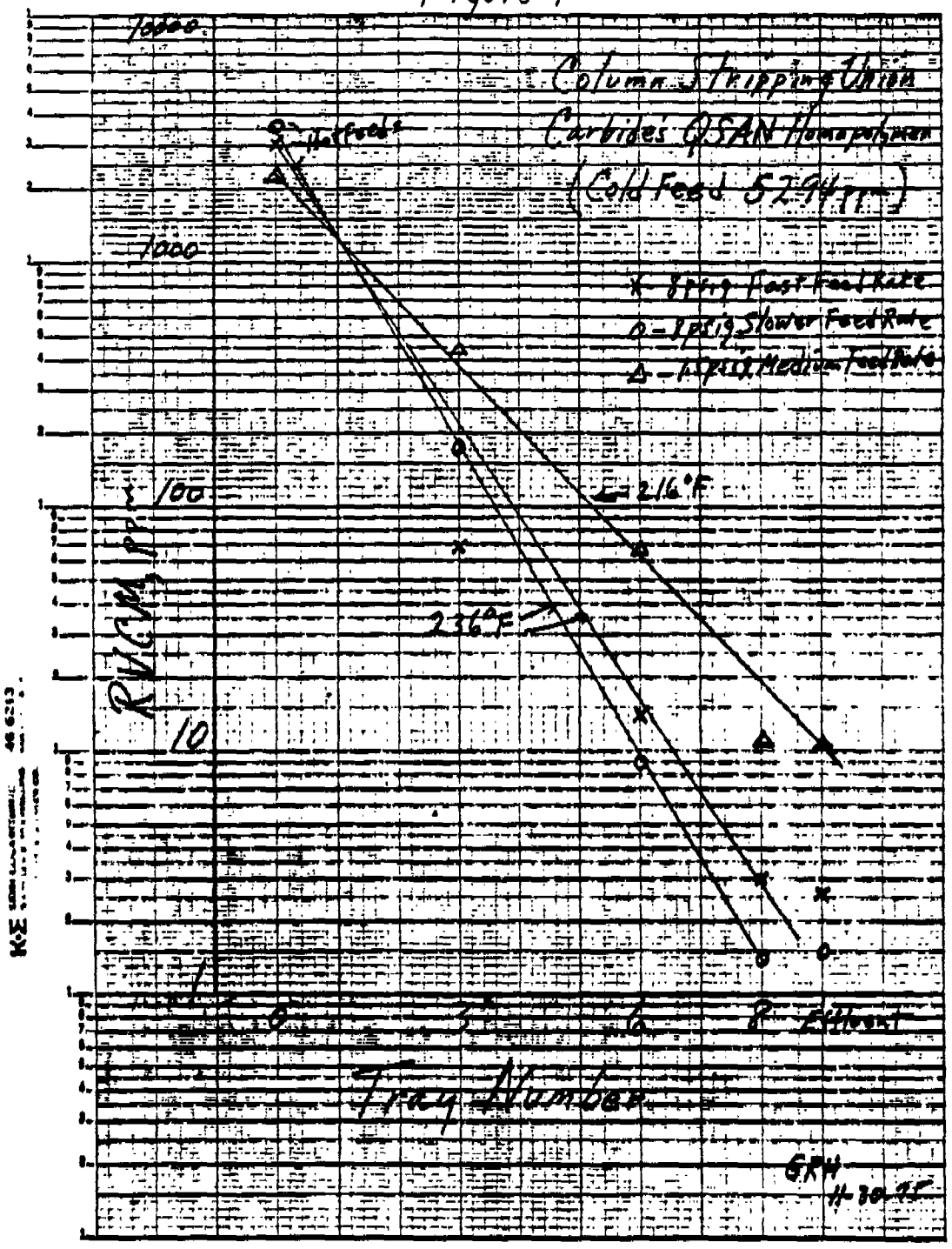

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Figure 1A

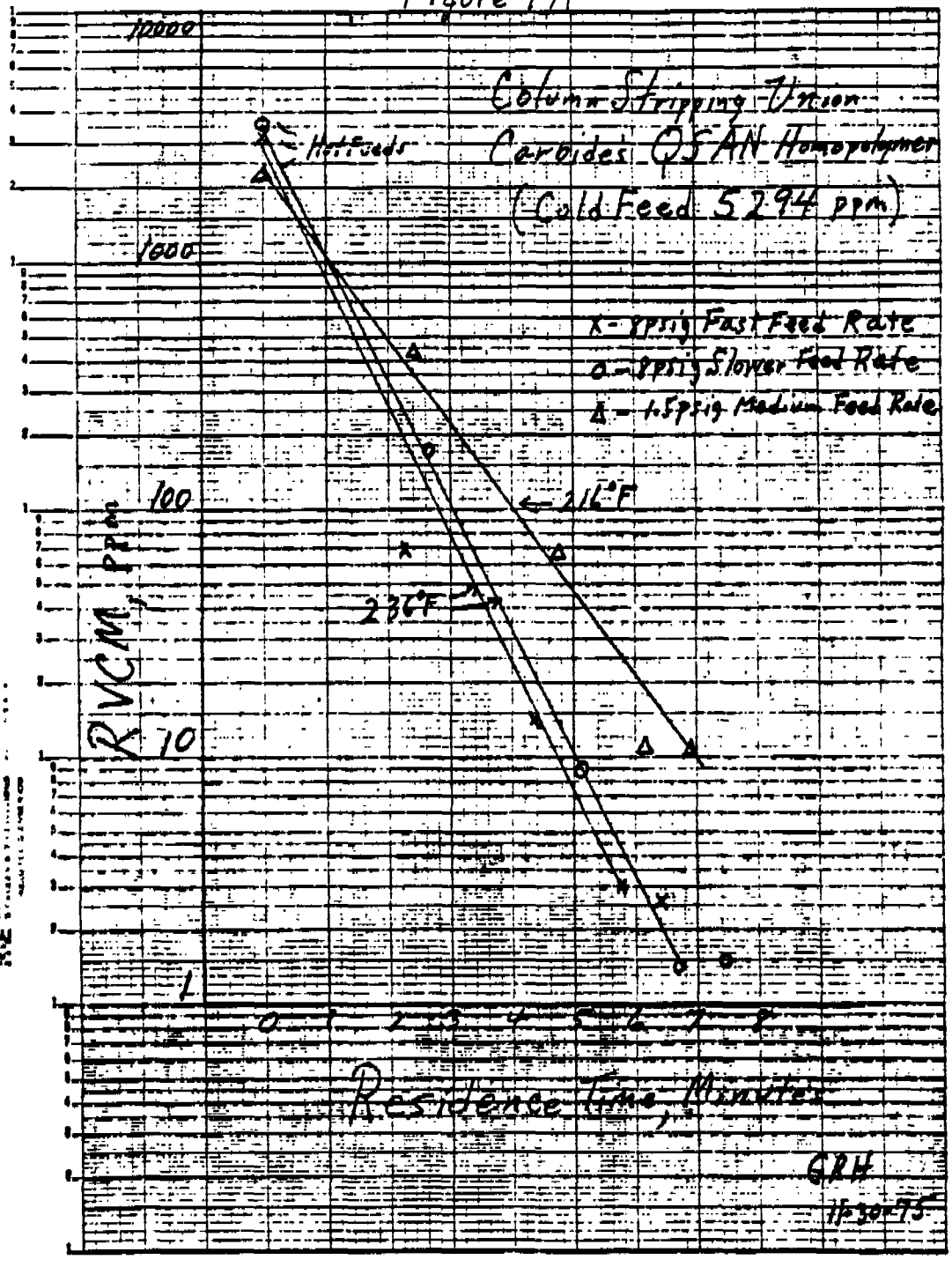

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Figure 2

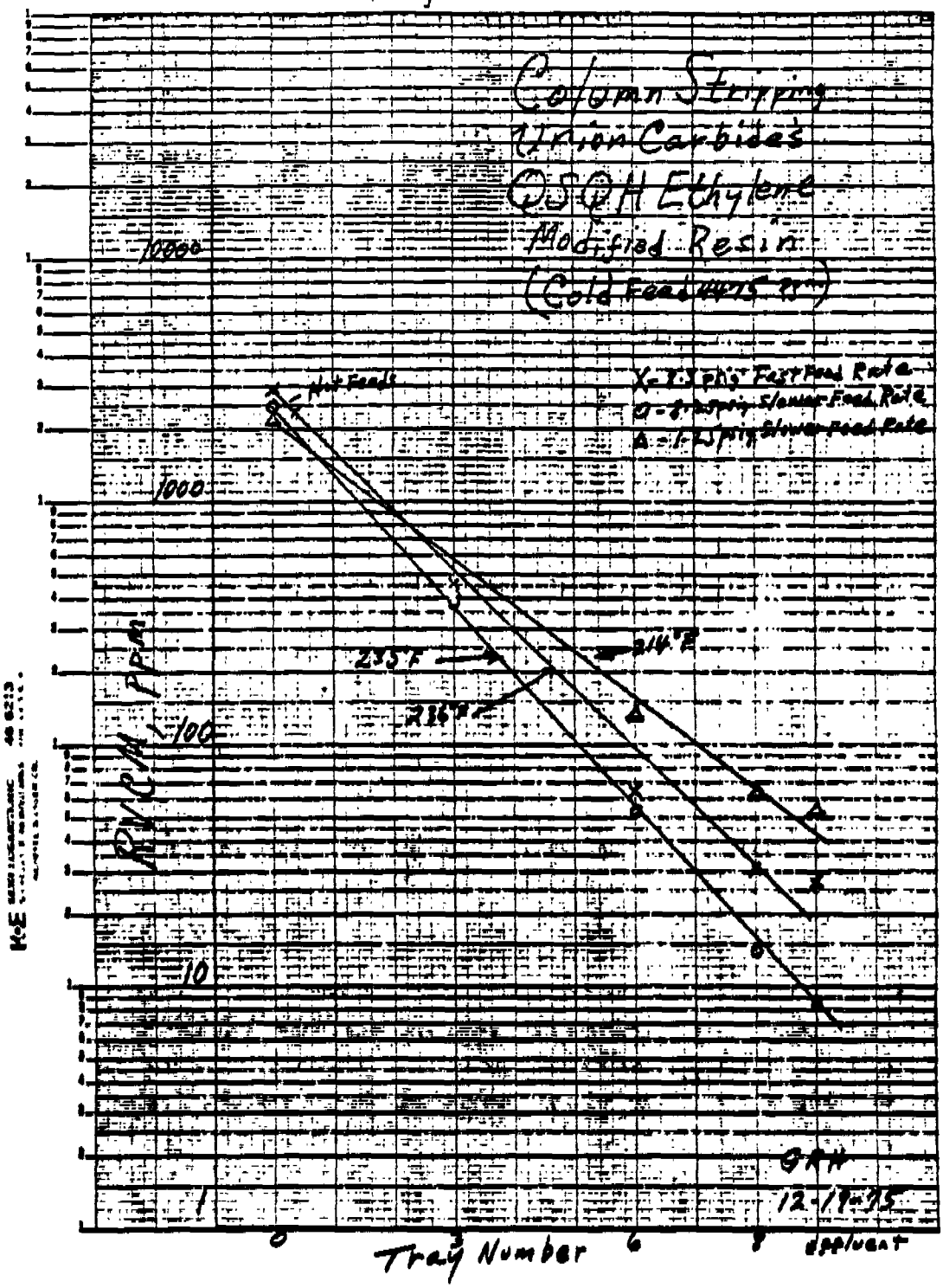

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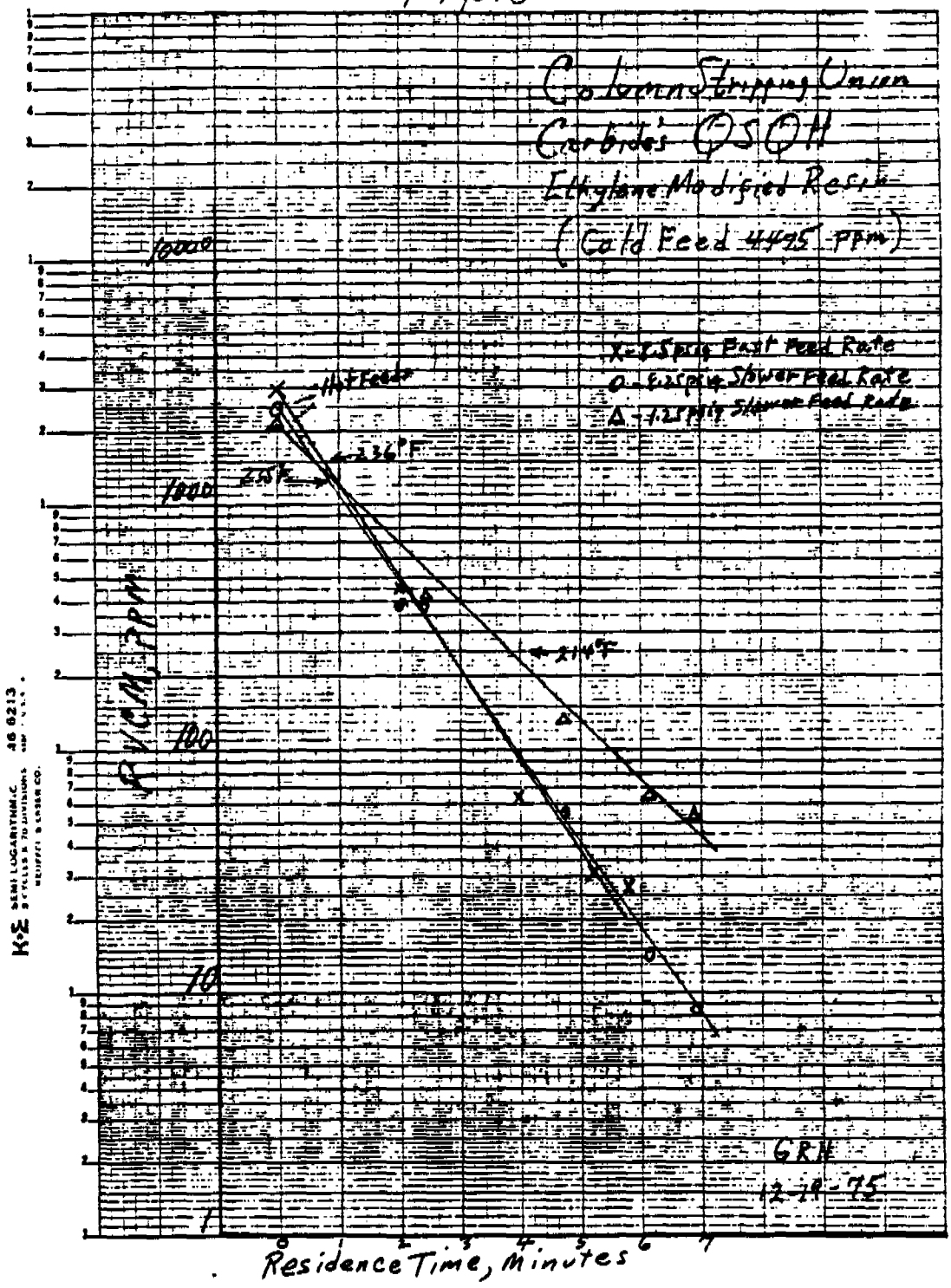
Figure 2A



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