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41726

**STRIPPING TESTS ON DIAMOND SHAMROCK'S
PVC RESIN SLURRIES IN THE 6-INCH
DEVELOPMENT COLUMN**

by

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

21486001

BFG14358

Project 7716-5
October 6, 1975

Stripping Tests on Diamond Shamrock's PVC Resin Slurries
in the 6-inch Diameter Development Column

by

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

SUMMARY

Diamond Shamrock, 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. The three resins were: a low molecular weight homopolymer with 0.10 porosity, a high molecular weight homopolymer with 0.22 porosity; and a vinyl acetate copolymer.

These resin slurries were stripped in the 6-inch countercurrent steam stripping column at Brecksville under various operating conditions and 5-gallon samples of stripped slurry from each run were sent to Diamond Shamrock. Residual vinyl chloride data were also provided.

The vinyl acetate copolymer handled satisfactorily at 180°F under vacuum but at a low stripping rate. Under less vacuum at 200°F, there was significant agglomeration of the resin particles. Successful stripping at 180°F would require a column with more trays or multipasses through the short column.

The two homopolymer resins handled satisfactorily at atmospheric pressure and at 8 psig, but there was some evidence of resin discoloration. Part of this may be caused by iron contamination from the steel shipping drums since the polyethylene liners were broken in all shipments, but it appears that the Diamond Shamrock resins are more heat sensitive than other resins that have been stripped in the column. Discoloration was avoided in retests by going to a lower temperature on the feed slurry tank.

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OBJECTIVE

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

CONCLUSIONS

Diamond Shamrock's low molecular weight homopolymer resin can be reduced from 5000 ppm to less than 10 ppm in one pass through the column at 8 psig if the feed is preheated to column operating temperature. When feed was heated only to 135-150°F, the vinyl chloride was reduced to 15 ppm in one pass. At atmospheric pressure, the resin was stripped to 20 ppm in one pass with the higher feed temperature but only to 150 ppm at the lower feed temperature. Adequate stripping can be attained by using a column with more trays.

The high molecular weight homopolymer was readily stripped to less than 10 ppm at atmospheric pressure even with low preheat to the feed.

The vinyl acetate copolymer was handled satisfactorily without agglomeration under vacuum at 180°F, but the stripping rate was slow. It is projected that 33 trays would be required to reduce the vinyl chloride to less than 10 ppm at 180°F. Stripping rate was doubled at 200°F, but there was significant particle agglomeration and plugging of the downcomers.

Stripping rates of Diamond Shamrock homopolymers are comparable to those of B. F. Goodrich resins having similar molecular weight and porosity.

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

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60-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. 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.

Diamond Shamrock sent 55-gallon drum samples of three of their slurries for testing. 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 CAGE 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 wiper to hold $1\frac{1}{2}$ " depth on the tray. This represents a holdup volume about .1734 gallons per tray and 1.3872 gallons total. Each tray has 17 holes $\frac{1}{4}$ " diameter on a $1\frac{1}{2}$ " 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 pounds 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 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 rather severe discoloration in the resin during the first run with the low molecular weight homopolymer when feed was heated to column operating temperature, heat on the feed slurry tank was reduced to 135-150°F for the remaining runs. To compensate for steam condensation on the top tray, 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

Diamond Shamrock reported the following data for the three products.

Diamond Shamrock Resins

Drum Number Resin Type	3A, 3B Homopolymer	4, 4B Homopolymer	5 Vinyl Acetate Copolymer (14% Vinyl Acetate)
Inherent Viscosity	0.7	1.35	0.59
Porosity	0.1	0.22	--
% Retained on 100 mesh	20	47	46
% Through 200 mesh	8	2	trace
Residual Vinyl Chloride	3,000-10,000 ppm	6,300 ppm	3,000 ppm

III. Column Operation

Before adding feed to the column, it is allowed to reach equilibrium with the atmosphere with steam flow at the desired rate. A portion of the steam condenses because of heat loss and the condensate discharges from the bottom of the column. The condensate rate is measured. Steam passing through the column is condensed and the rate measured. When feed is started, new measurements are taken. The effluent rate less the original condensate is the feed rate. Corrections to this value are needed if either condensation or evaporation results from the entering feed. This correction is determined by the difference in steam condensate from the condenser before and after feed is started.

Residence time in the column was estimated tray by tray, assuming that the condensate occurs equally on each tray. Volumes of the feed plus condensate were calculated with consideration of densities of the components. True residence time is somewhat less than the calculated values because contents on the trays are frothed by the steam. Use of the residence times for relative comparisons should be acceptable.

After sufficient time for steady state operation to be established, samples were taken from trays 3, 6 and 8 and from the effluent. Five gallons of the stripped slurry from each run were collected and sent to Diamond Shamrock for their evaluation.

IV. Operating Data and Analytical Results

A. Low Molecular Weight Homopolymer

Drum 3B was selected for testing since it contained more vinyl chloride than 3A. The contents of the drum were reslurried and loaded into the feed tank at 32.4% total solids. Slurry was received in a steel drum with thin polyethylene liners which leaked some and were completely destroyed by the agitator during loading to the feed tank. As a result, there was some contamination with iron. The slurry was heated to 220°F in the feed tank and samples showed significant resin discoloration before feeding to the column. Discoloration was not increased by passing through the column, but it did increase with time in the feed tank.

Runs were made at 8 psig, 235°F and two feed rates. Vinyl chloride level was reduced to less than 10 ppm in each run. A third run was made at 2.5 psig, 221°F and vinyl chloride was reduced to 18 ppm under these conditions. Data from these runs are shown in Table I. Figure 1 shows log VCM content plotted against tray number and Figure 1A shows the same values plotted against residence time. In both cases, the effluent values were considered as occurring after one additional tray.

Because of the discoloration, it was decided to make similar runs with drum 3A but to heat the feed to a lower temperature, about 135°F. Under these conditions, vinyl chloride was reduced to 16 ppm at 8 psig, 234°F at a normal feed rate but only to 72 ppm under the same conditions at a very fast feed rate. At 1.75 psig, 216°F the vinyl chloride was reduced to 148 ppm at a normal feed rate. With feed at 135°F, it is projected that 13 trays would be needed to reach 10 ppm at 8 psig and the fast feed rate and 10 trays at the normal rate. At 1.75 psig, 17 trays would be needed.

The contents of drum 3A also got some contamination from the drum. Discoloration was not evident in the stripped resin, but the serum had some discoloration, possibly from contamination by other use of the column.

Data for the three runs are shown in Table I and Figures 2 and 2A.

B. High Molecular Weight Homopolymer

The contents of drum 4 were reslurried and loaded into the feed tank at 28.9% solids. Some contamination from the drum occurred because of broken liners. When loaded to the slurry tank, the serum was essentially colorless, but after heating to 145°F, it became bluish-gray, but the resin

did not appear discolored. Color of the serum after stripping was about the same as that of the warm feed.

Two runs were made at 8 psig, 235°F at different feed rates and one run at 2 psig, 217°F. In all three runs, the vinyl chloride content was reduced to 5 ppm or less. Data for the three runs are shown in Table II and Figures 3 and 3A.

Contact with Diamond Shamrock indicated that the serum discoloration was unexpected so they sent another drum of material labeled 4B for additional tests. This sample was in a fiber drum with polyethylene liners. Contents of the drum were loaded to the feed tank at 30.2% total solids.

Two runs were made at 5 psig, 235°F at different feed rates and one run at 1.75 psig, 216°F. In all three runs, the vinyl chloride content was less than 0.6 ppm. The feed contained only 684 ppm compared to 4038 ppm for drum 4, so the lower levels are as expected. Data for the three runs are shown in Table II and Figures 6 and 6A.

There was no discoloration in serum or resin so it is concluded that the color formation in drum 4 was caused by trace contamination left in the feed tank when used in other service.

C. Vinyl Acetate Copolymer

The contents of drum 5 were reslurried and loaded into the feed tank at 37% total solids. Some contamination from the drum occurred. Slurry was heated to 145-150°F and fed to the column which was under vacuum to keep temperature low. Two runs were made at a 13-inch vacuum, 180°F and different feed rates. Another run was made at a 6-inch vacuum, 200°F. The resin handled with no difficulty at 180°F, but there was significant agglomeration of particles at 200°F. The agglomerates plugged the downcomers which have fairly narrow clearance from the plates. At 180°F vinyl chloride content was reduced to about 400 ppm at the faster rate and 300 ppm at the slower rate. From the data it is estimated that 30 to 40 trays would be required to reduce the vinyl chloride content to 10 ppm at 180°F. This could be achieved by two passes through a 20-tray column. At 200°F, 18 trays would be required, but this temperature is apparently too severe for the copolymer resin particles.

Data for the three runs are shown in Table III and Figures 4 and 4A.

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V. Discussion of Results

From Figures 1, 2, 3, 4 and 6, equations of the type $C = C_0 e^{-AN}$ were derived. C represents the predicted vinyl chloride content in ppm at tray N when starting with a feed containing C_0 ppm. The slope of the line is -A, and this value can be considered a rate of stripping factor. Similarly, from Figures 1A, 2A, 3A, 4A and 6A, equations of the type

$C = C_0 e^{-Bt}$ 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 the equation: $B = \frac{A(8)}{t \text{ (for 8 trays)}}$.

By using these equations, the number of trays required to strip slurry from one level of vinyl chloride to any other level can be calculated. In using these equations, C_0 should be taken as the vinyl chloride content actually received by the top tray. 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. For these tests the C_0 or hot feed value was determined by allowing a sample of the heated feed to flash to the atmosphere. It became apparent during these tests that in most cases the hot feed vinyl chloride content decreased, apparently from leaks in the feed tank. For later runs, a hot feed sample was taken during the actual run. This was done for drums 3A, 4B and 5 but not for 3B and 4. For drums 3B and 4, the hot feed content was estimated by extrapolation of the tray data.

When two feed rates are used under the same operating conditions, data from the two runs give a line with essentially the same slope when plotted against tray number. This indicates 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. This is demonstrated in the fast feed rate run with drum 3A where the slope of the line is significantly different from that at the slow feed rate. The very fast feed rate apparently did not allow sufficient time for monomer diffusion.

In many of the plots, the vinyl chloride content as measured for tray 3 falls well below the line. This can be explained by considering the operating characteristics of the column. Feed is added by a pulse valve which is open for 1 second, then closed for 44 or 59 seconds, depending on feed rate desired. The size of the pulse depends on pressure differential

between the column and the feed pump discharge. As a result, the first tray receives a slug of feed which gradually works its way down the column. When the feed is significantly colder than operating temperature there is considerable frothing and holdup on the top tray and often the second tray to a lesser extent as the feed heats to operating temperature. Often the trays barely recover before the next pulse. This results in more residence time on the top two trays than that estimated from the normal level. In addition, the heating of the feed removes appreciably more vinyl chloride than would be achieved if the feed were already at the operating temperature. These factors cause the analytical values at tray 3 to be below the operating line. In production equipment where a steady feed rate is achieved and the feed can be heated in line to the column, this problem is eliminated. Ideally a steady feed should be provided for the development column but it is extremely difficult to handle the 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.

The pulse effect is dampened out by the first two trays and flow discharge from trays further down the column is fairly steady with no indication of a pulse in the effluent from the bottom tray.

Rate factors from the ten figures are listed for comparison.

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<u>Polymer</u>	<u>Stripping Temperature, °F</u>	<u>Slurry Rate lbs./hr.</u>	<u>-A</u>	<u>-B</u>
Low Molecular Weight Homopolymer	235	99.5	0.674	0.787
Drum 3B	235	65.8	0.672	0.566
	221	76.1	0.377	0.360
Drum 3A	234	162.9	0.473	0.935
"	234	74.3	0.598	0.592
"	216	85.4	0.343	0.389
High Molecular Weight Homopolymer	235	110.1	0.872	1.228
Drum 4	235	100.6	0.868	0.978
	217	108.7	0.589	0.813
Drum 4B**	235	73.5	1.151	1.093
"	235	58.0	1.151	0.984
"	216	65.3	0.895	0.876
Vinyl Acetate Copolymer	180	97.5	0.119	0.125
Drum 5	180	85.5	0.147	0.150
"	200	101.8	0.266	0.302

**This resin shows much faster rate on a tray basis than Drum 4.

The A rate factors are plotted against stripping temperature in Figure 5. This plot shows the high molecular weight homopolymer with high porosity to be much faster stripping than the low molecular weight lower porosity resin. To obtain comparable rates, the low molecular weight resin must be stripped at about 20°F higher temperature. Stripping rate for the vinyl acetate copolymer is intermediate between the two but at a safe temperature of 180°F the rate is very slow, requiring more trays or multipasses through the shorter column.

Once stripping rates are established, the number of trays needed to accomplish reduction of vinyl chloride from C_0 to C can be estimated by:

$$N = \frac{-\ln C/C_0}{A}$$

VI. Comparison of Diamond Shamrock Stripping Rates with B. F. Goodrich and Air Products' Resins

Rate factors derived for several BFG resins from earlier data in the 6-inch and 30-inch columns and for Air Products' resins in the 6-inch column are listed for comparison in the following table:

<u>Resin</u>	<u>Porosity</u>	<u>BFG Stripping Temperature, °F</u>	<u>Rate Factors (A)</u>	
			<u>6-inch column</u>	<u>30-inch column</u>
103EPF76	0.12	214-217	0.415*	0.365*
103EPF76	0.12	231-237	0.550*	0.486*
105EP	0.05	215-220	-	0.118*
105EP	0.05	225-237	-	0.165*
102EPF3	0.30	216-218	-	0.525*
102EPF3	0.30	236-237	-	0.820*

*average of several values

<u>Air Products</u>				
Homopolymer	0.10	220	0.384	-
0.85 L.V.	0.10	236	0.602	-
Propylene modified Resin, 0.627 L.V.	.093	217-218	0.491	-
Vinyl Acetate	.035	180	0.148	-
Copolymer, 16.4%	.035	200	0.285	-
Vinyl Acetate, 0.564 L.V.	.035	217	0.415	-

<u>Diamond Shamrock</u>				
Homopolymer	0.1	216-221	0.360, 0.389	-
0.7 L.V.	0.1	234-235	0.598, 0.673	-
Homopolymer	0.22	216-217	0.589, 0.895**	-
1.35 L.V.	0.22	235	0.870, 1.151**	-
Vinyl Acetate				
Copolymer, 14%		180	0.147	-
Vinyl Acetate, 0.59 L.V.		200	0.266	-

**The resin in Drum 4B stripped much faster than that in Drum 4 when evaluated on a tray basis.

These data show comparable rates between the Air Products and Diamond Shamrock resins at 0.1 porosity with F76. Diamond Shamrock's resin at 0.22 porosity strips at a rate comparable to F5. The two vinyl acetate copolymers show very similar rates and at a safe temperature of 180°F, they strip at a rate near the same as 105EP does at 237°F.

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Table III
Vinyl Acetate Co-
polymerization

Run	Down Number	Monomer, 9.7 L.V., 0.1 Porosity	3A	Monomer, 1.35 L.V., 0.22 Porosity	4B	Monomer, 1.35 L.V., 0.22 Porosity	5
Column Pressure, psig	0	0	0	0	0	0	13"
Bottom Temperature, °F	236	236	234	235	235	235	13"
Feed, pounds/hour	99.5	66.6	76.1	162.9	74.3	86.4	180
Slurry, % Solids	-	32.4	-	-	31.04	-	200
Booth, pounds/hour	32.7	21.3	24.7	56.6	23.1	26.5	97.5
Steam, pounds/hour	54.5	54.6	57.0	48.5	55.8	58.7	85.5
Steam/Booth Ratio	1.69	2.54	2.31	0.96	2.42	2.22	101.8
Feed Temperature	217	219	219	133	133	127	-
R.VCM, ppm, Cold Feed	-	5664	-	-	4882	-	-
R.VCM, ppm, Hot Feed Flashed	2269	8000	6460	3581	3440	3300	-
R.VCM, ppm, tray 3	199	00	00	637	254	845	-
R.VCM, ppm, tray 6	26	11	47	163	78	364	-
R.VCM, ppm, tray 8	10	3	30	80	24	157	-
R.VCM, ppm, Effluent	10	2	18	72	16	148	-
Reaction Time, minutes, tray 3	2.49	3.96	3.51	1.52	3.22	2.92	-
" " " " " " " "	5.19	7.54	6.77	2.99	6.21	5.67	-
" " " " " " " "	6.78	9.74	8.81	3.94	8.99	74.2	-
" " " " " " " "	-	-	-	5.77	6.29	6.04	-
" " " " " " " "	-	-	-	4.40	4.81	4.60	-
" " " " " " " "	-	-	-	2.27	2.48	2.36	-
" " " " " " " "	-	-	-	0	5	6	-
" " " " " " " "	-	-	-	122	206	206	-
" " " " " " " "	-	-	-	3253	-	-	-
" " " " " " " "	-	-	-	684	-	656	-
" " " " " " " "	-	-	-	13.8	3.75	32.7	-
" " " " " " " "	-	-	-	0.47	0.65	1.45	-
" " " " " " " "	-	-	-	0.08	0.04	0.53	-
" " " " " " " "	-	-	-	6.3	0.1	0.52	-
" " " " " " " "	-	-	-	3.18	3.94	3.73	-
" " " " " " " "	-	-	-	6.11	7.54	7.19	-
" " " " " " " "	-	-	-	7.94	9.75	9.37	-
" " " " " " " "	-	-	-	-	604	-	-
" " " " " " " "	-	-	-	147	106	106	-
" " " " " " " "	-	-	-	145	144	144	-
" " " " " " " "	-	-	-	55.5	56.5	60.0	-
" " " " " " " "	-	-	-	32.8	30.0	32.4	-
" " " " " " " "	-	-	-	22.2	17.5	19.7	-
" " " " " " " "	-	-	-	36.1	31.6	17.7	-
" " " " " " " "	-	-	-	55	55	51	-
" " " " " " " "	-	-	-	1.52	1.74	1.35	-
" " " " " " " "	-	-	-	147	126	153	-
" " " " " " " "	-	-	-	-	1450	-	-
" " " " " " " "	-	-	-	-	1206	1122	-
" " " " " " " "	-	-	-	-	717	347	-
" " " " " " " "	-	-	-	-	583	492	-
" " " " " " " "	-	-	-	-	489	111	-
" " " " " " " "	-	-	-	-	426	278	-
" " " " " " " "	-	-	-	-	2.93	3.33	-
" " " " " " " "	-	-	-	-	5.77	6.55	-
" " " " " " " "	-	-	-	-	7.62	8.64	-

o-Vinyl chloride was being lost from feed tank during the run.

...many companies were being re-planned or re-organized.

consequent tests by the Analytical Group indicate that vinyl acetate copolymers require longer equilibration time in the head space method than PVC homopolymers. As a result, the values reported below may be low by 25-40%. This will not affect the rate factors since slopes of the lines will not be changed, only the actual level at each plotted point.

B. F. GOODRICH
Research Center

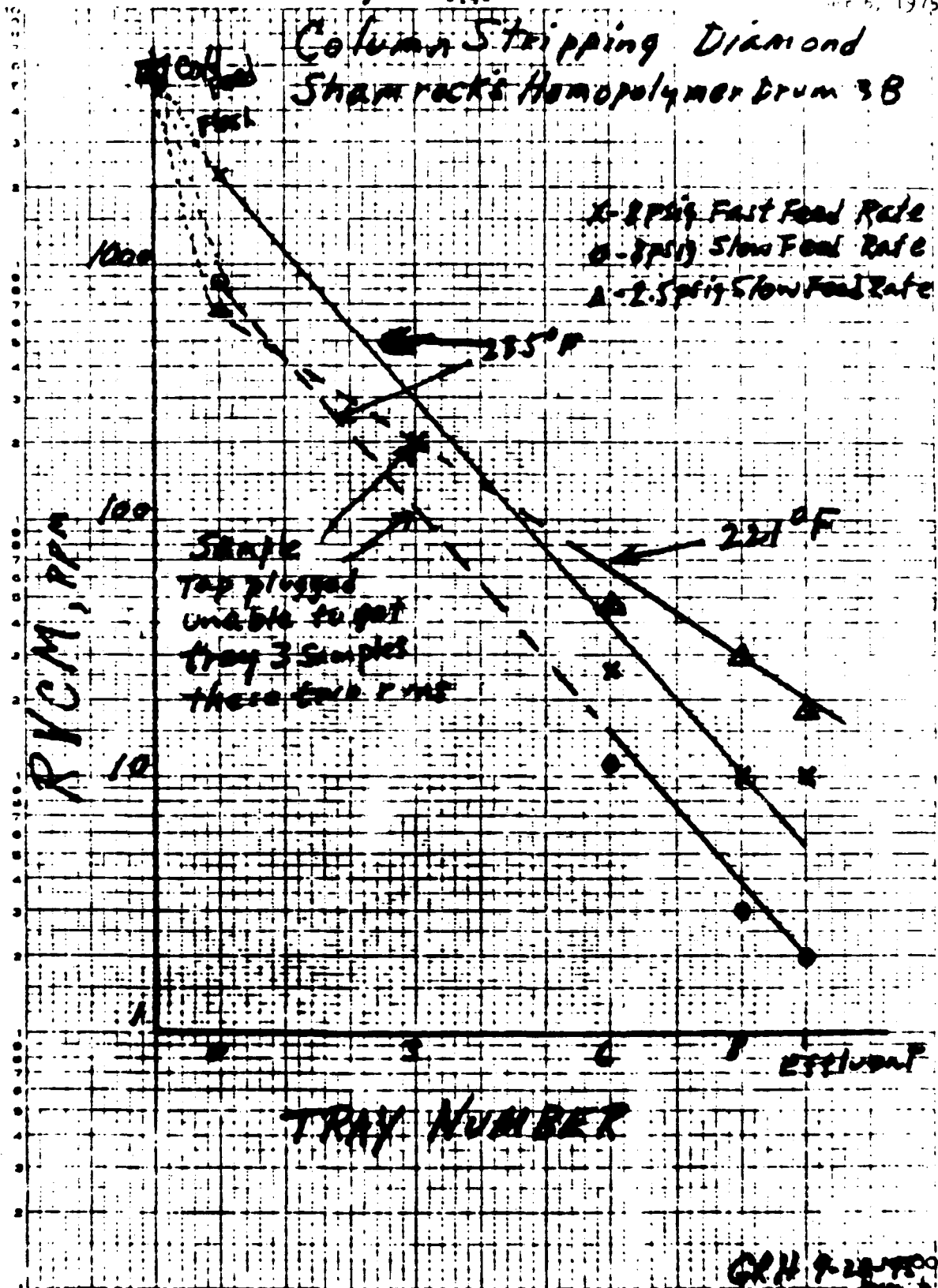
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Figure 1

Ref. 7716-75
Mar 5, 1975

Column Stripping Diamond
Shawrock's Homopolymer Drum 3B



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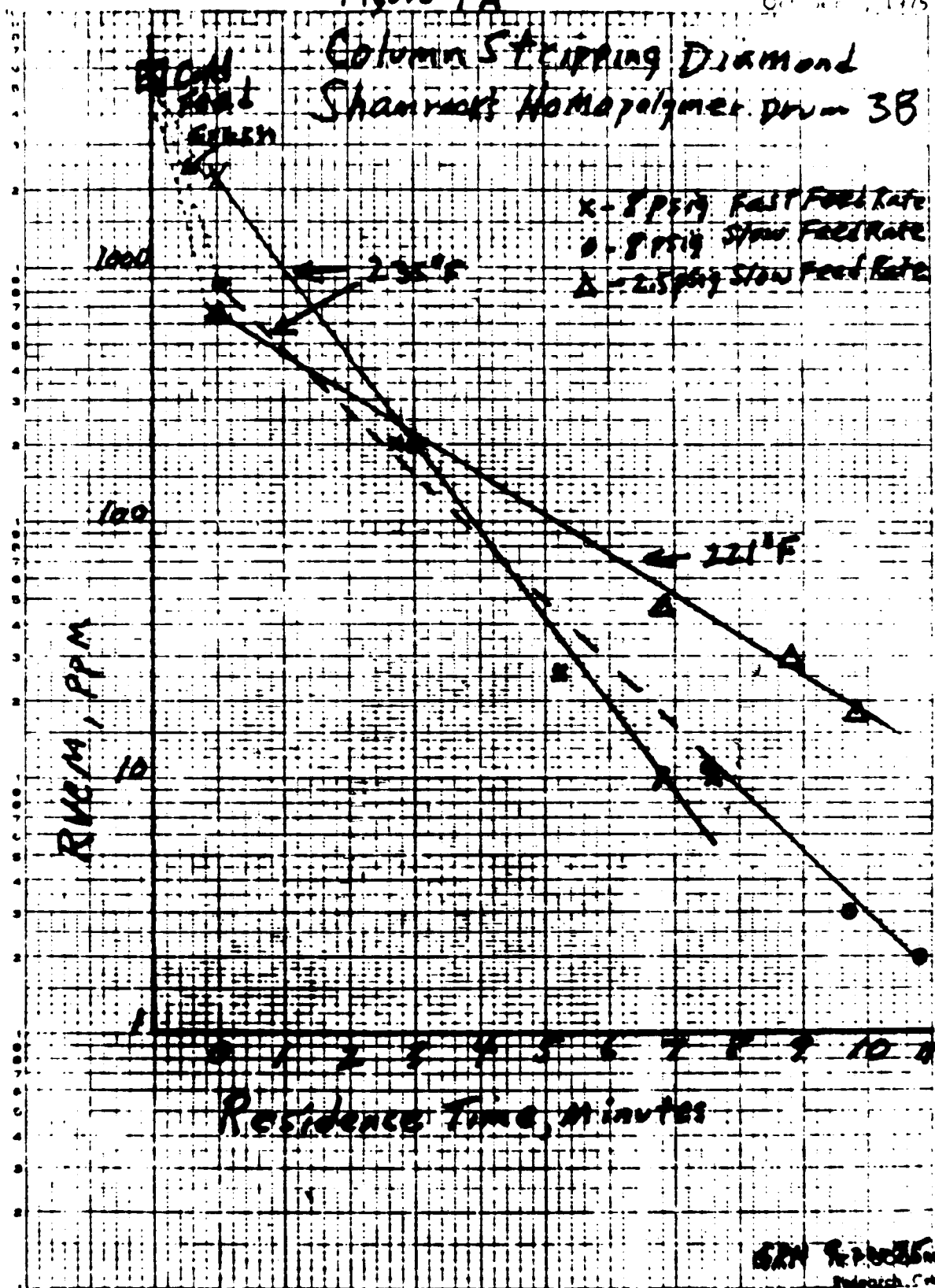
GRN 9-24-75 OODRICH
Mar 5, 1975

BFG14372

Figure 1A

Project 214B-75
October 1, 1975

Column Stripping Diamond Shamrock Homopolymer Drum 3B



EUCKING DISTIBEN CO.
MADE IN U. S. A.

NO. 340-B10 DISTIBEN GRAPH PAPER
SEMI-LOGARITHMIC
5 CYCLES X 10 DIVISIONS PER INCH

SRM Research Center

214B6016

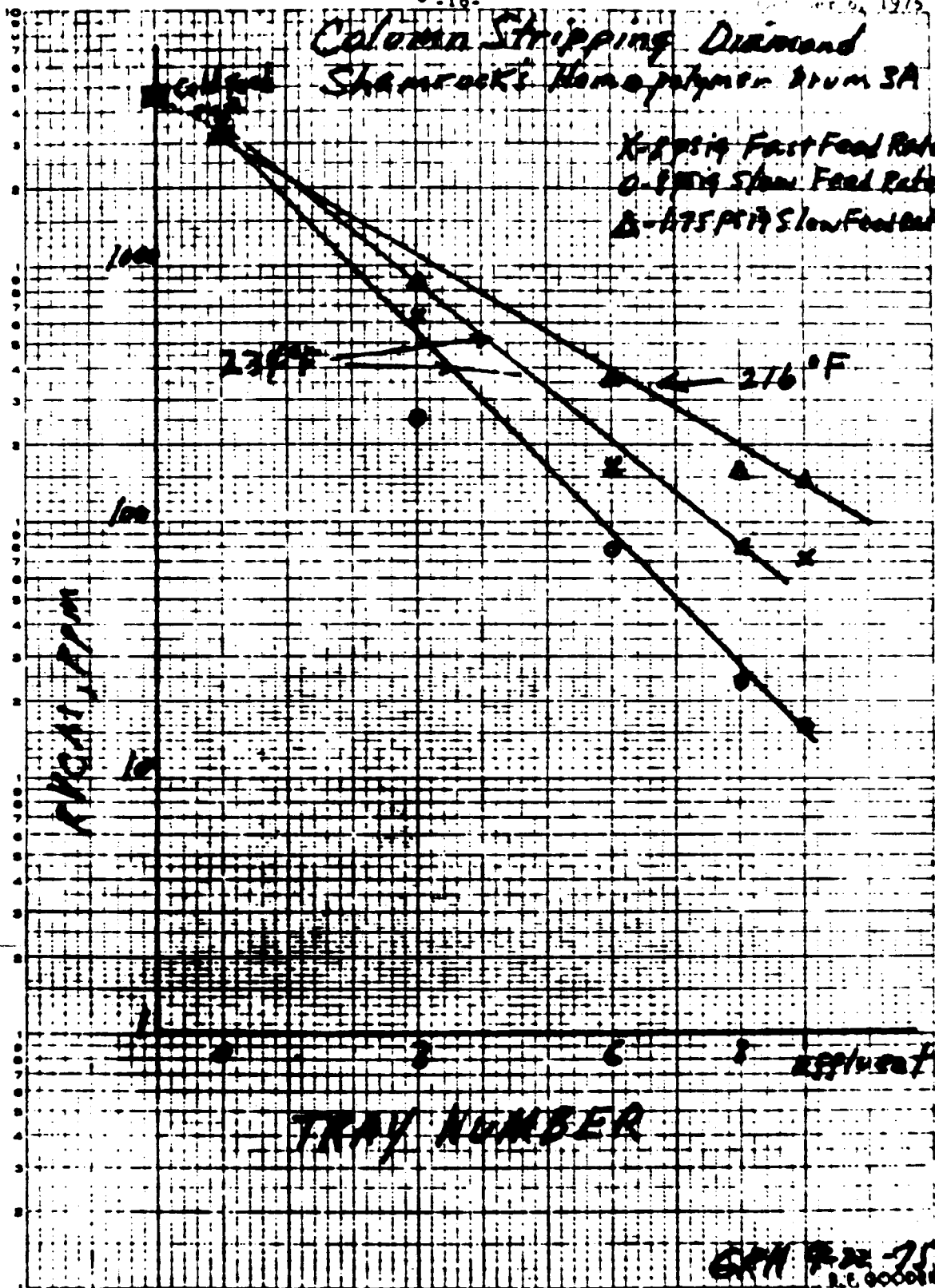
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Figure 2

7716-75
1975

Colman Stripping Diamond
Shamrock Homopolymer Drum 3A

X-87519 Fast Feed Rate
O-87519 Slow Feed Rate
B-87519 Slow Feed Rate



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

NO. 340-LS-11 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
5 CYCLES X 10 DIVISIONS PER INCH

GRN 7-22-75
R.E. GOODWIN
Research Center

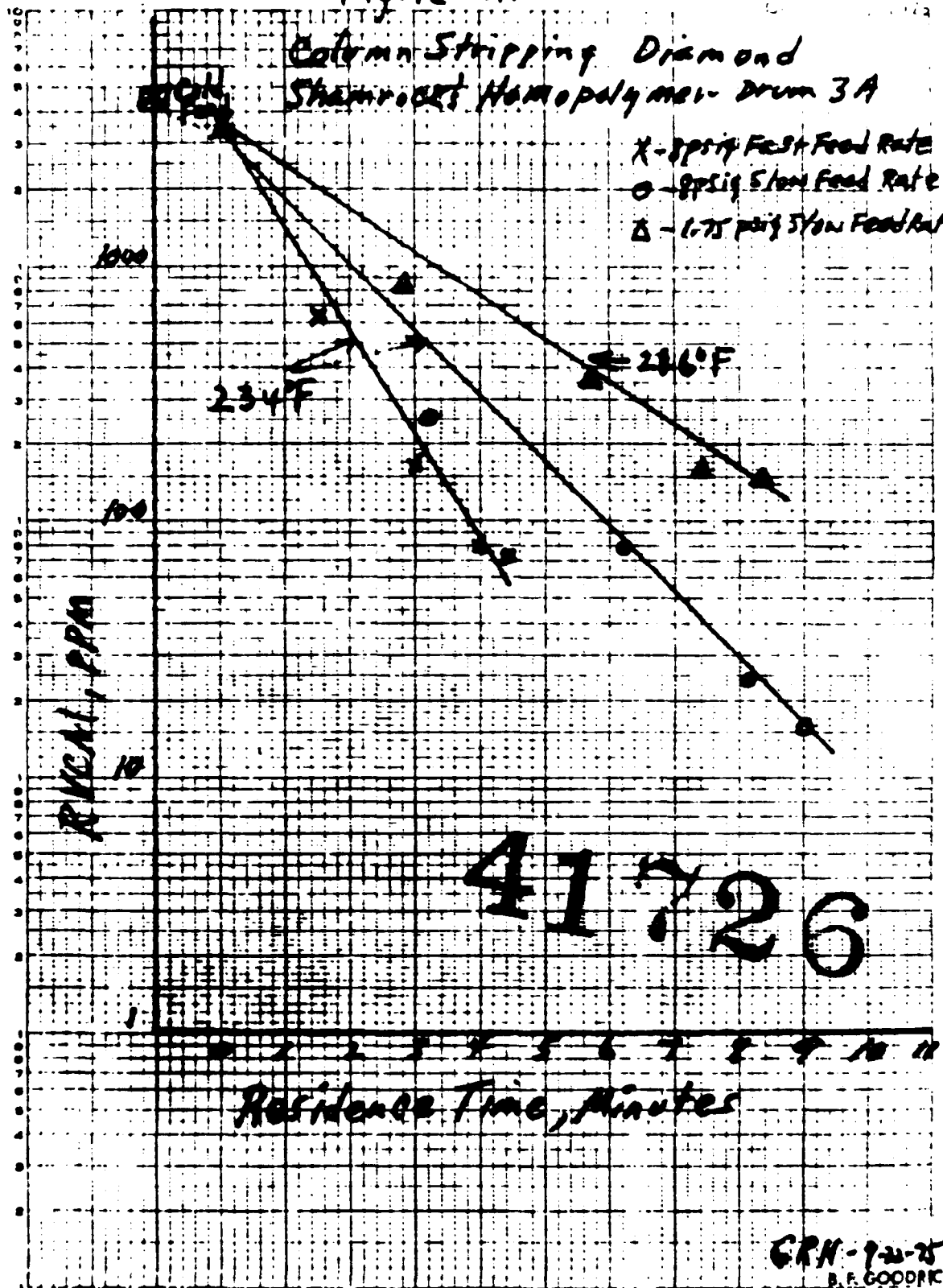
21A86017

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Figure 2A

Column Stripping Diamond
Shamrock's Homopolymer- Drum 3A

- X - 8 psig Fast Feed Rate
- O - 8 psig Slow Feed Rate
- Δ - 1.75 psig Slow Feed Rate

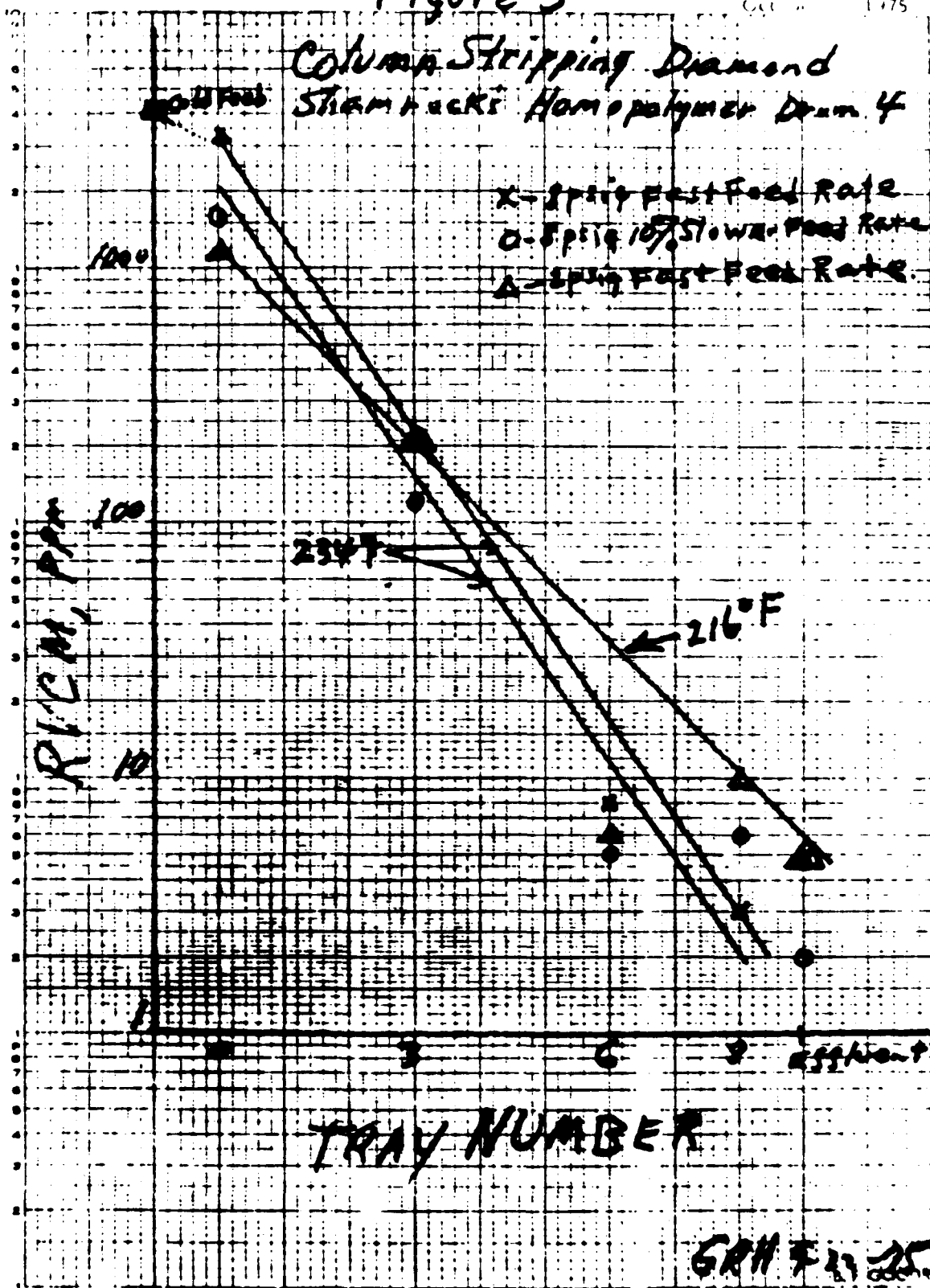


GRN-9-25
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Figure 3

PR 100-75
CCL 100-75



LUBRICATION SYSTEMS CO.
MADE IN U.S.A.

NO. 240-10 SYSTEM GRAPH PAPER
NEW LUBRICATION SYSTEMS CO.
A DIVISION OF DIVISIONS PER INCH

GRH 7-15
Research Center

21486019

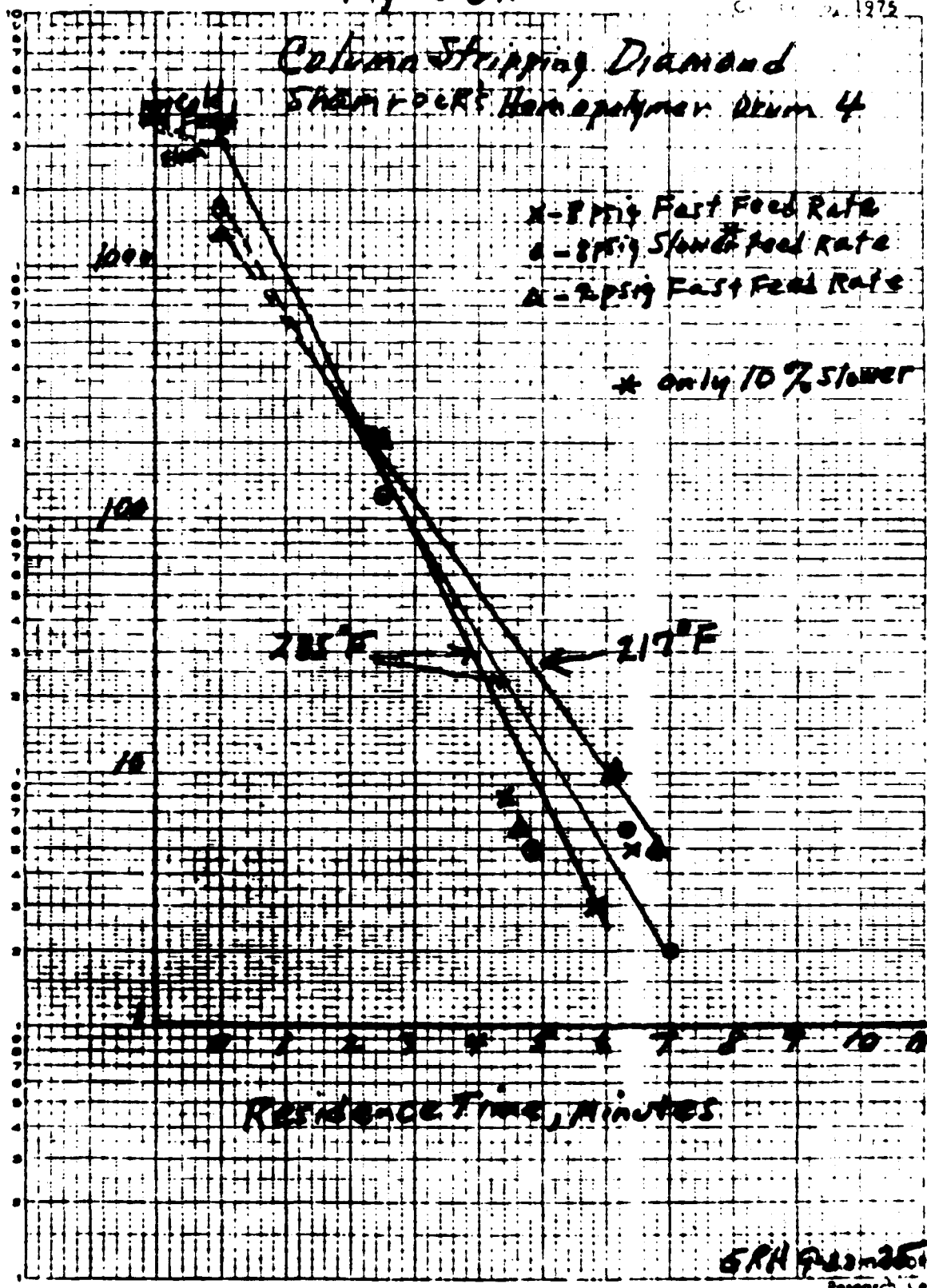
BFG14376

Figure 3A

216-75
Oct. 1972

CLUBINE ENCYCLOPEDIA
MADE IN U.S.A.

NO. 248-LS-111 ENCYCLOPEDIA GRAPH PAPER
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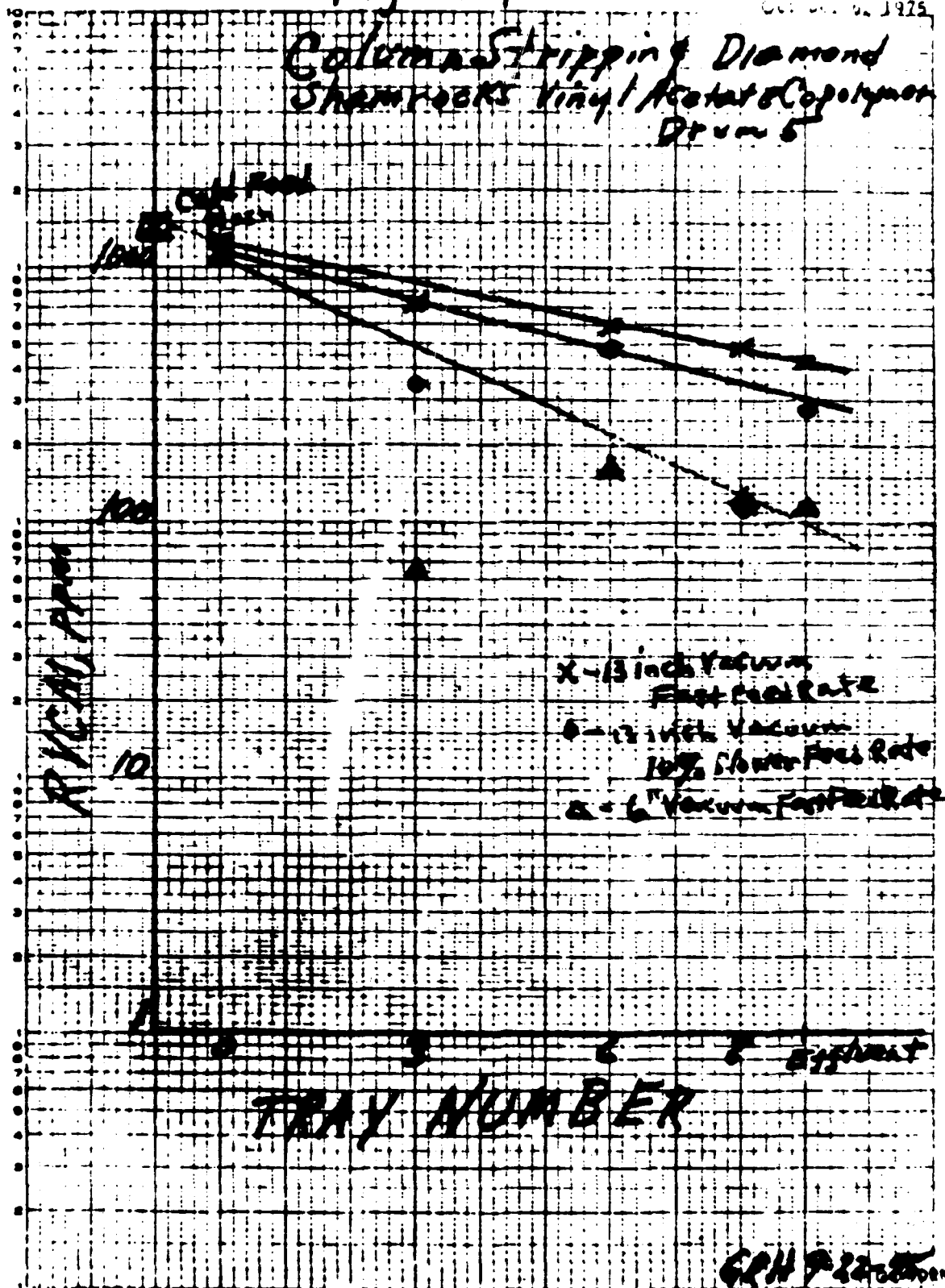
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Figure 4

716-75
Oct. 10, 1975

Column Stripping Diamond
Shawcross Vinyl Acetate Copolymer
Drum 5



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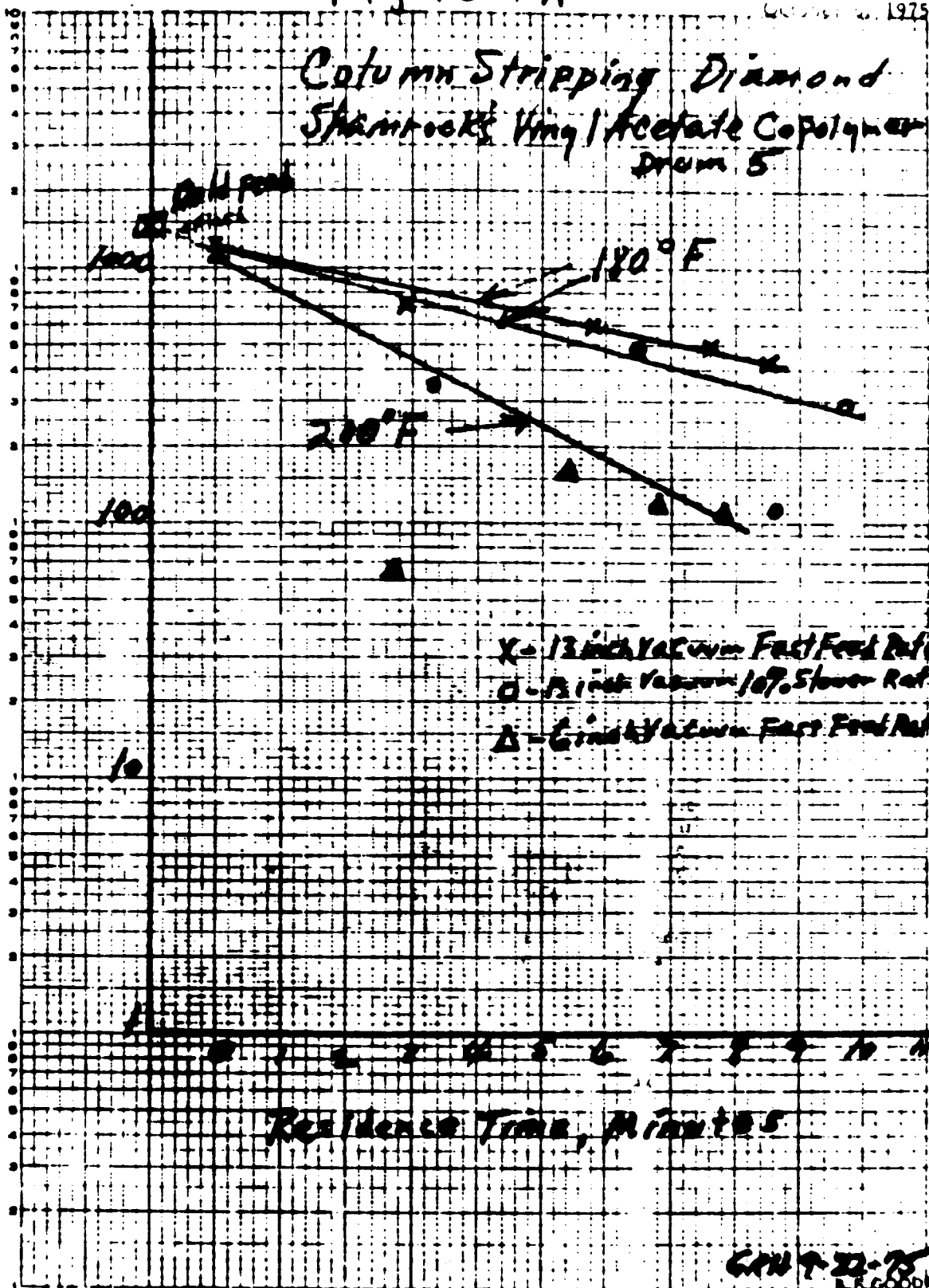
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Figure 4A

P- 7716-75

CO- 1975

Column Stripping Diamond
Shamrock Vinyl Acetate Copolymer
Drum 5



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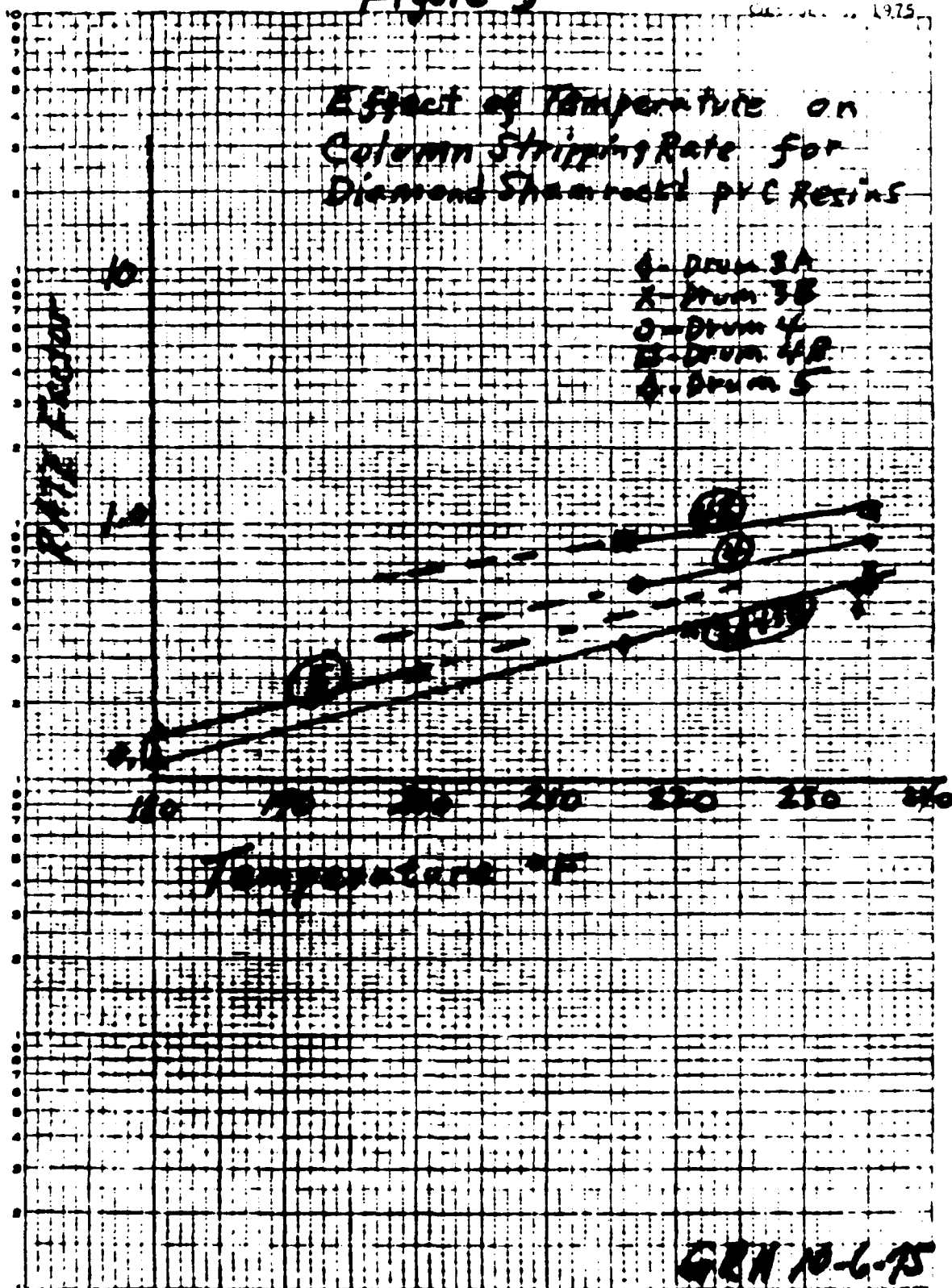
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-22-
Figure 5

Project 2216-75
October 1975

Effect of Temperature on Column Stripping Rate for Diamond Shearrock PCE Resins



ENGINE DIVISION
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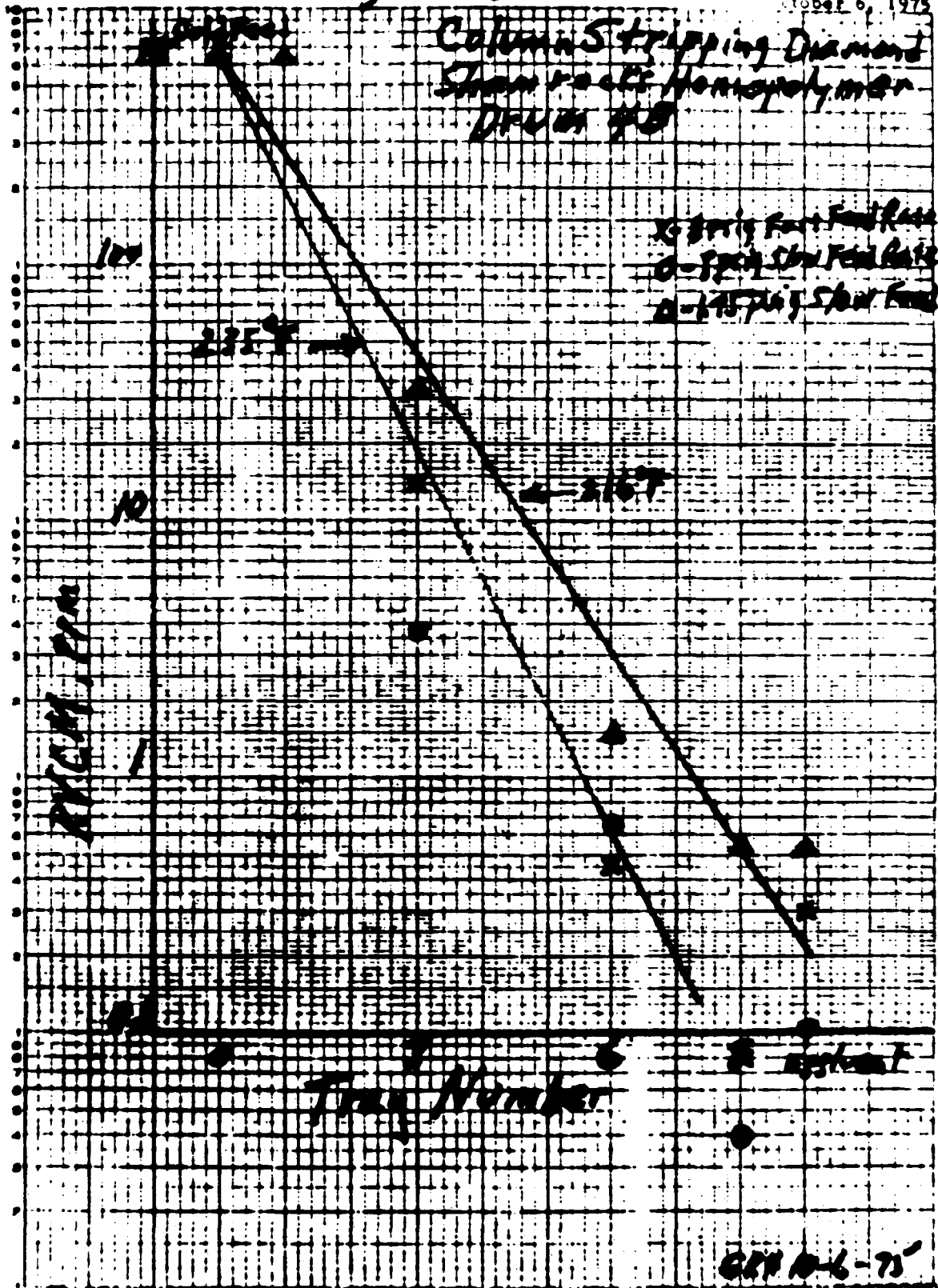
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Figure 6

Project 7716-75

October 6, 1975

Column Stripping Diamond
Shore 60 Homopolymer
Drum #0



Current Output of
100 to 1

1000 to 1000000
1000000 to 10000000
10000000 to 100000000
100000000 to 1000000000

EXP 10-6-75

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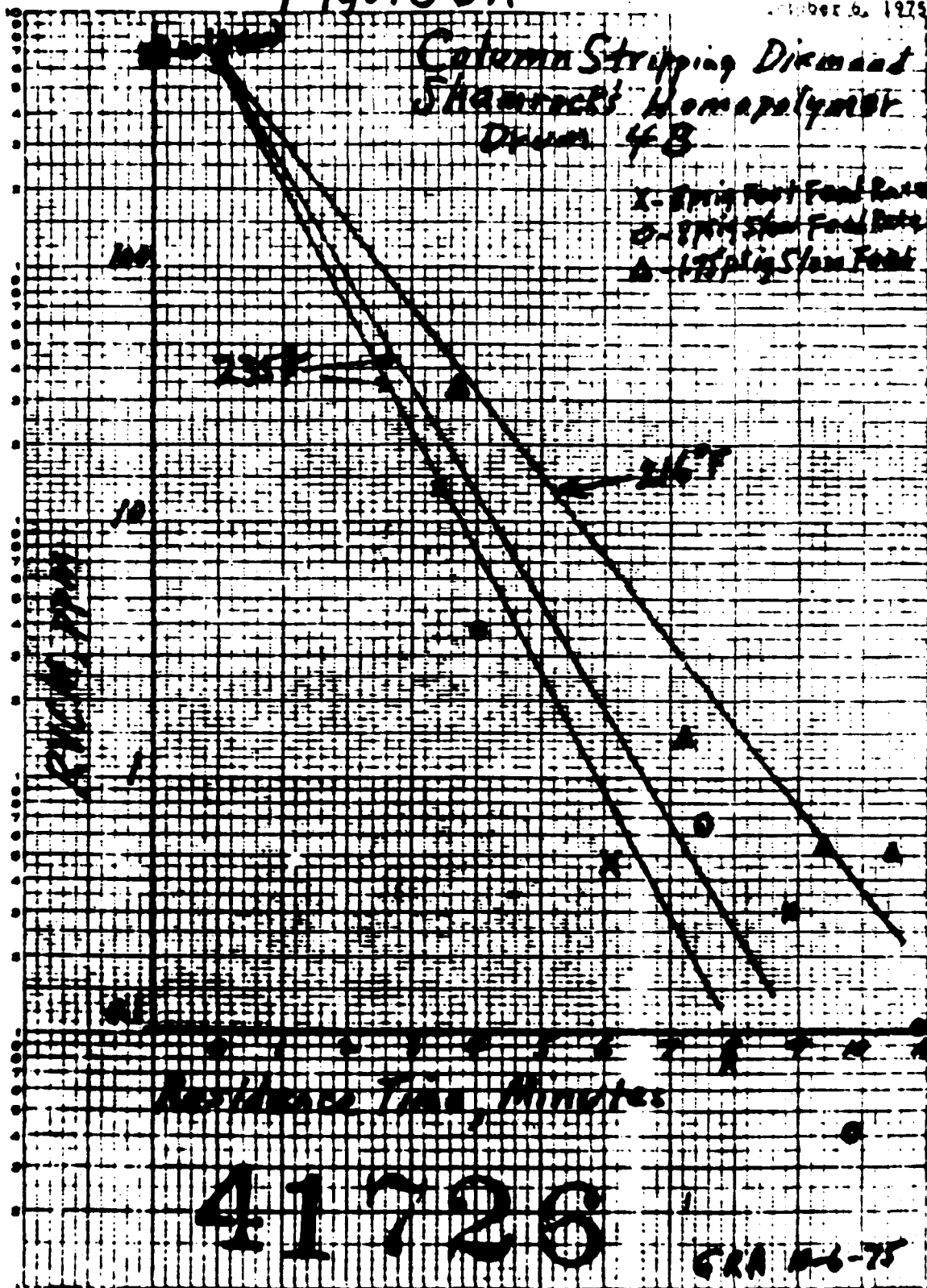
Figure 6A

Project 7716-75

October 6, 1975

Catena Stripping Dickman
Shamrock Homopolymer
Drum 4B

X - Spring Port Feed Rate
O - 8PM Slam Feed Rate
Δ - 175 plg Slam Feed



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GRA 4-75

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VII. Addendum

A. Introduction

Diamond Shamrock requested additional tests with their vinyl acetate copolymer resin which was identified as Drum 5 in the original report. Specifically they requested that it be run at a slow feed rate to allow at least 15 minutes retention time in the column. To provide more margin of safety in preventing agglomeration and column plugging, these tests were made at 170°F instead of 180°F. Extrapolations of the data were made to predict results for 180°F based on the factors established with the first drum of material.

Some changes in procedure had been made since the earlier run. A small stream of water was added to the steam feed to remove superheat and prevent drying on the lower trays which had been a severe problem at low feed rates. When drying or concentration occurred, there was considerable agglomeration and plugging of the downcomers. Adding the water was effective in minimizing the problem but injection of water through the sample tape was necessary several times at the very slow feed rate.

The analytical procedure was changed to allow much longer equilibration time in the head space method. Studies by Whitney had shown that the vinyl acetate copolymers require much longer than homopolymers to reach equilibrium at 90°C. Insufficient time resulted in low and erratic values for the earlier tests. The second drum of resin had a much higher level of vinyl chloride than the first drum.

Diamond Shamrock was interested in methods to obtain 10 ppm in a 20 tray column. Projections are shown on potential methods for reaching this goal.

B. Operating Data and Analytical Results

Stripping tests were made on November 12, 1975. The slurry, as loaded to the feed tank, showed a solids content of 31.3% and 6360 ppm vinyl chloride.

To obtain the slower feed rates desired, the pulse timer was set to open the feed valve for a fraction of one second. Three runs, at widely different feed rates, were made without appreciable difficulty. Table IV shows data for the three runs.

Table IV

Column Operating Data, Diamond Shamrock's Vinyl
Acetate Copolymer, Second Drum

Run Number	1112A	1112B	1112C
Column Vacuum inches Hg	17	17	17
Bottom Temperature, °F	170	170	170
Feed, pounds/hr	24.9	51.8	137.3
Seconds between pulses	40	20	10
Resin, pounds/hr	7.79	16.21	42.97
Steam, pounds/hr	36.4	33.6	32.8
Steam/Resin Ratio	4.67	2.07	0.76
Feed Temperature, °F	114	116	116
RVCN, ppm, Cold Feed	6360	6360	6360
RVCN, ppm, Hot Feed Flashed	4326	3786	4076
RVCN, ppm, tray 3	2302 *	2557 *	2769 *
" " tray 6	1491	2024	2431
" " tray 8	1215	1556	2003
" " Effluent	1250	1377	1770
Residence Time, minutes			
tray 3	10.35	4.90	1.94
tray 6	20.27	9.69	3.87
tray 8	26.65	12.84	5.15
Effluent	29.81	14.40	5.79

* The analyst had difficulty and was not able to report a specific value. Results were listed as more than the values shown.

C. Discussion of Results

The data are plotted as log vinyl chloride content against tray number in Figure 7 and against residence time in minutes in Figure 7A. From these plots rate factors A and B were derived as discussed earlier in the report. These data show that increasing the residence time by a factor of 5.15 increased the tray stripping rate by only 1.66. (Compare runs A and C) Comparing runs A and B, increasing residence time by a factor of 2.07 increased the tray rate by 1.2 and comparing runs B and C, increasing residence time by a factor of 2.49 increased tray rate by 1.38. These data suggest a relationship:

$$\left(\frac{\text{time 1}}{\text{time 2}} \right)^x = \frac{\text{rate 1}}{\text{rate 2}}$$

Using the data from the three runs and solving for x shows: For A - C, x = 0.31; for A - B, x = 0.25 and for B - C, x = 0.36; average x = 0.307.

The rate factors from Figures 7 and 7A are:

Slurry Rate, pounds/hour	-A Factor	-B Factor	Trays Required*
24.9	.1477	.0449	41
51.8	.1231	.0763	49
137.3	.0889	.1359	67

* To reduce vinyl chloride from 4000 ppm to 10 ppm

From the dependence of rate on temperature as shown in Figure 5, the projected rate factors were estimated for 180°F at the three feed rates and trays needed to reduce vinyl chloride from 4000 to 10 ppm were estimated:

	-A factor at 180°F	Trays Needed
Slow feed	0.199	30
Medium feed	0.166	36
Fast feed	0.120	50

No problem is anticipated for this resin at 180°F, but there was appreciable agglomeration in the earlier run at 200°F so 180°F is near the safe operating temperature limit.

D. Operation of a 20 Tray Column to Obtain Less than 10 ppm Residual Vinyl Chloride

Diamond requested projections on how a 20 tray column could be used to reach 10 ppm. Several projections were made based on the development column data. There are no direct comparison data between production columns and the development column on tray rate factors yet, but comparison between the 30 inch column and the 6 inch column shows similar A factors. Initial data from the new 60 inch plant columns are in the range predicted by the 30 inch column so the rate factors generated in the development tests are expected to be comparable to those of the production columns. Several options exist for reaching 10 ppm in a 20 tray column. These are discussed.

1. Lower Vinyl Chloride Content in Feed to the First Tray

This can be accomplished by more batch stripping before feeding to the column and/or heating the feed to column operating temperature in line to the column. With the higher feed temperature there will be a larger percentage flash removal of vinyl chloride as the slurry enters the column. Even that with a cold feed of 6340 ppm the level was reduced to the range of 4000 by heating only to 116°F. The level could be reduced further by heating to 180°F in line without adding significant heat history to the slurry. Table V shows that even with the slow feed rate, a vinyl chloride concentration of 535 would be required to the first tray to reach 10 ppm.

The feed required can be calculated by:

$$C_f = 10/e^{-AN}$$

2. Make Two Passes Through the Column

Another method to achieve the low vinyl chloride level desired would be to make two passes through the column. In this case the equation would be $C_p = 10/e^{-A_2N}$ and at the slow feed rate a level of 28,640 ppm could be accepted and reduced to 10 ppm in two passes. Some values are shown in Table V.

3. Recycle Part of the Slurry

In this mode of operation, a portion of the slurry would be taken from the bottom of the column as stripped product while the remainder would be returned and mixed with fresh feed for another pass. This method may be preferable to making two separate passes since it would not require extra holding tanks. The equation for predicting feed concentration and recycle fraction is:

$$10 \text{ ppm} = [C_p X_p + 10 (1 - X_p)] e^{-AN}$$

When C_p is the vinyl chloride concentration in the feed to the top tray and X_p is the fraction of new feed. This equation can be used by setting either the feed concentration or the feed fraction and calculating the other. With a feed containing 4000 ppm the fresh feed fraction is .132 at the slow rate and at 1000 ppm the feed fraction is .53. Some values are shown in Table V.

Table V

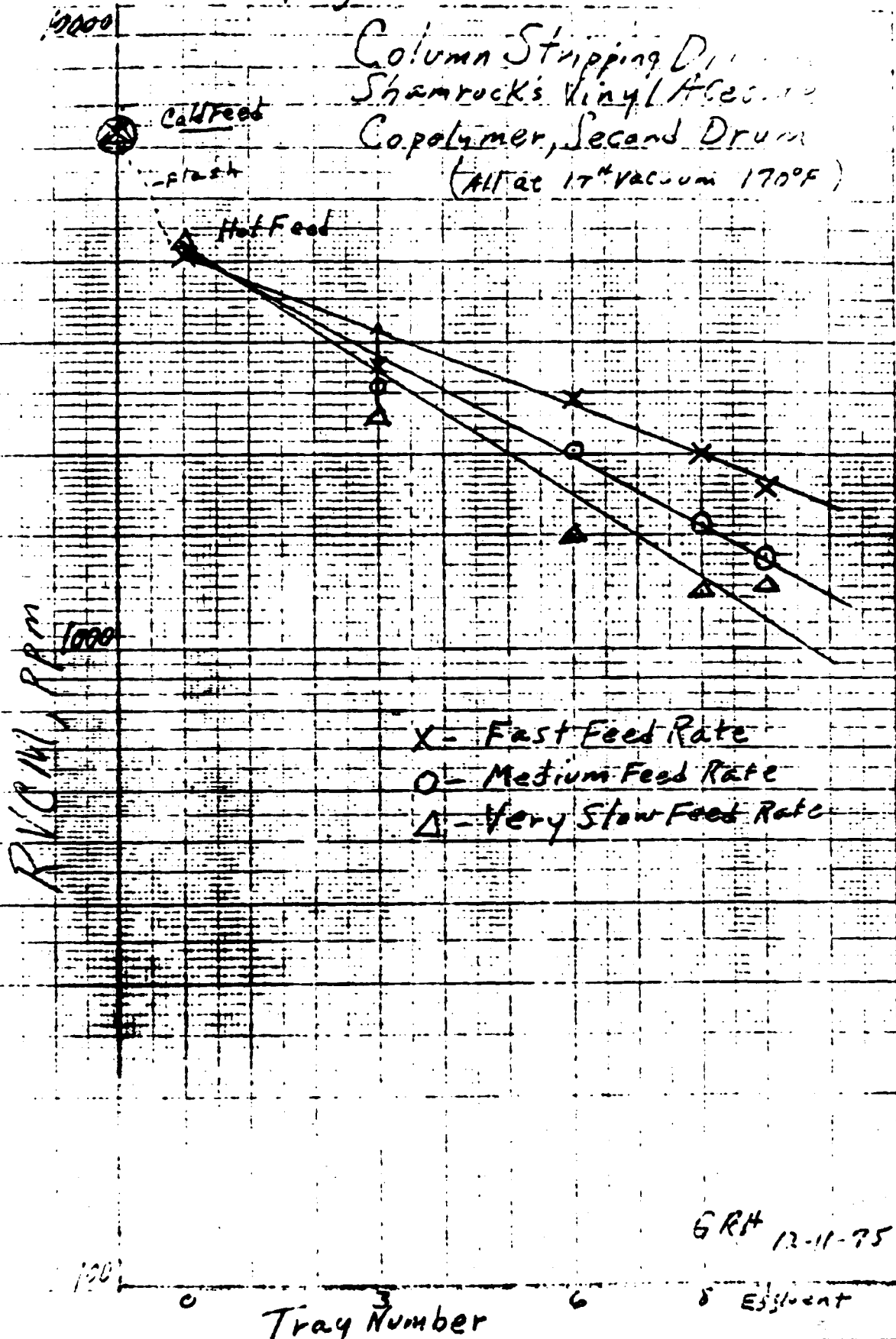
Projections for a 20 Tray Column at 180°F

<u>RVCM to First Tray</u>	<u>32000</u>	<u>16000</u>	<u>8000</u>	<u>4000</u>	<u>2000</u>	<u>1000</u>	<u>500</u>
<u>Fast Feed Rate - A Factor 0.120</u>							
RVCM One pass	2903	1452	726	363	181	91	45
RVCM Two passes	263	132	66	33	16	8	4
<u>Recycle Mode</u>							
98% recycle RVCM	59	30	15	8	5	2.7	1.8
75% recycle RVCM	726	364	182	91	46	23	12
50% recycle RVCM	1452	726	363	182	91	46	23
25% recycle RVCM	2178	1089	544	271	136	68	34
<u>Medium Feed Rate - A Factor 0.166</u>							
RVCM One pass	1157	578	289	145	72	36	18
RVCM Two passes	41	21	10	5	2.6	1.3	0.65
<u>Recycle mode</u>							
98% recycle RVCM	23	12	6	3.2	1.5	1.1	0.7
75% recycle RVCM	289	145	72	36	18	9.3	4.8
50% recycle RVCM	579	290	145	72	36	18.3	9.2
25% recycle RVCM	868	434	217	108	54	27.2	13.6
<u>Slow Feed Rate - A Factor 0.199</u>							
RVCM One pass	598	299	149	75	37	19	9
RVCM Two passes	11	6	3	1.4	0.7	.35	0.17
<u>Recycle mode</u>							
98% recycle RVCM	12	6	3.2	1.7	0.93	0.6	0.37
75% recycle RVCM	150	75	37.5	19	9.5	4.8	2.5
50% recycle RVCM	299	150	75	37	19	9.4	4.8
25% recycle RVCM	448	224	112	56	28	14	7.1

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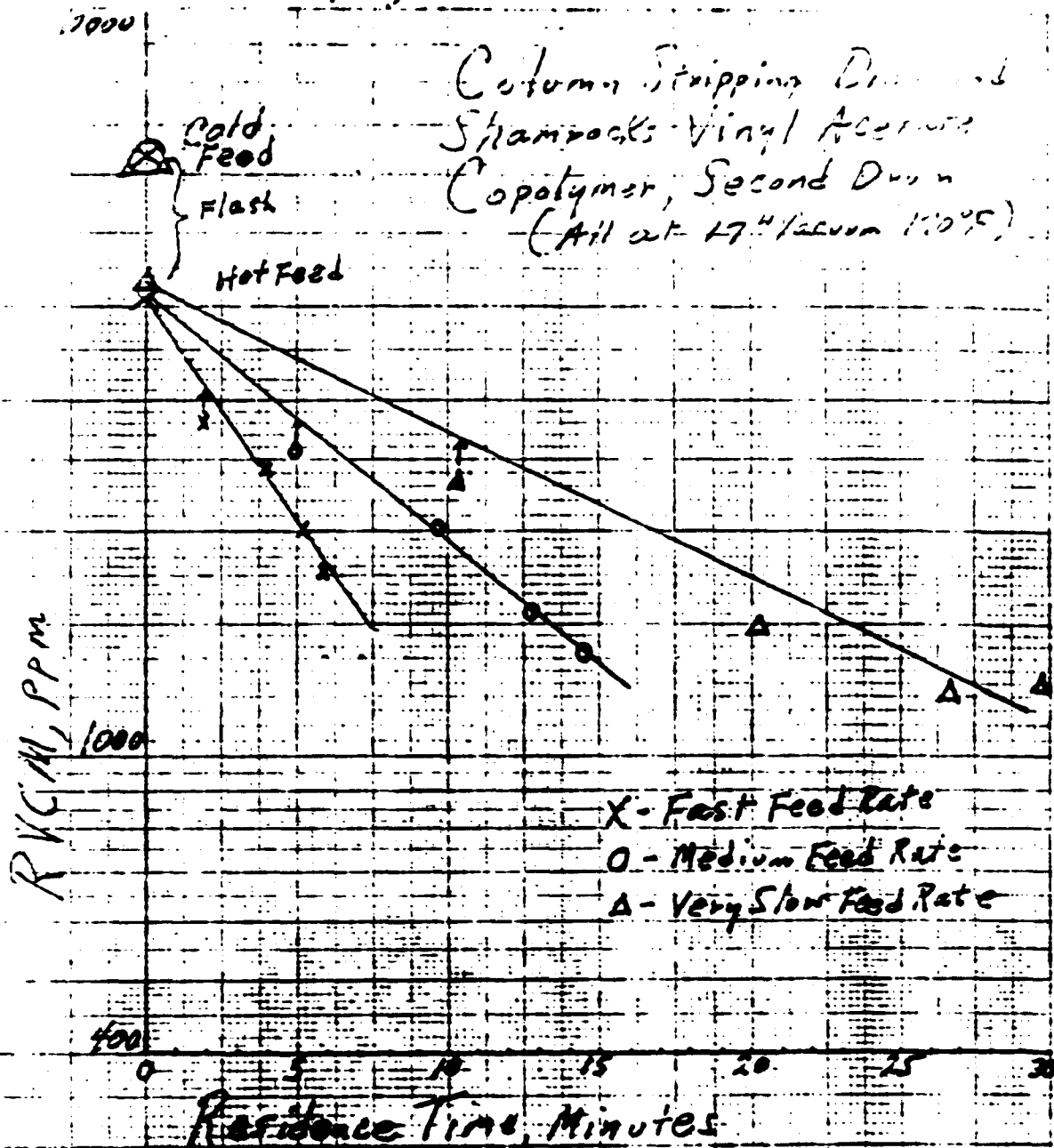
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Figure 7



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Figure 7A



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