"Not Responsive" tag is ~~for~~ a different case R Bernstein 1/25/95

Not responsive

UCC
049047

Maliko, et al vs Union Carbide Corporation
51 of Third Supplemental Interrogatories

2,6

UCC
049048

Not Responsive

"Not Responsive" tag is for a different case A Burnstein 12/5/85

106

106

[illegible] RESIDUAL VCl

February 22 - March 15, 1975

Date	Bin	Conditions	Residual VCl, ppm
2/27	603	Normal stripping while pumping	1,504
2/28	602	through vacuum stripper at 70°C	1,629
2/28	601		1,425
2/28	605		1,017
[illegible]	604		918
3/1	602		1,773
3/1	605		842
3/2	603		1,136
3/2	601		1,179
3/2	604		1,403
3/3	602		1,077
3/3	606		1,557
3/3	603		1,253
3/4	604		949
3/4	601		917
		Average	1,239
3/5	603	Batch vacuum stripped, unknown temp.	232
3/6	605	and time because of bad thermocouple	178
3/6	602	- off-color resin	110
		Average	173
[illegible]	606	Batch vacuum stripped, at 85°C, 30-	215
3/7	605	minutes at 10-15 inches Hg vacuum,	278
3/7	604	acceptable color resin	270
3/8	601		191
		Average	239
3/8	602	Batch vacuum stripped at 90°C, 30 min.,	69
3/9	601	acceptable color resin	111
3/9	603		153
3/9	605		173
3/9	602		160
3/10	606		158
3/10	601		83
3/11	603		53
3/12	602		103
3/12	601		91
3/13	603		188
		Average	122

106

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QSQF BIN DATA OF RESIDUAL VCl

Date	Bin	Residual Monomer	Stripping Conditions
3/13	606	946	90° - 30 minutes
3/14	609	155	90° - 30 minutes
3/15	606	727	80° - 90° - 30 minutes
3/15	603	735	80° - 30 minutes
3/16	606	690	80° - 30 minutes
3/16	602	977	80° - 30 minutes
3/16	603	671	80° - 30 minutes
3/17	601	930	80° - 30 minutes
3/18	602	995	80° - 90° - 30 minutes
3/18	601	1,847	90° - 30 minutes
3/18	603	497	90° - 30 minutes
3/19	604	240	90° - 30 minutes
	Average	687	

BIN DATA - RESIDUAL MONOMER PPM

Date	Bin	Residual Monomer	Stripping Conditions
QSAN			
2/10	709	78	Continuous 80°C
2/11	706	70	Ditto
2/11	707	185	Ditto
2/15	705	108	Ditto
2/15	702	90	Ditto
2/16	703	50	Ditto
2/17	709	73	Ditto
2/17	704	104	Ditto
2/18	707	111	Ditto
2/18	703	115	Ditto
2/23	703	122	Ditto
2/23	705	200	Ditto
2/23	702	112	Ditto
2/23	703	96	Ditto
2/24	706	80	Ditto
2/25	705	156	Ditto
2/25	411	104	Ditto
	Average	109	
QSAL			
2/19	709	227	Continuous 80°C
2/19	707	216	Continuous 80°C
2/20	702	292	ditto
2/20	707	277	ditto
2/21	708	256	ditto
3/9	408	211	ditto
3/9	409	280	ditto
3/9	702	190	ditto
3/10	705	133	ditto
	Average	231	
VSKK			
3/13	707	603	Continuous 75°C
3/13	704	1,448	ditto
3/13	709	800	ditto
3/14	706	1,239	ditto

Date	Bin	Residual Monomer	Stripping Conditions
VSKK (continued)			
3/14	707	960	Continuous 75°C
3/15	709	1,418	ditto
3/16	706	924	ditto
3/16	708	909	ditto
3/16	703	846	ditto
3/18	704	806	ditto
3/18	707	1,11[illegible]	ditto
3/18	708	[illegible]10	ditto
3/19	701	1,125	ditto
3/19	709	1,035	ditto
3/19	706	809	ditto
3/20	703	1,102	ditto
3/20	701	1,783	ditto
3/21	704	2,016	ditto
3/21	707	3,514	ditto
3/21	701	785	ditto
	Average	1,189	

UC 149-2

UNION CARBIDE INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

T (NAME) Mr. A. A. Peterson
COMPANY Building 114
L CATION TEXAS CITY PLANT

DATE December 11, 1975

COPY TO Dr. J. C. Chaty
Mr. M. E. Eisenhour
Mr. R. L. Fraitz
Dr. D. R. Mortgomery
Mr. R. W. Sesler
Mr. G. F. Tacquard
Mr. R. N. Wheeler - 514

SUBJECT Results of B. F. Goodrich Stripping System to Remove Residual Vinyl Chloride from UCC Suspension Resins

Dear Adolph:

Samples of QSQH-7 and QSAN-7 were supplied to B. F. Goodrich's Research Center, Brecksville, Ohio, for pilot plant tests to remove residual vinyl chloride via their patented continuous stripping operation. These samples were obtained from the blow down tanks before vacuum stripping. Both resin samples contained residual VCM exceeding 10,000 ppm.

These resins were subjected to varying residence times and temperatures at Goodrich in an effort to remove the maximum amount of residual vinyl chloride. Samples were taken at each test condition and returned to Texas City for evaluation. Results of these resin samples after stripping are shown in the attached Table.

Reduction of the residual VCM, particularly with regard to QSQH-7, is considered to be a slight improvement over the current UCC production. However, the extreme stripping conditions (> 100°C) also resulted in severe resin degradation as shown by the high yellow factors. Stripped samples of VSJE-10 supplied to Goodrich have not been received.

Please let me know if additional information is desired.

Very truly yours,

R. M. Arnold

/kw
Attachment

UCC
049054

RESULTS OF B. F. GOODRICH PILOT PLANT PROGRAM

CONTINUOUS STRIPPING OF UCC SUSPENSION VINYL RESINS TO REMOVE VINYL CHLORIDE MONOMER

Resin Type	Sample Designation	Test Conditions (Minutes/°F)	Residual VCM, ppm		Yellow Factor
			Initial	After Stripping	
QSAN-7			11,690		1.0
	1104 A	6.4/236		6	7.8
	1104 B	7.4/236		3	9.0
	1104 C	6.9/216		21	9.1
QSQH-7			20,283		1.0
	1120 A	5.8/236		32	7.0
	1120 B	6.9/235		11	9.9
	1120 C	6.9/214		61	7.2

UCC 049055

RMA:kw

12/11/75

UNION CARBIDE INTERNAL CORRESPONDENCE

RECEIVED
JUN 19 1975
R. N. WHEELER, JR.

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

TO (NAME) Mr. R. N. Wheeler
COMPANY Building 189 - Room 301
LOCATION SOUTH CHARLESTON PLANT

DATE June 13, 1975

COPY TO Mr. M. E. Eisenhour
Mr. R. L. Frantz
Mr. R. W. Sesler
Mr. G. T. Tacquard

SUBJECT VCM Concentrations in QSAL-7 Slurry

Dear Nick:

At your request, a limited study to determine the VCM concentrations in the vapor above the suspension resin surge (slurry) tanks has been made. A sample was obtained of QSAL-7 from the surge tank in a glass sample bomb. The sample was placed in an oven maintained at 75°C (approximate slurry temperature) and a vapor sample withdrawn after 0, 1 and 6 hours storage for VCM analysis. The sample bomb was filled at 50% capacity.

At the time the sample was taken, the stripping temperature for QSAL-7 was 90°C for thirty minutes. The resin portion of the slurry analyzed 875 ppm VCM. QSAL-7 samples taken from the surge tank and dryer approximately one hour after this slurry sample was obtained had the following analysis:

Date	Time	Sample	VCM, ppm
6/4/75	9:00 a.m.	No. 5 BDT	626
		No. 5 Dryer Spot	209

Therefore, during the production of QSAL-7 having approximately 200 ppm VCM, the vapor above the BDT would have VCM concentrations which closely approximate the results from this study as shown in the attached graph.

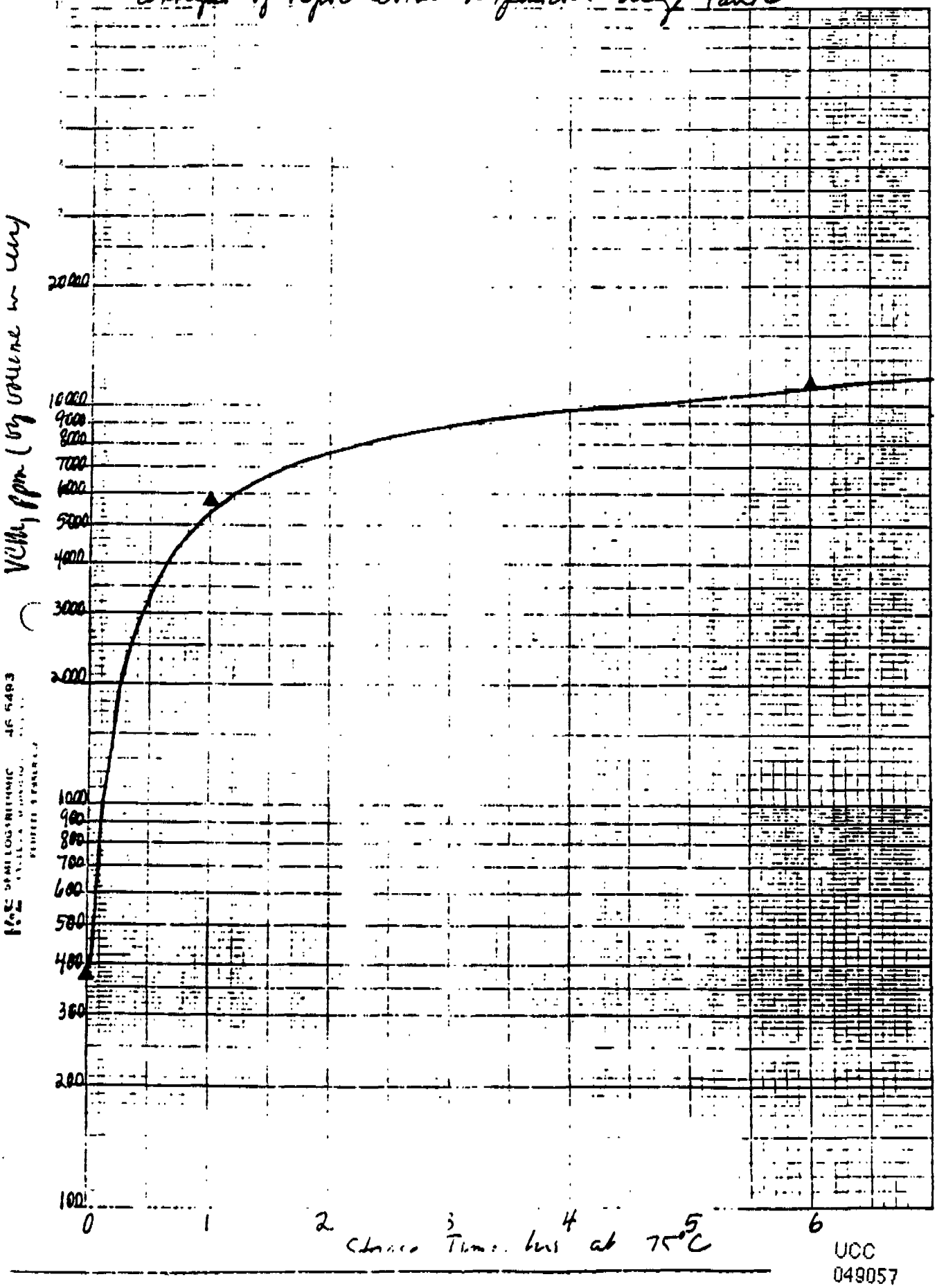
QSAL-7 stripping conditions were changed soon after these samples were obtained so that comparative data was not generated. Please let me know if additional information would be desirable.

Very truly yours,

R. M. Arnold

/kw
Attachment

Analysis of Vapor Phase Suspension Surge Tank



UCC
049057

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UNION CARBIDE INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

TO (NAME) Dr. R. J. Anderson, 312
COMPANY Mr. M. E. Eisenhour
LOCATION Mr. R. L. Frantz
Dr. W. R. Manning, 511
Dr. C. E. Moyer
Mr. G. F. Tacquard

COPY TO
Mr. R. M. Arnold
Dr. F. H. Covitz, 312
Mr. S. A. Dickerson
Mr. J. B. Hollingworth, NYO (28)
Dr. D. R. Montgomery
Mr. F. S. Provenzano
Mr. R. N. Wheeler, 514
Suspension Vinyl Staff

DATE February 23, 1977

SUBJECT Test Program To Reduce RVCM Levels in Suspension Resin Slurry

The recently published EPA regulation concerning vinyl chloride emissions included a requirement that vinyl resin contain less than 400 ppm residual vinyl chloride monomer (RVCM) when it leaves our blowdown tanks (BDT's). An intensive effort is underway to accumulate the necessary data and define a program that will allow us to meet this new regulation. The purpose of this letter is to summarize the work completed to date and to outline the work remaining to be completed.

The data first collected on RVCM levels of the various Suspension resins showed wide scatter and could not be correlated with any of the stripping conditions employed. This data was obtained from spot samples after the slurry had been stripped in the BDT and as it was being pumped to the dryer building. This scattered data resulted in a change in the sampling method from spot samples to continuous sampling during the stripping and pumping operation.

Analysis of the data from continuous sampling (see Figure I) resulted in two major observations: 1) that suspension homopolymer could consistently be stripped with existing equipment and procedures to levels less than 400 ppm RVCM, and 2) that re-pressuring the BDT's with the "15-lb. vent header" resulted in a significant increase in the RVCM level to well above the 400 ppm level. Copolymer resin slurries at this time were still above the 400 ppm level after stripping with existing equipment and procedures, but also showed the same trend of increasing RVCM levels while pumping under the "15-lb. vent header" pressure (see Figure II).

At this point two tests were performed to determine if the low RVCM levels could be maintained if the slurries were pumped without re-pressuring with the "15-lb. vent". The first test was carried out while pumping the slurry from the BDT to the dryer building under vacuum conditions. These results showed that by maintaining a vacuum on the BDT, the RVCM levels would continue to drop during pumping. However, this pumping procedure resulted in more than doubling the pumpout time of the BDT. Since the BDT's are presently production limiting, this pumping procedure was felt to be an unsatisfactory solution to the increasing RVCM problem.

The second test involved re-pressuring the BDT after vacuum with nitrogen. These results (see Figure I) were also very good with the RVCM levels remaining fairly constant below the 400 ppm level. Again, however, problems arose that involved limiting production capacity. The nitrogen in the system added two problems: 1) the volume of nitrogen had to be pumped through the monomer recovery system which is already loaded and this resulted in an increased stripping time, and 2) the excess nitrogen caused the MEK absorber to lose efficiency in the recovery of VCM from the off-gas recovery system. While both of these tests proved that re-pressuring the BDT's with the "15-lb. vent header" was the cause of the increasing RVCM levels, they did not provide satisfactory alternatives at the time.

Another concern that arose during these early tests was color degradation of the resin. While we had shown that most all homopolymers could be stripped below the 400 ppm level we were still concerned with copolymers. We felt that temperatures above those presently being used (85°C) would be required to sufficiently strip copolymer slurries but that these higher temperatures would cause resin color degradation. Two suggestions were made to try to prevent this color degradation and lower the RVCM levels to less than 400 ppm: 1) that the slurry be cooled immediately after stripping at the high temperatures (90-95°C) and 2) that sodium nitrite be used to "kill" the polymerization in the autoclaves after the desired termination point had been reached. The first suggestions was based on long experience that showed resin color degradation was a function of total heat applied to the resin. By raising the stripping temperature but shortening the time at temperatures above 60°C, the total heat applied to the resin could be lowered and should not cause a color degradation problem. The second suggestion resulted from R & D work which showed a lower color degradation rate for resins "killed" with sodium nitrite than for those not treated.

Since the only equipment we had in the production unit that could be both heated and cooled was the autoclaves themselves, it was decided to test the first suggestion of cooling the resin in an autoclave. The autoclave D-3 was chosen for the test since it was

equipped with steam heatup. One test was conducted in January but enough data was not collected. Since the samples were more than twenty-four hours old before they were delivered to the Lab, no RVCM levels were measured. However, the color index measured after stripping at 95°C for thirty minutes was only 2.9 which was encouraging. This test was performed on QSAN resin, not a copolymer, because the steam heatup was only connected to D-3 autoclave. We had hoped to obtain enough information from testing QSAN resin to indicate if test on copolymers would be worthwhile. Again, however, this test ran into trouble as the steam heatup piping was disconnected and lost when contractors made new tie-ins for the steam heatup system on the North and East lines. This test program has, therefore, been temporarily discontinued until the steam injection system is complete.

We then developed a program to test the effects of sodium nitrite addition on color at a temperature of 90°C on copolymer resin. These tests were conducted in existing production unit equipment with VSJE resin. R & D test had shown some problem with the addition of sodium nitrite to slurries containing other color stabilizers used in the unit such as EPO, Bis-Phenol A, and Irganox 1076. These were eliminated from the VSJE recipe to prevent this color formation problem between these stabilizers, and sodium nitrite.

To date four tests have been conducted. The first was somewhat of a failure as the operator added Bis-Phenol A to the BDT and the resin turned green. This did confirm, however, the problems noted in the R & D test. The RVCM level on this batch did look promising with low reading of 30 ppm. The second test was more closely supervised and no green resin was noted. The color readings on this batch were very promising with essentially little change from beginning to end of the stripping operation which took over two hours. The initial color on this batch was somewhat high at 7.8, our normal range is between 4.0 and 8.0 for stripped batches at 85°C. RVCM levels for this batch were not very good with low reading of only about 500 ppm. Careful examination of these two test revealed a difference in stripping procedure which may be significant. The first batch was heated to 90°C after being placed under vacuum and the second was heated to 90°C before vacuum. Since little heat is lost in this operation, this indicates that steam was being vigorously sparged into the slurry while under vacuum on the first test (see Figure III) but this did not occur on the second test (see Figure IV).

With this observation in mind our third and fourth tests were planned to try to duplicate the first two tests. Data from these tests could then be used to determine if vigorous steam sparging during vacuum caused a significant drop in RVCM levels. Results of the third test supported this idea with RVCM levels down to 10 ppm being

noted. However, color index reading from this test were not as good with the color rising from an initial 4.0 to 6.0 after two hours. While RVCM during the fourth test dropped to a low of about 50 ppm, the overall data indicated that RVCM levels did not drop as fast as those during vigorous steam sparging under vacuum. Comparison of the data showed that with vigorous steam sparging under vacuum the RVCM levels were between 200 and 400 ppm only 30 minutes after starting vacuum (see Figure III) whereas without vigorous steam sparging the RVCM levels were between 800 and 1,000 ppm at thirty minutes (see Figure IV). Additional tests to be conducted concerning this procedure will be outlined later in this letter.

During this same time period a couple of other ideas were tested which related to RVCM levels. One was trying to re-pressure the BDT's with steam. This proved unsuccessful after thirty minutes and the idea was abandoned. Another idea was to pump copolymer slurry from the BDT into the foam trap where it would enter the top of the tank through a sparger. This, it was hoped, would give better liquid-vapor contact and thus help VCM removal. Results from two tests were not very encouraging. The RVCM levels were somewhat lower than those from normal operation (400 to 500 versus 500 to 600) but not low enough to meet EPA requirements. Therefore, this idea was not considered pratical at present and no futher tests are scheduled.

Another area that was tested during the very early stages of this study was the effect of polymerization termination point on RVCM levels. However, the data collected was so scattered that no conclusions could be reached. With the encouraging results that have recently been obtained it is not felt that additional tests are necessary at this time in this area.

The following is an outline of additional tests that are currently being considered in the study of RVCM levels:

1. Sodium Nitrite Addition

A major test of the effect of sodium nitrite on copolym r color has been postponed since the Lab color analyzer is presently out of service. As soon as this analyzer is functional we will proceed with a test program to produce about two van boxes of copolymer that has had the polymerization terminated with sodium nitrite. This material will be isolated from other copolymer material produced at the same time to help determine any differences in the two resins. The resin terminated with sodium nitrite will be stripped at 90 - 95°C in the BDT's versus 85°C for the other material. These materials will be dried on separate dryer systems but at hopefully similar conditions.

Since this test will probably be conducted during the VSKK run, we will not only collect data on color index and RVCM but also haze. Completion of this test is expected by March 4, 1977.

2. Revised Stripping Procedures (With Pumpout Under Vacuum)

The normal steam stripping procedure for resin slurries will be revised to provide for vigorous steam sparging while under vacuum conditions. Incorporated with this different steam stripping procedure will be instructions to pump the slurry from the BDT to the surge tank under vacuum, not with re-pressurization from the "15-lb." vent header. The purpose of this test will be to determine how fast RVCM can be stripped from the slurry to a level below 400 ppm average while still maintaining an acceptable color index. We will also determine what production rate is lost, if any, by pumping the BDT's out under vacuum. This test will be conducted on only one autoclave line at a time. This will allow us to develop the best stripping cycle under these conditions for each resin types that will meet the EPA regulation. Completion of these tests is expected by March 11, 1977.

3. Revised Stripping Procedures (With Pumpout Under N_2 Pressure

Should the results from Step 2 show that the production lost with pumping under vacuum is unacceptable we will proceed with these tests. This procedure will be basically the same as Step 2 but will provide for pressuring the BDT with nitrogen prior to pumping. Again, this test would be conducted with only one line at a time initially. After each line is tested separately, all three lines will be tested simultaneously to determine if any problems exist while operating all three lines under this procedure. Completion of these test, if required, would be March 18, 1977.

4. Steam Stripping Followed By Cooling

No tests are planned at this time.

While not all the data collected thus far has been presented in this report, an attempt has been made to summarize all the important work completed in this study to date. Any questions concerning this report or request for additional data should be directed to me. Your comments about any facet of the test program or conclusions reached from the data are also welcomed.

Many thanks go to Steve Dickerson and his Lab Technicians for their help in collecting and analyzing the samples.

Sincerely,

K. E. Bowen

KEB/st

Attachments

Figure 1

QSAN

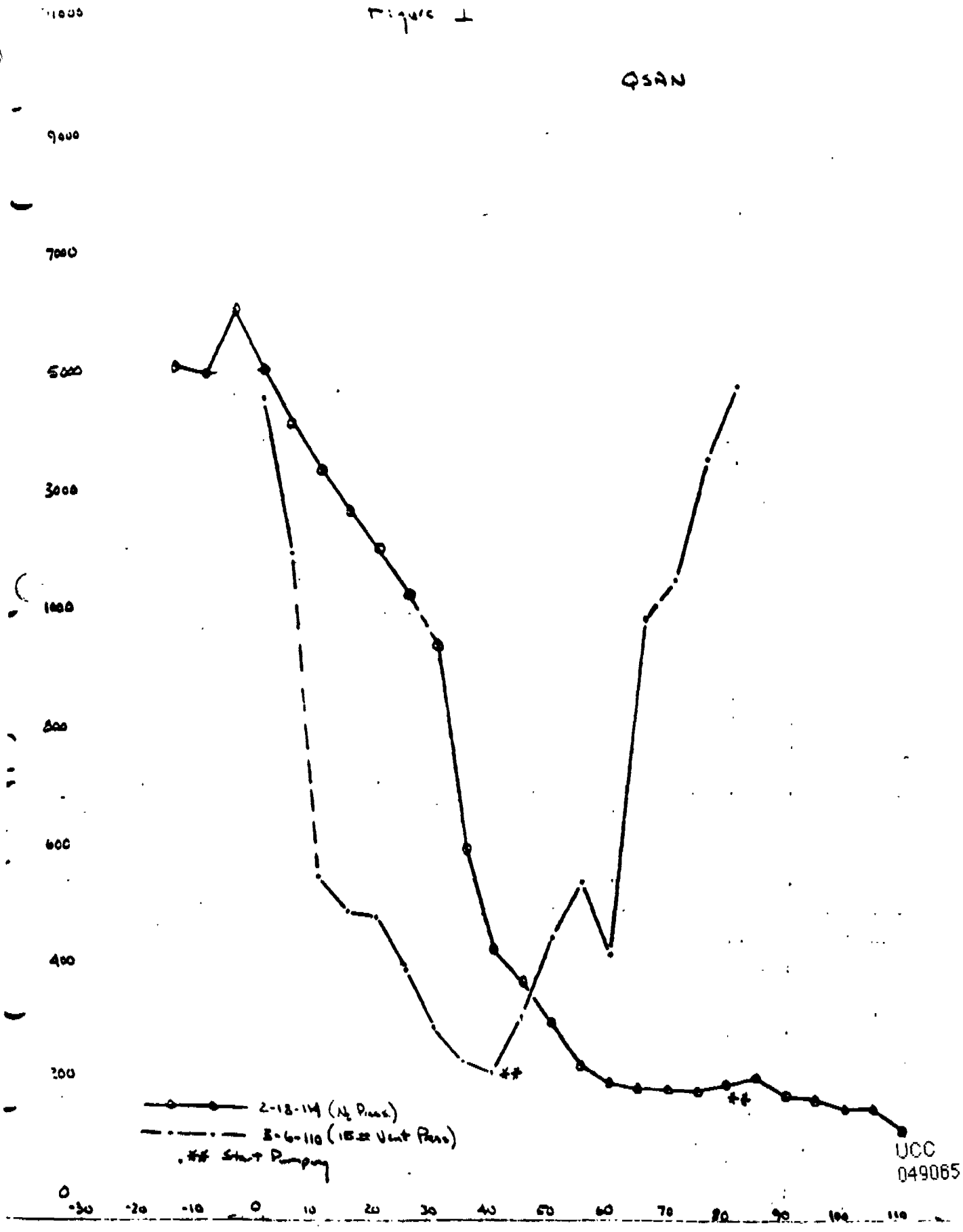

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Figure 11

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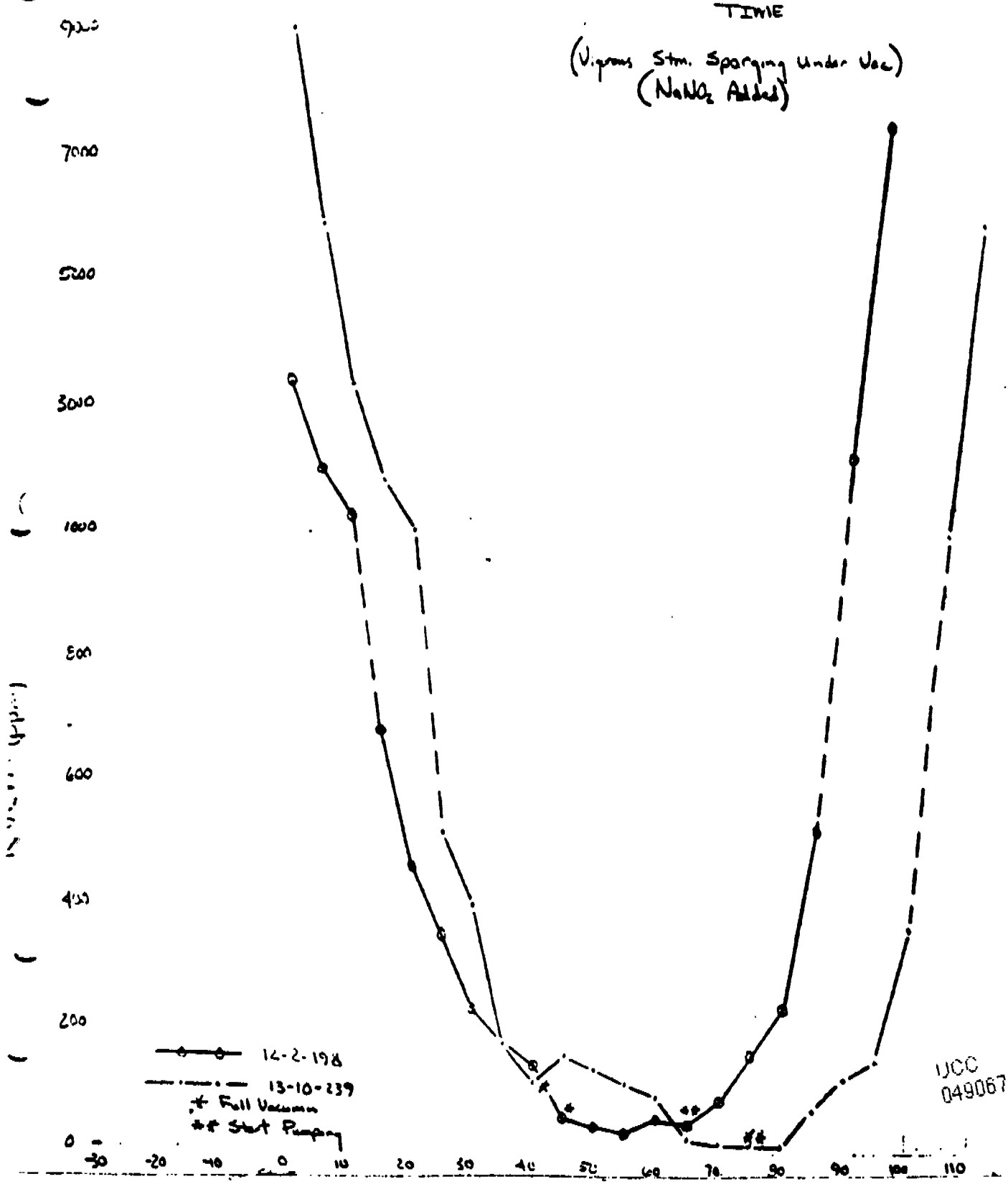
Figure III

RVcm of VSJF
vs
TIME
(Vigorous Stm. Sparging under Vac)
($NaNO_2$ Added)



UCC
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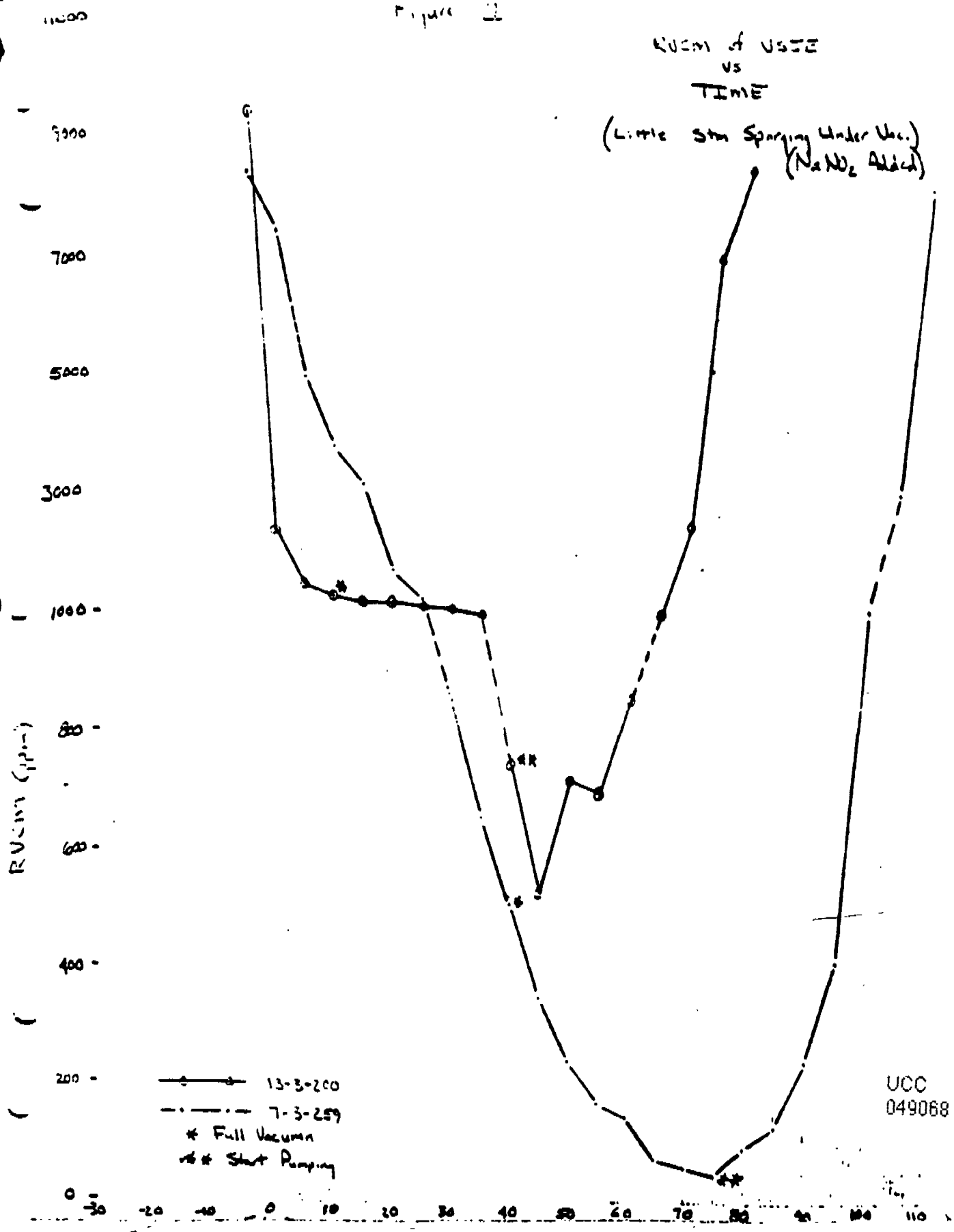
Figure 2


RVOM of USTE
vs
TIME
(Little Stm Sparging Under Vac.)
($NaNO_2$ Added)
RVOM (ppm)
11000
9000
7000
5000
3000
1000
800
600
400
200
0
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
13-3-200
7-3-259
* Full Vacuum
** Start Pumping
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106

UCC
049069

BUSINESS CONFIDENTIAL PROJECT REPORT

SUSPENSION VINYL RESINS

RETARDATION OF COLOR FORMATION AT STRIPPING TEMPERATURES

AUTHOR: D. R. Montgomery

SUPERVISOR: C. E. Moyer, Jr.

DATE: May 4, 1977

PROJECT NO.: 216B12

FILE NO.: 23577

SUMMARY A series of tests have been run to define color stability of PVC resins as a function of time and temperature. These tests were run to simulate slurry stripping conditions plus surge tank residence time in order to find a way to maintain acceptable color while minimizing residual vinyl chloride monomer (RVCM) in suspension resins. A number of additives were evaluated to see if any of them could stabilize PVC resins to the extra thermal abuse needed for better stripping.

The best of these potential stabilizers was found to be sodium nitrite. It has been found that its addition to copolymer slurries (VSJE and VSKK) stabilizes them sufficiently that they can be stripped at temperatures 10-15°C higher than normal with color comparable to conventional resins. These results have been verified in plant trials and resulted in resins with satisfactory color and a significant reduction in the RVCM in the product. Resins from these plant runs have been shown to behave normally in typical enduse formulations.

It has also been found that the addition of other stabilizers (such as Mark C, Mark M, or Bisphenol A) to a sodium nitrite terminated slurry results in significantly accelerated rates of color formation due to reaction of the excess nitrite with the other stabilizers. Obviously cross-contamination of sodium nitrite containing slurries and these other materials, particularly Bis A, must be avoided

Several potential problems with full scale use of this procedure are recognized and further work is planned.

RESEARCH AND DEVELOPMENT DEPARTMENT
CHEMICALS AND PLASTICS
UNION CARBIDE CORPORATION
TEXAS CITY, TEXAS

INTRODUCTION The elevated temperatures required for effective stripping of unreacted monomers from our suspension copolymers, combined with the residence time in the surge tanks and the additional heat during drying, has historically given us trouble with excessive color formation. The recently issued EPA regulation governing vinyl chloride emissions requires a maximum of 400 ppm VCM (calculated on a contained dry resin basis) in slurry leaving the blowdown tanks (BDT). The regulation does allow averaging over all suspension resin production on a twenty-four hour basis. Our copolymer resins (VSJE and VSKK) have very low porosity and are therefore the most difficult resins among our major products from which to strip VCM. Unfortunately, they also have the poorest color stability against thermal abuse. Consequently, we have been unable to utilize the rigorous stripping temperatures that are required to achieve low VCM levels within reasonable times because of resin color limitations. Analyses of RVCM on BDT samples show large fluctuations, ranging from a few hundred to over 10,000 ppm. (Recent data have shown BDT RVCM to be a strong function of when the sample is tak n.) Analyses of dried resin in the bin samples for the first three month of this year indicate an average of approximately 1,200 ppm for VSJE and 1,800 ppm for VSKK. The dried resin RVCM must be lower than the BDT values; a reasonable estimate for an average value of the latter is probably 2-3000 ppm. Certain modifications to the stripping procedures are being investigated which will help, but we also obviously need to be able to utilize higher stripping temperatures if we are to meet the 400 ppm with a reasonable cycle time in the BDT.

RESULTS Color kinetics runs were made at 92°C; a more detailed explanation of the procedure followed and the technique used in evaluating the results is given in the Experimental Section. The primary criteria for comparing results was d(YI)/dt, the change in Yellow Index per hour. The bulk of the work was done with VSJE slurry and unless indicated otherwise, the results reported are for VSJE.

Several potential stabilizers were screened and compared with unstabilized controls. Representative values for d(YI)/dt are given in Table I, along with a tabulation of the final YI obtained after 5½ hours. The most striking results were with slurries which had been killed with sodium nitrite at the termination point, which gave d(YI)/dt considerably less than 1 and final YI ≤10. Other runs with $NaNO_2$ under slightly different conditions actually gave values as low as 0.1 and 6.6, respectively. The results compare quite favorably with the control, 2.2 and 14+. The run containing Irganox 1076 (an antioxidant) was virtually superimposable with the control. Inclusion of EPO (epoxidized soybean oil), used routinely in Production as a stabilizer, actually increased d(YI)/dt to 2.7. This rather surprising result was later duplicated with a completely different batch of slurry. Post-addition of Thermolite 25 (a commercial organo-tin vinyl stabilizer) and Bis Phenol A (used by Production as a short stop and possible stabilizer) gave modest improvements to 1.7. Mark M (a commercial Ba/Cd vinyl stabilizer) gave somewhat b tter results, 1.2. Mark C (an organo phosphite ch lator)

showed substantially improved results initially, 0.4, but then had a break to a higher rate, 1.0.

The results of attempts to combine the $NaNO_2$ treatment with some of the other moderately effective stabilizers, looking for an additive or synergistic effect, were disappointing, An adverse interaction was found with all of the additives tested except EPO, and the rate of color formation became quite high, as illustrated in Table II. This extreme color was subsequently shown co be due to reaction of the excess of aqueous $NaNO_2$ (or HNO_2-the slurries normally exhibit a pH of ~4) with the stabilizers. See Table III for the results of heating aqueous $NaNO_2$ with some of the other additives. Dry resin from $NaNO_2$-treated slurries shows no adverse interactions with the usual stabilizers in end-use tests.[1,2,3]

The possible effect of small amounts of iron was of concern since the Production blowdown tanks are stainless steel. Add d ferric iron at 250-500 parts per billion was shown (Table IV) to have an adverse but not catastrophic effect on the rate of color formation both with and without $NaNO_2$. The presence of a 1 w concentration of disodium ethylenediamine tetraacetic acid (Na_2EDTA) moderates but does not eliminate this effect.

Addition of $NaNO_2$ at the termination of the polymerization was found to be effective at slowing color formation in VSKK also, as shown in Table V. The color retardation was similar to the VSJE results, although not quite as pronounced.

QSAF is the most difficult to strip and was therefore selected to illustrate the benefits which might be possible with the homopolymers. The results, shown in Table VI, indicate a positive effect but since the "control" rate is lower, the benefits are also less spectacular. The initial rate in the Na_2EDTA run was comparatively high but it leveled off quickly and the final color was only 6.5. Polivic S202 is a potential additive to increase porosity[4] and was checked for possible adverse interactions; obviously none were found.

The amount of $NaNO_2$ added to a slurry influences the degree of stabilization achieved although this is not a spectacular effect. Figure 2 shows d(YI)/dt vs $NaNO_2$ concentration for VSKK. These data represent three separate polymerizations in which varying amounts of $NaNO_2$ solution were added to the autoclave at the end of the polymerization with duplicate color kinetics runs on one of them. The average final color (5½ hours) was 9.5. Data on a variety of VSJE slurries shows a large amount of scatter in plots of d(YI)/dt vs $NaNO_2$ concentration although the general trend is toward a stronger effect at higher concentrations. In retrospect there are other factors besides $NaNO_2$ concentration per se that appear to affect its effectiveness at retarding color formation. These factors were not recognized at the time many

of the experiments were designed and thus not adequately controlled. Specifically, acidity of the slurry is of overriding importance. A sodium nitrite treated slurry lost over half of its apparent stabilization when it was neturalized to pH=7 with $NaHCO_3$ before heating. Comparative data are given in Table VII. A rationale for this effect will be offered in the discussion of mechanistic interpretations.

Aliquots of the same slurry were run at 92°C, 80°C and 70°C for both VSJE and VSKK to derive an activation energy for the color forming reaction. The data are tabulated in Table VIII and plots of log (d(YI)/dt) vs 1/T are given in Figure 3. Derived Ea's are 19 and 22 kcal/mole, respectively.

DISCUSSION

Mechanistic interpretations

Several tentative conclusions as to the mechanisms of color development and its retardation can be drawn from the results described above. Further confirmation will be sought for some of the key points. The rate of color development at 70-92°C, as measured by d(YI)/dt, gives reasonable results when treated as a pseudo first order reaction. This does not mean, however, that the actual reactions taking place which give rise to the color are necessarily first order. The commonly accepted source of color when PVC is heated is conjugated carbon-carbon unsaturation due to dehydrochlorination along the backbone of the polymer. On this basis the "percent completion" of the total potential reaction is extremely low and the normal treatments of kinetic data which require several half-lives of the reaction are obviously not applicable. Also, YI is not necessarily a linear function of the extent of dehydrochlorination. Even with these limitations several interesting conclusions can be made.

The firmest conclusion at this point involves the basis for the pH effect on the effectiveness of $NaNO_2$ as a color retarder. This is almost certainly a matter of the concentration of a species which can penetrate the resin particles to where the pertinent reactions are occurring. Nitrite ion per se should be transported very inefficiently, at best, into the resin particle from an aqueous medium. On the other hand, HNO_2 (or nitrogen oxides derived from it) should have a much improved rate of penetration. Calculations indicate addition of 0.003 moles/liter of $NaNO_2$ to an unbuffered pH=4 slurry would result in approximately 3% hydrolysis with a HNO_2 concentration of $8.7X10^{-3}$ and pH=4.9. If this slurry had its pH raised to 7, the HNO_2 concentration would drop to $6.7X10^{-7}$. One would then conclude that the only reason the neutralized slurry retained even as much stability as it did would be because it had existed as an acidic slurry with HNO_2 in it for a considerable time before the neutralization and HNO_2 in partially effective concentration had already penetrated the resin

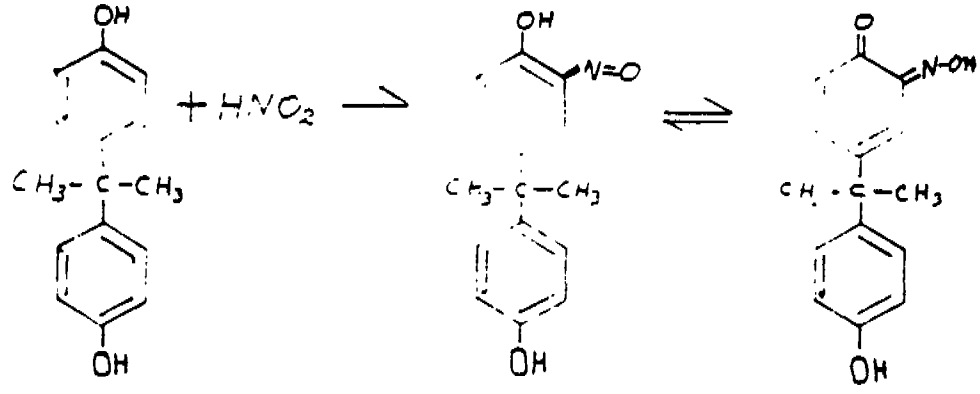
and was not completely neutralized. This HNO_2-as-effective-ingredient interpretation is consistent with reports that $NaNO_2$ is ineffective as a short-stop reagent for those who practice a buffered polymerization. As a corollary to the reduced effectiveness in neutralized slurry, if the pH were lowered to 3, the same amount of $NaNO_2$ would be 28% hydrolyzed with a HNO_2 concentration of $8.3X10^{-4}$. Alternatively, only about 5% as much $NaNO_2$ would have to be added to give the same effective HNO_2 concentration in a pH3 slurry as compared to a pH4 slurry. For example, if the slightly lower pH could be tolerated, addition of 2 lbs of 35% HCl (appropriately diluted) and 0.5 lb of $NaNO_2$ per production batch should give approximately the same stabilizing effect as the 10 lbs of $NaNO_2$ per batch used in the plant tests. The same principle should also apply to the emergency short-stop procedures. It should be noted, however, that acidified solutions of $NaNO_2$ could probably not be made up in advance and stored for extended periods of time because of the instability of nitrous acid. The importance of pH was not recognized early in the experimentation described above, therefore was not controlled, and likely accounts for much of the variability observed when attempting to correlate $NaNO_2$ concentration with d(YI)/dt.

The fact that the rate of observed color development decreases with time within the frame of our measurement even though the percentage loss of HCl is very low suggests that some species is present in low concentration which is substantially more reactive than the bulk of the resin and that this concentration does decrease significantly. It would then be this reactive species which must be intercepted to provide color stability during our stripping and drying operations. The mechanisms of thermal degradation of PVC and of its stabilization have been extensively studied for many years and the literature is replete with conflicting theories. For a recent review with extensive references, see for example Reference 5. It is obviously beyond the scope of this work to settle these controversies; I can only speculate based on what I observed. The fact that HNO_2 is a very potent retarder for color development strongly suggests that a radical is involved since nitrite is a potent free-radical inhibitor and is in fact used in the suspension vinyls unit to kill "hot" reactions. The radical could be involved in the propagation of the dehydrochlorination, as espoused by Gupta and St. Pierre[4], or, alternatively, the initiation of the reaction could involve primary radicals generated from the residual peroxide which is present in the resin. The residual peroxide could be an appropriate species which is present in low concentration and would disappear at a significant rate at the temperatures utilized.

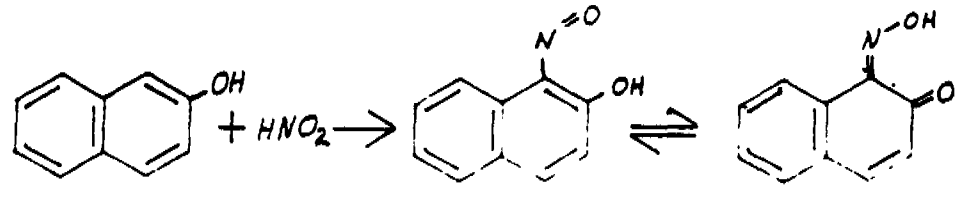
The 20 kcal activation energy observed for the overall color formation process is consistent with usual values for organic reactions[7]; free-radical reactions in general would be expected to be somewhat higher[8]. Attempts to derive an entropy of activation for further information as to type of reaction were unsuccessful, since such calculations are dependent upon

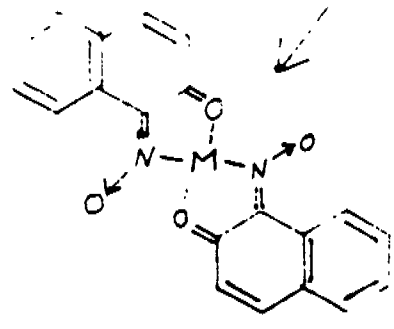
the absolute value of the [illegible] constant, and all that is available in this case is a pseudo-first-order rate coefficient, the magnitude of which is dependent on the units used by the measuring device.

The green color observed when Bisphenol A and $NaNO_2$ are used in the same slurry is likely due to acid-catalyzed nitrosation of the phenolic ring as follows:



Close analogies exist in the literature, e.g., the reaction with β-naphthol.[10]





Metal lake of nitroso-β-naphthol green with M=Fe

The specific reactions between NO_2^- and Mark C and Mark M are not so obvious but it is clear that all of these highly-colored reactions involve the excess NO_2^- (HNO_2) present in the water and there are not sufficient residues on the resins after drying to cause any problems.

The destabilizing effect of EPO at 92 , although disturbing, is not necessarily inconsistent with its presumed stabilizing effect during ambient temperature storage. The author has had previous experiences in solvent vinyls where propylene oxide definitely stabilizes color of varnishes at ambient temperatures but ethylene oxide in a solution heated at 60°C caused an increase in color formation. Epoxides are frequently used as vinyl stabilizers, presumeably functioning as HCl traps. However, the epoxy group possesses considerable basicity and it appears likely that at higher temperatures it may function as a strong enough "pull" to accelerate the dehydrochlorination reaction.

Practical Applications

The laboratory studies have shown that addition of $NaNO_2$ to copolymer slurries after the prescribed termination pressure drop has been reached will provide a significant retardation in the rate of color development at stripping temperatures. This increment of stabilization can be utilized either to provide improved color at normal stripping temperatures or to allow higher temperatures, and thus faster removal of RVCM, with comparable color. In either case no contact of the nitrited slurry with Bisphenol A can be allowed because of the side reaction leading to a green color. The $NaNO_2$ can be used in combination with EPO if this is felt to be desireable for color stability during dry resin storage, although the color generated during stripping with EPO will be slightly higher than without it. (The latter statement holds whether $NaNO_2$ is used or not.) Low concentrations of Na_2EDTA can also be included in the polymerization without adverse interaction with the $NaNO_2$. The nitrite treatment is more effective in a "normal" moderately acidic reaction slurry (pH ∿4) and loses much of its benefits in a buffered or neutralized recipe. It would be equally effective at reduced concentrations in a more acidic slurry, e.g., pH ∿3.

Short term trials have been made at the production unit with both VSJE and VSKK. Representative data from these tests are given in Tables IX and X. (Data courtesy of Mr. Steve Dickerson.) These tests demonstrated clearly that significantly higher than "normal" stripping temperatures can be utilized while still maintaining good resin color, if the slurry is treated with $NaNO_2$. As anticipated, the RVCM levels drop much more rapidly at the higher temperatures. Resin from these tests was recovered and subjected to several end-use tests. In all cases it was found to be indistinguishable from "normal" resins.[1,2,3] It is therefore recommended that an extended plant trial be undertaken for a more comprehensive evaluation of the benefits which can be derived from this technique (as well as a reading on the seriousness of some potential problems). During this trial, the entire copolymer line should be run on the test, to avoid any cross-contamination. The test should be of sufficient duration to obtain reliable answers to questions of optimum conditions and procedures in the production equipment and what quality (RVCM vs color)of resin can be produced under our best currently available technology. In regards to timing, it might well be desireable

to wait until the new transfer system from the blowdown tanks to the surge tank is available on the North line, to allow routine pumpout under vacuum without suffering a loss in capacity.

Several production-related problems remain to be answer d.

1.) Bird effluent water is normally used to rinse the autoclaves between batches. If we run $NaNO_2$ routinely on one (or more) lines, will we see retardation of subsequent polymerizations due to traces of $NaNO_2$ in the rinse water?

2.) Nitrites in the water to the waste treatment plant could potentially be a problem. The concentrations that would be present would be extremely low and should not be a significant hazard. However, we intend to pursue this point in detail with the EP Department.

Experimental

The resin slurries for the tests were prepared in the Suspension Vinyls Pilot Plant. Some of the stabilizers test d were added to the initial charge (if normally employed in that manner), some were added to the autoclave after the polymerization was completed, and others were added to the slurries in the laboratory. All slurries were stripped thirty minutes at 85°C in the Pilot Plant blowdown tank, then portions were saved for subsequent laboratory experiments.

The color kinetics experiments were carried out in th laboratory in a jacketed resin kettle equipped with an agitator and a bottom stopcock for periodic withdrawal of samples. Wat r was heated in an auxilliary kettle and circulated through the jacket. Most of the experiments were run at 92°C slurry temperature, the maximum at which we could conveniently control. The apparatus was glass except for the agitator which was stainless steel.

The procedure followed was to preheat the jacket water, then add the slurry (approx 2700 g) to the kettle. The first sample was taken when the slurry reached 80°C (about forty-five minutes after heating started). The slurry reached the control temperature of 92°C in about another 20-25 minutes. Subsequ nt samples were taken at intervals for a total of 5½ hours. Th extended time was intended to simulate the thermal exposure production resin experiences in the blowdown tank plus the surge tank. The resin was recovered from the samples by filtration and dried in a circulating air oven at 40-45°C. The drying op ration did not significantly affect the color of the resin. The color of each sample was then determined with the Gardner XL 20 Colorimeter. This instrument shines white light on the sample, then measures green, amber, and blue components of the reflected light and computs a composite value called the "Yellow Index" (YI). This number is basically a measure of the yellowness of the resin although other colors do influence it. UCC internal specifications call for a 10 max YI for copolymers.

The results were evaluated by plotting YI vs time. These plots exhibit reasonable straight line characteristics for the early points (up to 60-150 min), before tending to flatten out at long times and/or high YI. The slope of a best-fit line through these early points, d(YI)/dt, units=change in yellow index per hour, was taken as a measure of the rate of color formation for purposes of comparing runs. Figure 1 illustrates typical plots. The final YI's after 5½ hours are also reported in the tabulated data, since the ultimate color at the end of processing is the important practical property.

Conclusions and Further Recommendations

The addition of sodium nitrite to compolymer slurry provides a remarkable retardation of color formations at temperatures useful for stripping residual monomer from the resin. Specifically, we should be able to raise our stripping temperature by as much as 10°C (e.g., from 80° to 90°) and retain as good or better color as we currently get.

Continuation of plant evaluation of the procedure is recommended, as outlined above.

Additional laboratory work is indicated to clarify several points regarding the mechanism of stabilization.

a.) Spectral examination of the resin to attempt to identify the chromophore.

b.) Test other free radical inhibitors to see if they provide substantial color retardation.

c.) Explore more fully the effect of pH upon nitrite stabilization.

Acknowledgements

The kinetic runs were carried out by H. R. Nowlin. Color measurements were made by S. A. Dickerson. Polymerizations were done by D. W. O'Daniel. Their assitance is gratefully acknowledged.

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[1]S. A. Dickerson, letter dated February 2, 1977, to D. R. Montgomery, Subject: "Color Development of $NaNO_2$ Killed VSJE in VAT Application."

[2]R. P. Braddicks, personal communication to D. R. Montgomery, March 3, 1977.

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[10]R. Q. Brewster, Organic Chemistry, Prentice Hall, 1948, p. 719.

D. R. Montgomery

D. R. Montgomery

/kw

Attachments

10 Tables
3 Figures

Manuscript Date: April 7, 1977
Revised: April 20, 1977

PRIVELEGED

DOCUMENT

Bates number UCC049080 – 049081 has been skipped

106

MEMORANDUM

EVALUATION OF

B. F. GOODRICH'S CONTINUOUS STRIPPING TECHNOLOGY

FOR

PVC RESIN SLURRIES

by

W. R. Manning

12-20-76

INTRODUCTION

This memorandum presents for record purposes an account of the evaluation that was made by Union Carbide in late 1975 and early 1976 of B. F. Goodrich's technology for continuous stripping of PVC resin slurries. The memorandum comprises a main section and four appendixes. The main body describes the maj r steps in the evaluation and presents the conclusions that were reached. The appendixes give pertinent details about each of the major steps.

DISCUSSION

In August of 1975, Dr. A. B. Steele, Operations Manager for Suspensi n Vinyl Resins, received a technical bulletin (copy attached as Appendix A) from Mr. Arthur L. Hastings, Licensing Manger for B. F. Goodrich Chemical Company, outlining a new continuous PVC slurry stripping process developed by Goodrich. Such a process was of possible interest to Union Carbide, as well as other PVC manufacturers, as an aid in complying with OSHA and proposed EPA regulations on the amount of vinyl chloride monomer that could be left in PVC resins or emitted to the environment.

After a secrecy agreement was executed between B. F. Goodrich and Union Carbide, Mr. A. A. Peterson and Dr. W. R. Manning visited the Avon Lake, Ohi plant of B. F. Goodrich on September 9, 1975 to receive additional details about the process, and to discuss the terms and conditions under which Union Carbide might acquire a license to use Goodrich's process. A copy of Mr. Peterson's report on this visit is also attached. (Appendix B).

Pursuant to Goodrich's offer to run samples of Carbide resin slurry through their six-inch, eight-tray pilot plant column to predict operating conditions and results for a production-sized column, we sent 55-gallon drums of three resin slurries from our production process:

QSAN	Homopolymer Resin
QSQH	Ethylene-Modified Resin
VSJE	Vinyl Acetate Copolymer Resin

The QSAN homopolymer resin and the QSQH ethylene-modified resin were run successfully in Goodrich's pilot-plant column, and samples of th stripped resin were returned to us. According to Goodrich, the VSJE vinyl acetate copolymer could not be run because of excessive foaming. (It should be noted that Goodrich developed their stripping technology primarily for homopolymers; they do not manufacture vinyl acetate copolymers.)

The results of our evalution of the stripped samples of QSAN and QSQH returned by B. F. Goodrich are shown in Appendix C (letter to A. A. P terson from R. M. Arnold, dated December 11, 1975). Briefly, the results showed that the Goodrich process achieved little or no improvement in residual vinyl chloride over our own batch vacuum stripping technology, and the resins stripped by the Goodrich process were much more highly colored than those from our process due to the heat-abuse of the resins in the Goodrich process.

CONCLUSIONS

The results of the B. F. Goodrich stripping tests were reviewed by the Vinyl Resins Operations Team at a meeting in Texas City on February 18 and 19, 1976. The team concluded that we should not pursue our investigation f the B. F. Goodrich process any further, because:

1. We were achieving low residual monomer on homopolymer with our batch vacuum stripping process, without excessive heat abuse of the resin.

2. Copolymers are even harder to strip than homopolymers (except low molecular-weight homopolymers) and Goodrich had been unsuccessful in running our copolymer in their pilot unit.

3. Goodrich did not seem really eager to license their process to us, as indicated by the slowness with which they provided results of their tests to us. The tests were run between November 4 and November 16, 1975. A formal report, dated December 28, 1975, was not received by us until February 25, 1976, and then only after a telephoned request on February 13, 1976. A copy of this report is attached as Appendix D.

W. R. Manning
12-20-76

APPENDIX C

JAN 16 1976

UNION CARBIDE

INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

TO (NAME) Mr. A. A. Peterson
COMPANY Building 114
LOCATION TEXAS CITY PLANT

DATE December 11, 1975

COPY TO Dr. J. C. Chaty
Mr. M. E. Eisenhour
Mr. R. L. Frantz
Dr. D. R. Montgomery
Mr. R. W. Sesler
Mr. G. F. Tacquard
Mr. R. N. Wheeler - 514

SUBJECT Results of B. F. Goodrich Stripping Residual Vinyl UCC Suspension Resins

106

Dear Adolph:

Samples of QSQH-7 and QSAN-7 were supplied to B. F. Goodrich's Research Center, Brecksville, Ohio, for pilot plant tests to remove residual vinyl chloride via their patented continuous stripping operation. These samples were obtained from the blow down tanks before vacuum stripping. Both resin samples contained residual VCM exceeding 10,000 ppm.

These resins were subjected to varying residence times and temperatures at Goodrich in an effort to remove the maximum amount of residual vinyl chloride. Samples were taken at each test condition and returned to Texas City for evaluation. Results of these resin samples after stripping are shown in the attached Table.

Reduction of the residual VCM, particularly with regard to QSQH-7, is considered to be a slight improvement over the current UCC production. However, the extreme stripping conditions (> 100°C) also resulted in severe resin degradation as shown by the high yellow factors. Stripped samples of VSJE-10 supplied to Goodrich have not been received.

Please let me know if additional information is desired.

Very truly yours,

R. M. Arnold

/kw
Attachment

Still have not been received.
1/14/76

UCC
049086

RESULTS OF B. F. GOODRICH PILOT PLANT PROGRAM

CONTINUOUS STRIPPING OF UCC SUSPENSION VINYL RESINS TO REMOVE VINYL CHLORIDE MONOMER

Resin Type	Sample Designation	Test Conditions (Minutes/°F)	Residual VCM, ppm		Yellow Factor
			Initial	After Stripping	
QSAN-7			11,690	BFC DATA	1.0
	1104 A	6.4/236 °C 113		6 2.6	7.8
	1104 B	7.4/236 "		3 1.5	9.0
	1104 C	6.9/216 102		21 11.0	9.1
QSQH-7			20,283		1.0
	1120 A	5.8/236 113		32 27	7.0
	1120 B	6.9/235 -		11 9	9.9
	1120 C	6.9/214 101		61 54	7.2

APPENDIX C

Typical QSAN, batch vacuum stripped 1/2 hr. at 85°C, has same or lower VCM content and color in 2.0-4.0 range. This is as yellow that it would be

RMA:kw

12/11/75

UCC 049087

106

UCC
049088

APPENDIX D

106

Project 7716-75
December 28, 1975

Stripping Tests on Union Carbide's PVC Resin Slurries in the 6-Inch Development Column

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

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 c - polymer.

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 ach 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.

APPENDIX D

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.

APPENDIX D

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

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 c lumn 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.

APPENDIX D

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 th 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, c llection 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 rat 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 rec ives 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 resid nce 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

APPENDIX D

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. Accurate 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 estimat s 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 n 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 c ld 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

APPENDIX D

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 col red.

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 add d 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 r sidence 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 to strip slurry from one level of vinyl chloride to any other level can be estimated. In using the.e 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 c lumn.

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 f trays is the controlling factor and not the residence time. Similar data were obtained during development work with the 30-inch, 17-tray c lumn. 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 als

APPENDIX D

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 the effluent discharge from the bottom tray. Because of higher levels and longer time on the two top trays plus heat up of the 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:

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

G. R. Huddleston

E. J. O'Connor

pl

Column Operating Data

Resin	Table I Homopolymer			Table II Ethylene-modified PVC			Table III Vinyl Acetate Copolymer
Identification Number	QSAN			QSQH			VSJE
Run Number	1104A	1104B	1104C	1120A	1120B	1120C	1113
Column Pressure, psig	8	8	1.5	8.5	8.25	1.25	17-inch Hg vacuum
Bottom Temperature, °F	236	236	216	236	235	214	170
Seconds between Pulses	45	60	60	45	60	60	run unsuccessful
Feed, #/hr.	108.1	91.9	105.5	99.5	78.7	87.0	
Slurry, % Solids	--------33.7---------			------- 23.8--------			
Resin, #/hr.	36.43	30.97	35.55	23.68	18.73	20.71	
Steam, #/hr.	51.9	53.1	57.8	50.3	51.3	57.3	
Steam/Resin Ratio	1.42	1.71	1.63	2.12	2.74	2.77	
Feed Temperature, °F	151	153	154	136	144	145	
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.

Project 7716-75
December 28, 1975

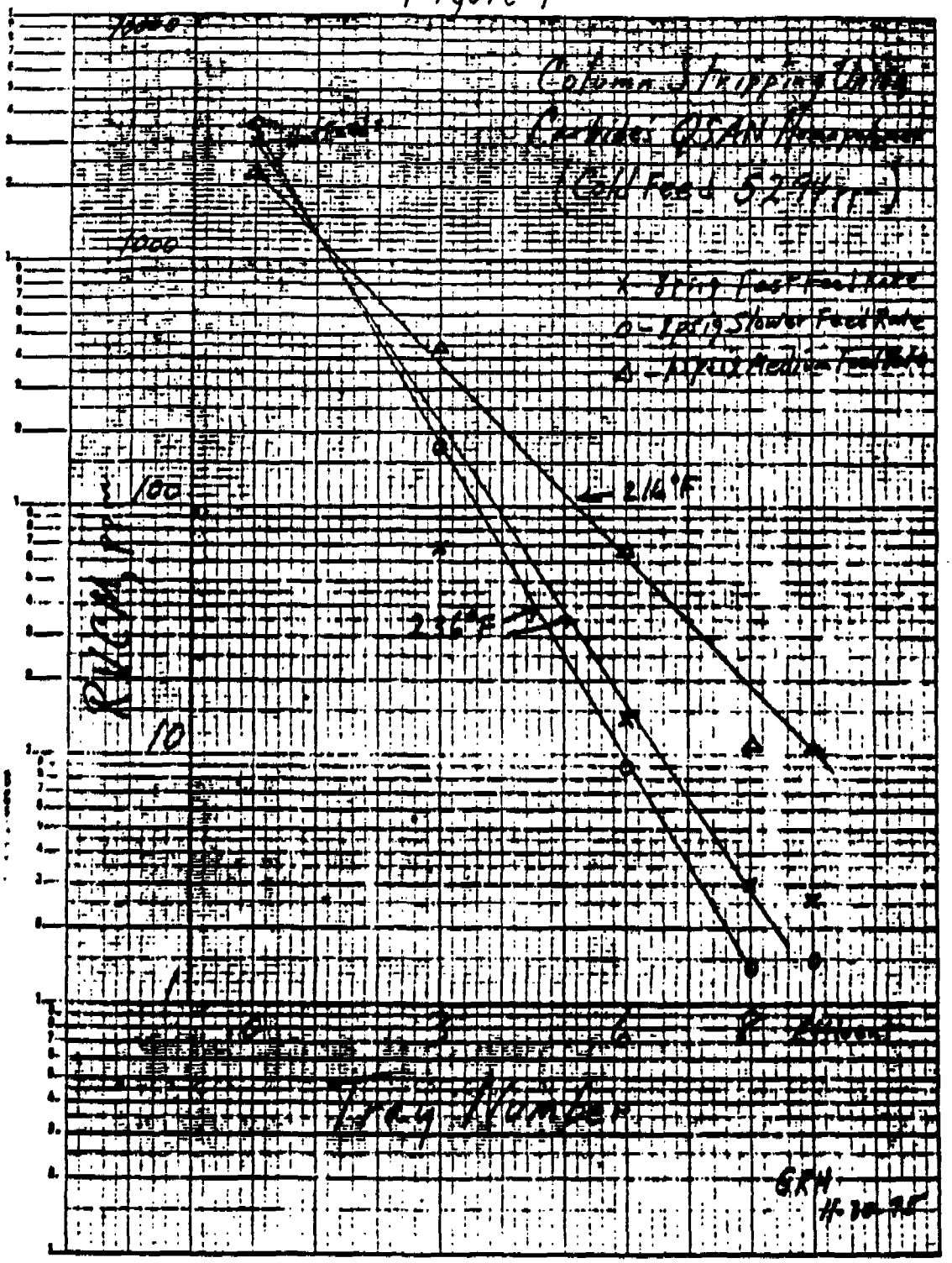
TABLE IV

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	

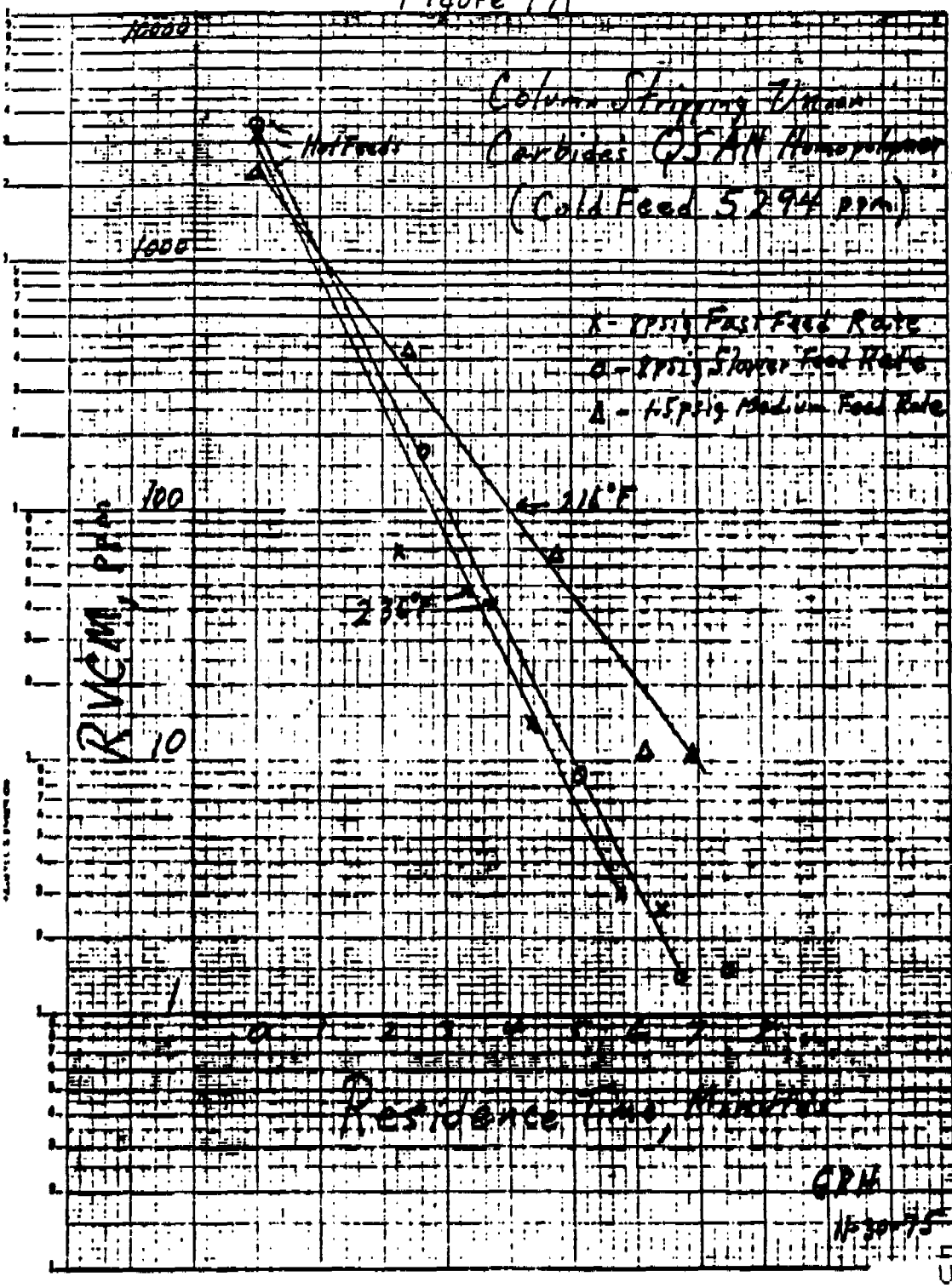
APPENDIX D

Figure 1



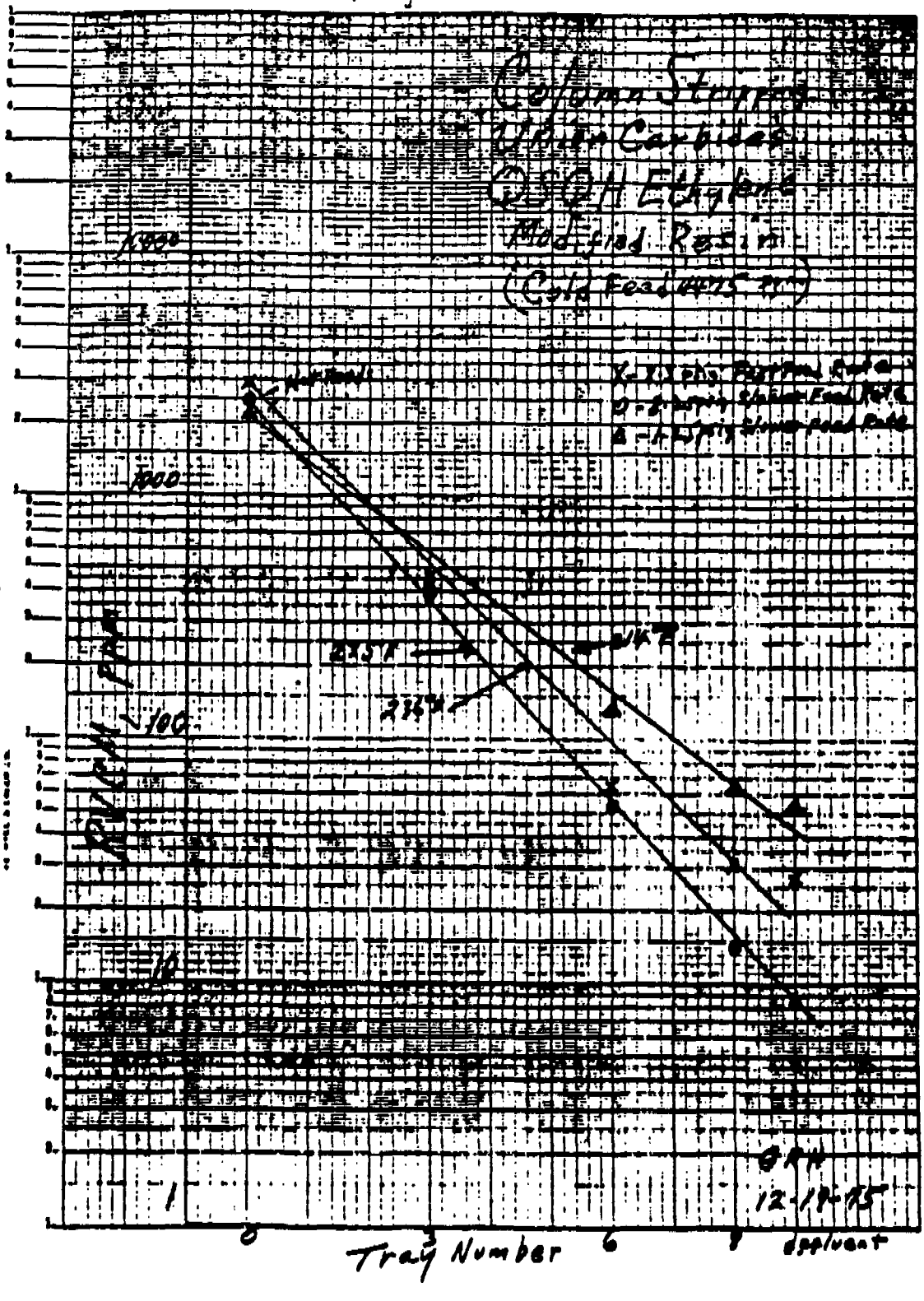
APPENDIX D

Figure 1A



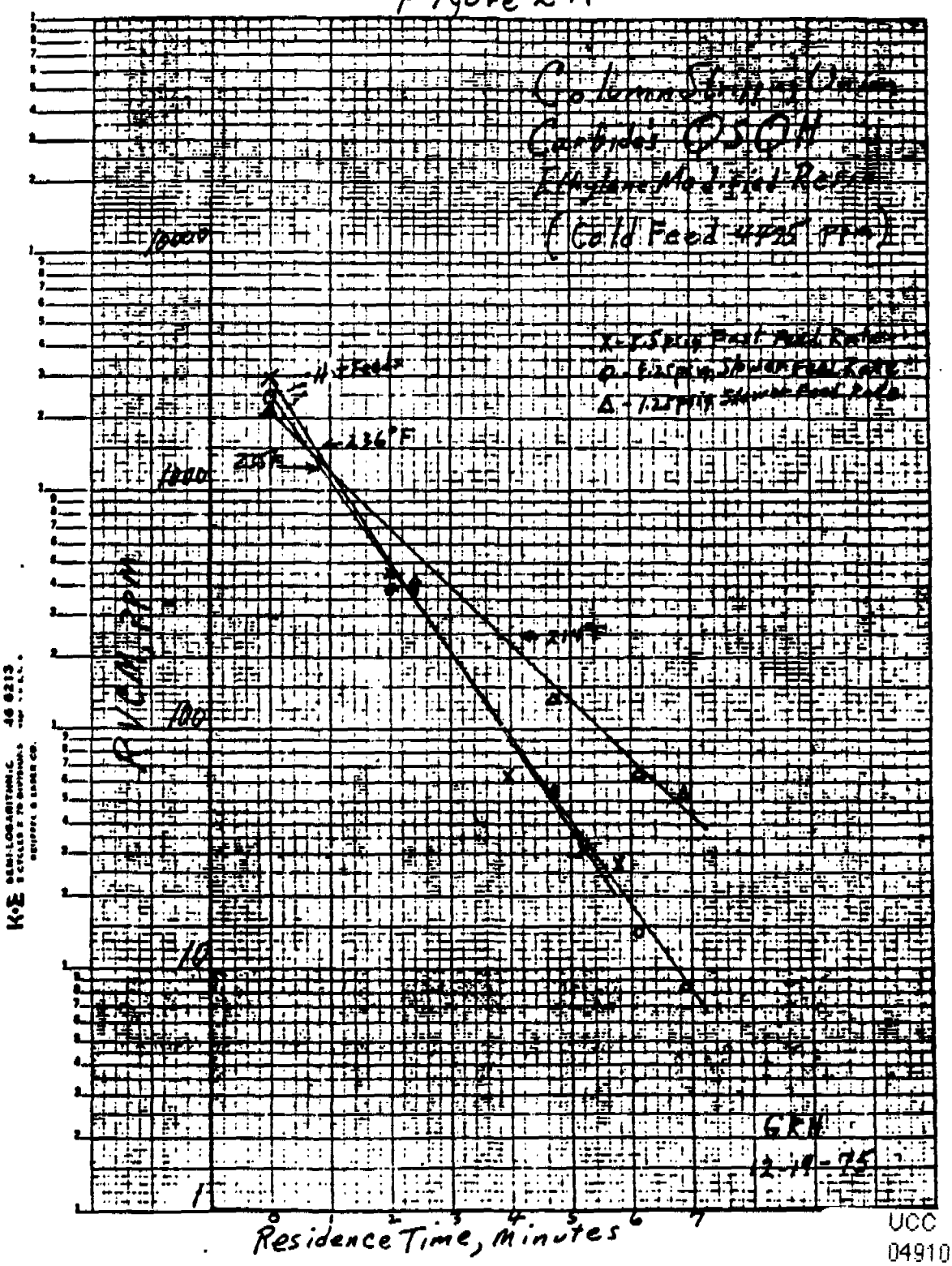
APPENDIX J

Figure 2



APPENDIX D

Figure 2A



106

UNION CARBIDE INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

TO (NAME) Mr. R. L. Frantz
COMPANY
LOCATION Texas City Plant

DATE January 13, 1976

COPY TO Dr. R. J. Anderson, 312
Mr. M. E. Eisenhour
Mr. J. B. Hollingsworth, NY (28)
Dr. D. R. Montgomery
Mr. F. S. Provenzano
Mr. G. F. Tacquard/S. A. Dickerson
[redacted]

SUBJECT Residual VCM After Stripping

JAN 17 1977

R N WHEELER JR.

For the past month samples of the slurry leaving the unit after stripping have been taken and analyzed for residual VCM and color in order to develop reliable information to determine exactly where we stand on meeting the upcoming EPA regulations limiting VCM concentrations to an average of 400 ppm leaving the stripping vessels. This letter is to update you on the information that has been collected to date.

With the Suspension slurries, duplicate samples of individual batches were taken, the batch number, termination pressure drop, BDT and stripping conditions were recorded. Likewise, single samples of the Non-Solvent slurry leaving the flash tank were taken and conditions recorded.

The complete results are listed in the following tables and summarized below:

106

Resin Type	Prescribed Stripping Conditions Temp	Time	Vacuum	Color	Residual VCM
QSAP	85°C	30 min	15"	3.4	78
VSJE	85°C	30 min	15"	6.3	1115
QSAL	85°C	30 min	15"	3.4	144
QSQF	85°C	30 min	15"	5.1	840
QSAN	85°C	30 min	15"	4.0	836
QSAN	80°C	30 min	15"	4.2	537
VSKK	80°C	30 min	15"	7.9	1455
QSAH	85°C	30 min	15"	5.6	1256
QYNL	83°-85°		11" - 14"	3.7	248

In looking at the complete data in the tables, the results in some cases are quite variable with several obvious inconsistencies. (Those results identified with an asterisk (*) were not included in the averages.) More information will be gathered to help resolve the discrepancies.

Rick Keefe

RK/st
Attachments

TABLE I

QSAP

Date	Batch No.	Δ P	BDT	Conditions Temp	Conditions Time	Conditions VAc	Color	VCM
12/6/76	6-10-187	-	-	85°	30 min	15"	3.4 3.3	81 76

Suspending Agents: F-50; K-J

Additives: Bis-A at 10# Δ P

TABLE II

VSJE

Date	Batch No.	ΔP	BDT	Conditions Temp	Time	VAc	Color	VCM
12/6/76	11-15-357	-	-	85°	30 min	15"	6.0 5.9	1091 1033
12/6/76	8-3-358	-	#3	85	25	15"	6.6 6.6	1256 1078

Suspending Agent: HEMC

Additives: Bis-A; EPO; Irg. 1076

TABLE III

QSAL

Date	Batch No.	Δ P	BDT	Conditions Temp	Time	VAc	Color	VCM
12/6/76	22-3-95	-	-	85°	30 min	15"	2.8 2.8	932* 938*
12/20/76	6-11-16	-	-	83	40	18"	3.8 3.8	169 166
12/21/76	2-12-22	-	#1	85	20	15"	3.0 3.0	119 121

Suspending Agents: F-50; K-J

Additives: EDTA

TABLE IV

QSQF

Date	Batch No.	Δ P	BDT	Conditions Temp	Time	VAc	Color	VCM
12/8/76	20-12-10	15#	-	85°	30 min	15"	-	496
			-				-	468
12/9/76	20-1-20	0#	-	85	45	15	-	1465
			-				-	1497
12/11/76	21-5-43	40#	-	85	30	18	5.2	1056
			-				5.2	1073
12/10/76	24-1-32	0#	-	85	30	12	4.9	4039*
			-				4.9	3572*
12/12/76	22-11-61	0#	-	86	40	19	5.3	204
			-					355
12/13/76	17-4-65	0#	-	86	45	16	4.7	540
			-					589
12/14/76	25-11-75	0#	-	85	30	16	5.0	339
			-					382
12/15/76	26-9-80	5#	-	85	25	16	4.3	860
								660
12/16/76	25-1-86	0#	-	85	40	18	5.6	1929
								1696
12/16/76	18-8-87	25#	-	83	40	18	5.5	1003
			-					942
12/17/76	24-6-97	10#	-	82	30	12	5.1	1549*
								1539*
12/17/76	18-9-98	10#	-	80	30	13	5.3	626
			-					635

Suspending Agents: F-50; K-J

Additives: Irg. 1076; Bis-A @ 20# Δ P

TABLE V

QSAN

Date	Batch No.	Δ P	BDT	Conditions Temp	Time	VAc	Color	VCM
12/8/76	2-9-6	12#	# 1	80°	30 min	15"	-	737
							-	252
12/10/76	4-9-27	45#	# 1	80	40	15	3.8	445
								408
12/11/76	5-9-30	10#	# 1	80	30	16	4.4	282
								280
12/13/76	1-6-46	6#	# 1	80	30	16	5.2	816
								953
12/14/76	2-3-53	0#	# 1	80	30	18	3.9	194
								198
12/15/76	6-7-57	5#	# 1	80	25	13	3.9	850
								252
12/16/76	4-1-66	10#	# 1	85	45	18		226
								213
12/17/76	2-7-74	25#	# 1	80	20	18	3.9	327
								550
12/17/76	3-6-76	15#	# 1	85	30	15	3.8	153
								149
12/20/76	17-2-5	12#		85	30	14	3.9	1488
								1243
12/20/76	18-1-6	20#		85	20	14	4.4	1642
								1574
12/12/76	1-5-36	0 #	# 1	80	30	15	4.2	1000
								1051

Suspending Agents: F-50; K-J

Additives: EDTA; Irg. 1076

TABLE VI

VSKK

Date	Batch No.	Δ P	BDT	Conditions			Color	VCM
				Temp	Time	VAc		
12/21/76	9-3-22	66#	#2	80°	40 min	15"	9.4	2824 1134
12/28/76	12-7-51	63#	#3	55	120	15	6.1	7239* 7359*
12/28/76	15-7-53	25#	#2	80	40	15	-	1520 1076
1/4/77	9-3-131	90#	#2	80	60	15	-	962 988
1/4/77	10-2-132	85#	#3	80	20	15	-	3391 1665
1/4/77	7-13-133	70#	#2	80	15	15	-	1275 1333
1/5/77	7-15-149	75#	#3	80	30	15	6.4	1175 1405

Suspending Agents: HEMC; F-50

Additives: Bis-A; EPO

TABLE VII

QSAH

Date	Batch No.	Δ P	BDT	Conditions Temp	Time	VAc	Color	VCM
1/4/77	20-5-42	90#	#3	85°	30 min	16"	-	385 416
1/4/77	17-8-45	120#	#5	85	30	15	-	696 653
1/5/77	22-6-46	30#	#3	85	30	15	5.6	2741 2624

Suspending Agents: F-50; K-J

Additives: EDTA; EPO

106

UC 149-

UNION CARBIDE INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

P. O. BOX 471, TEXAS CITY, TEXAS 77590

TO (NAME) Mr. R. H. May
COMPANY Building 114
LOCATION TEXAS CITY PLANT

DATE July 7, 1976

COPY TO Mr. M. E. Eisenhour
Mr. R. L. Frantz
Mr. A. A. Peterson
Mr. G. T. Pyle
Mr. G. F. Tacquard
Mr. R. N. Wheeler - 514

SUBJECT

JUL 12 1976

R N WHEELER JR.

Dear Ross:

At your request, spot samples of VYNW were obtained from the slurry tank, dryer feed (off the Bird) and dryer to determine residual vinyl chloride. These data are shown in the attached table.

The data indicate that a reduction of residual VCM from approximately 2000 ppm to < 50 ppm occurs during various drying stages at Building 120.

Please let me know if additional information is desired.

Very truly yours,

R. M. Arnold

/kw
Attachment

106

UCC
049116

106

BFG TECHNICAL DOCUMENT

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
Research Center

Project 7716-75
December 28, 1975

Stripping Tests on Union Carbide's PVC Resin Slurries in the 6-inch Development Column

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

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 stabl 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.

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.

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

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. Accurate 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 23.5%.

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

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 orarge 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 to 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

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 the effluent discharge from the bottom tray. Because of higher levels and longer time on the two top trays plus heat up of the 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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E. J. O'Connor

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Column Operating Data

Resin	Table I Homopolymer			Table II Ethylene-modified PVC			Table III Vinyl Acetate Copolymer
Identification Number	QSAN			QSQH			VSJE
Run Number	1104A	1104B	1104C	1120A	1120B	1120C	1113
Column Pressure, psig	8	8	1.5	8.5	8.25	1.25	17-inch Hg vacuum
Bottom Temperature, °F	236	236	216	236	235	214	170
Seconds between Pulses	45	60	60	45	60	60	run unsuccessful
Feed, #/hr.	108.1	91.9	105.5	99.5	78.7	87.0	
Slurry, % Solids	-------33.7---------			------- 23.8--------			
Resin, #/hr.	36.43	30.97	35.55	23.68	18.73	20.71	
Steam, #/hr.	51.9	53.1	57.8	50.3	51.3	57.3	
Steam/Resin Ratio	1.42	1.71	1.63	2.12	2.74	2.77	
Feed Temperature, °F	151	153	154	136	144	145	
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.

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	

Figure 1

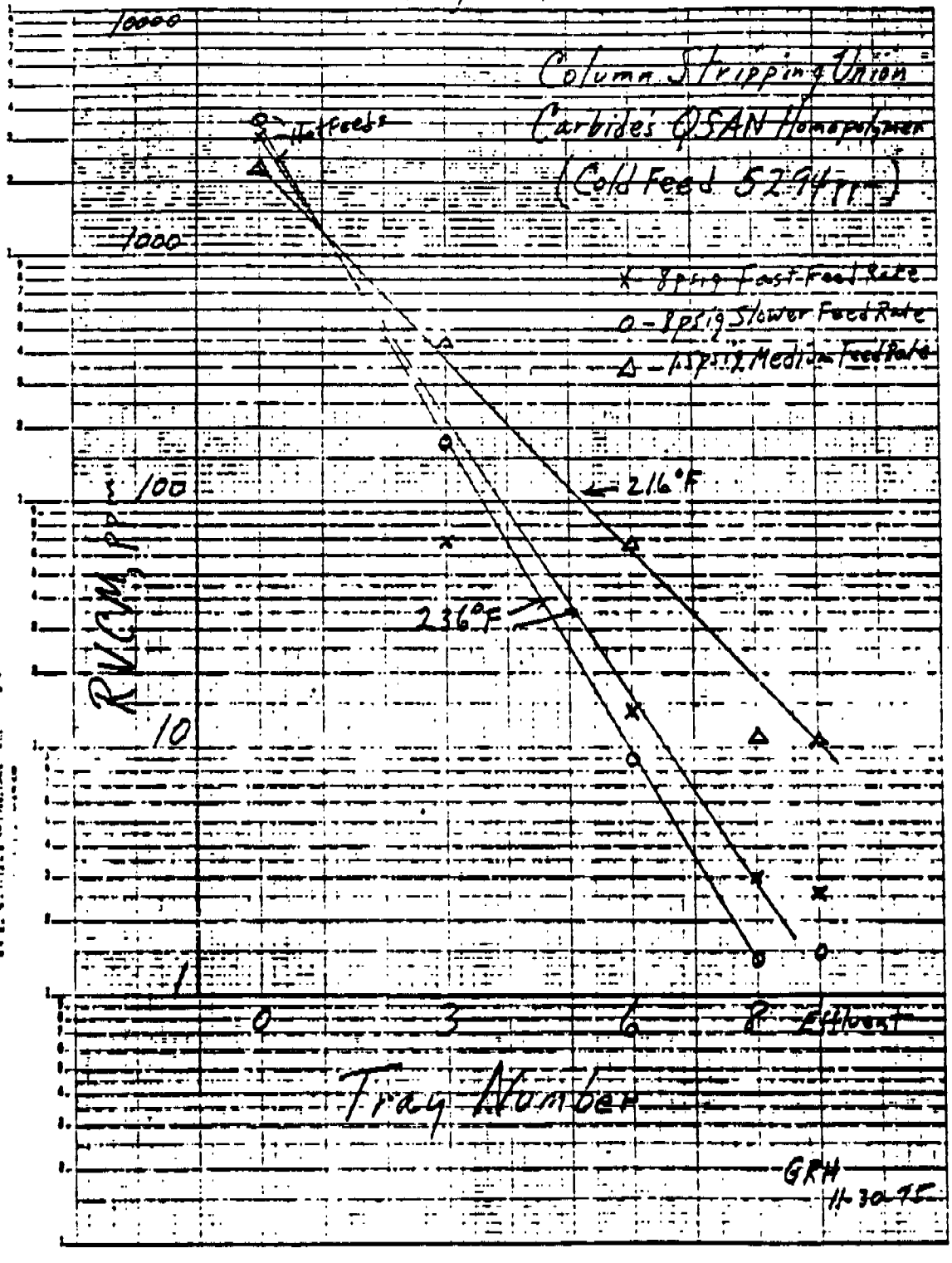


Figure 1A

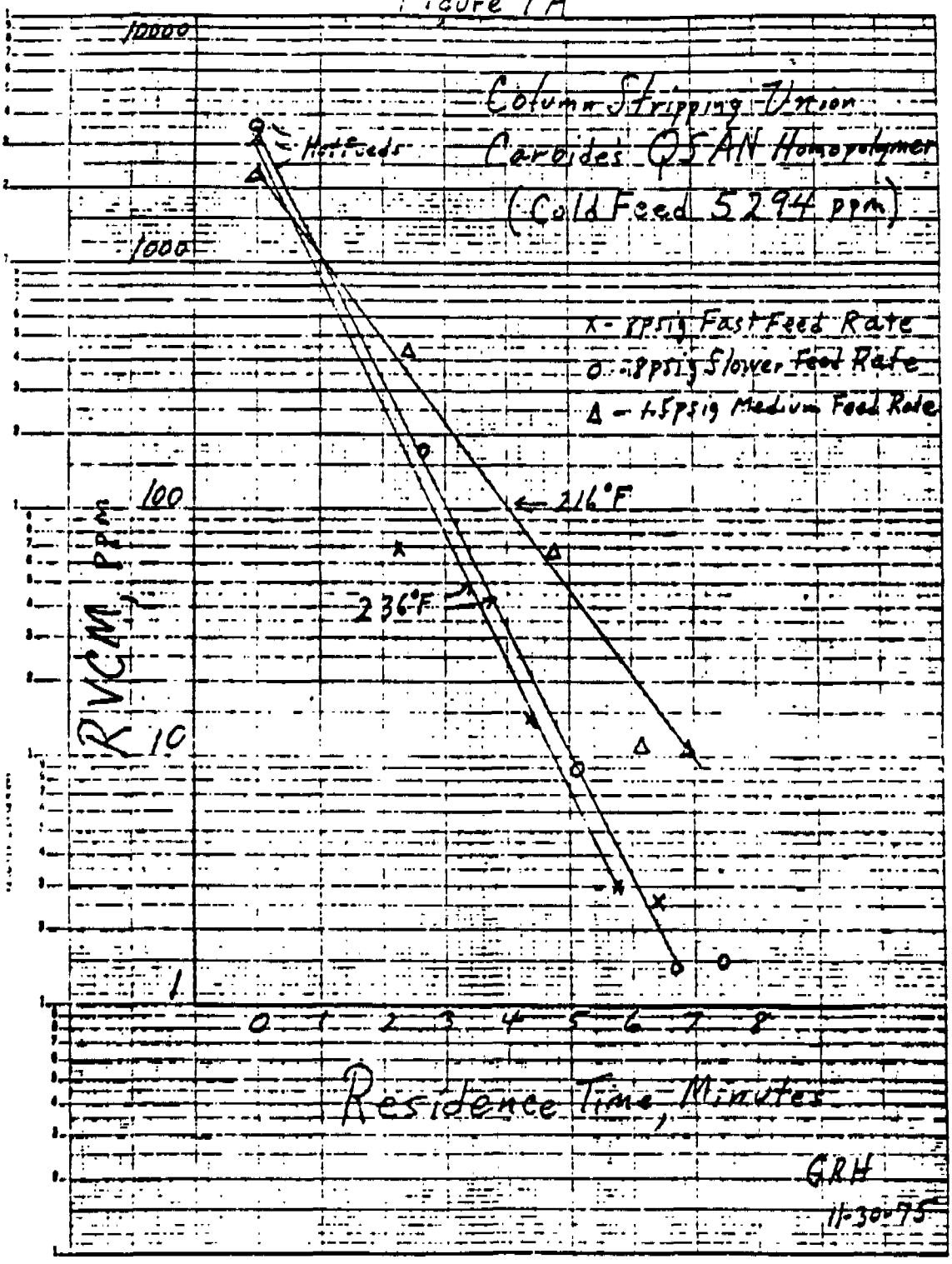


Figure 2

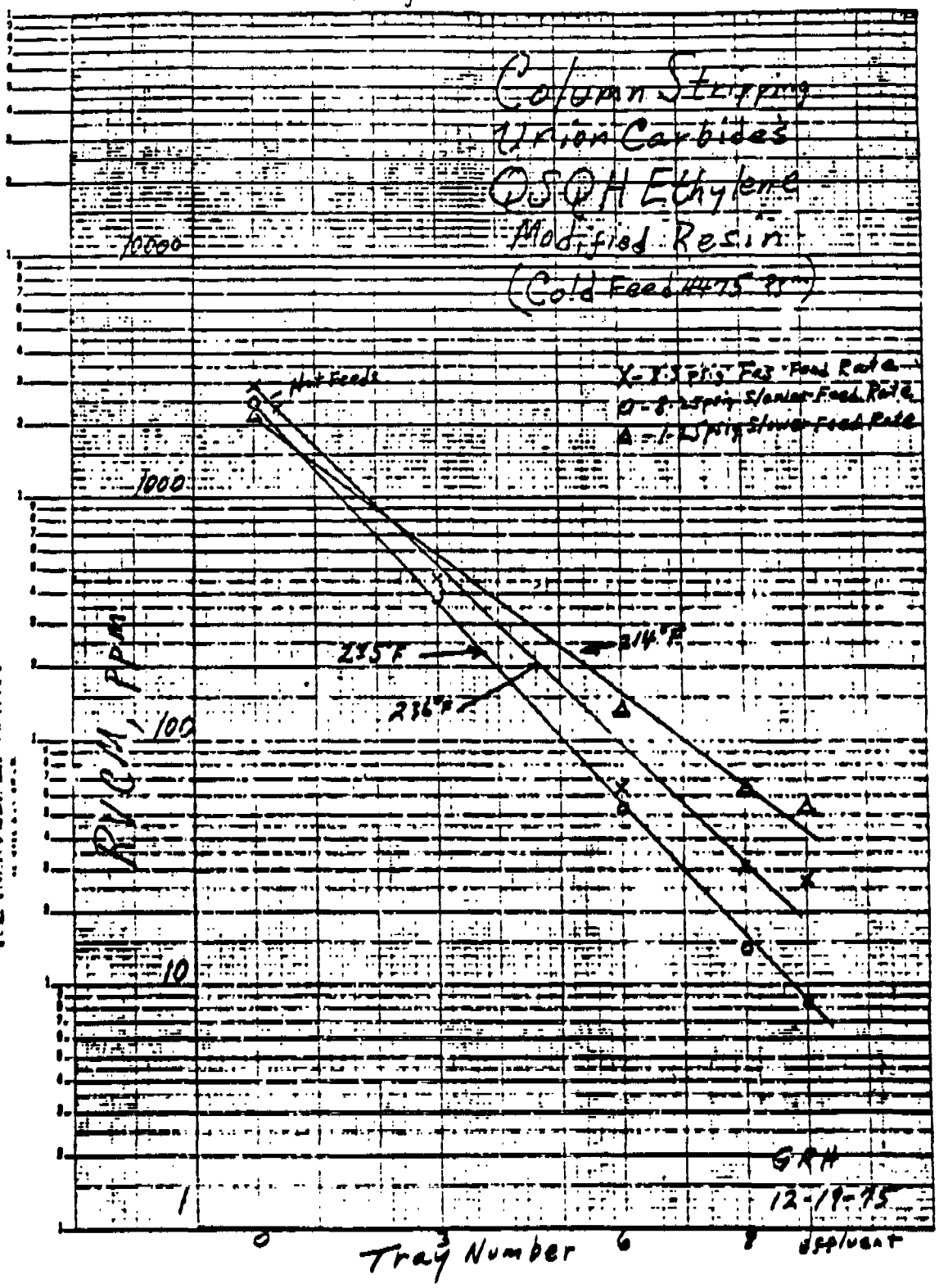
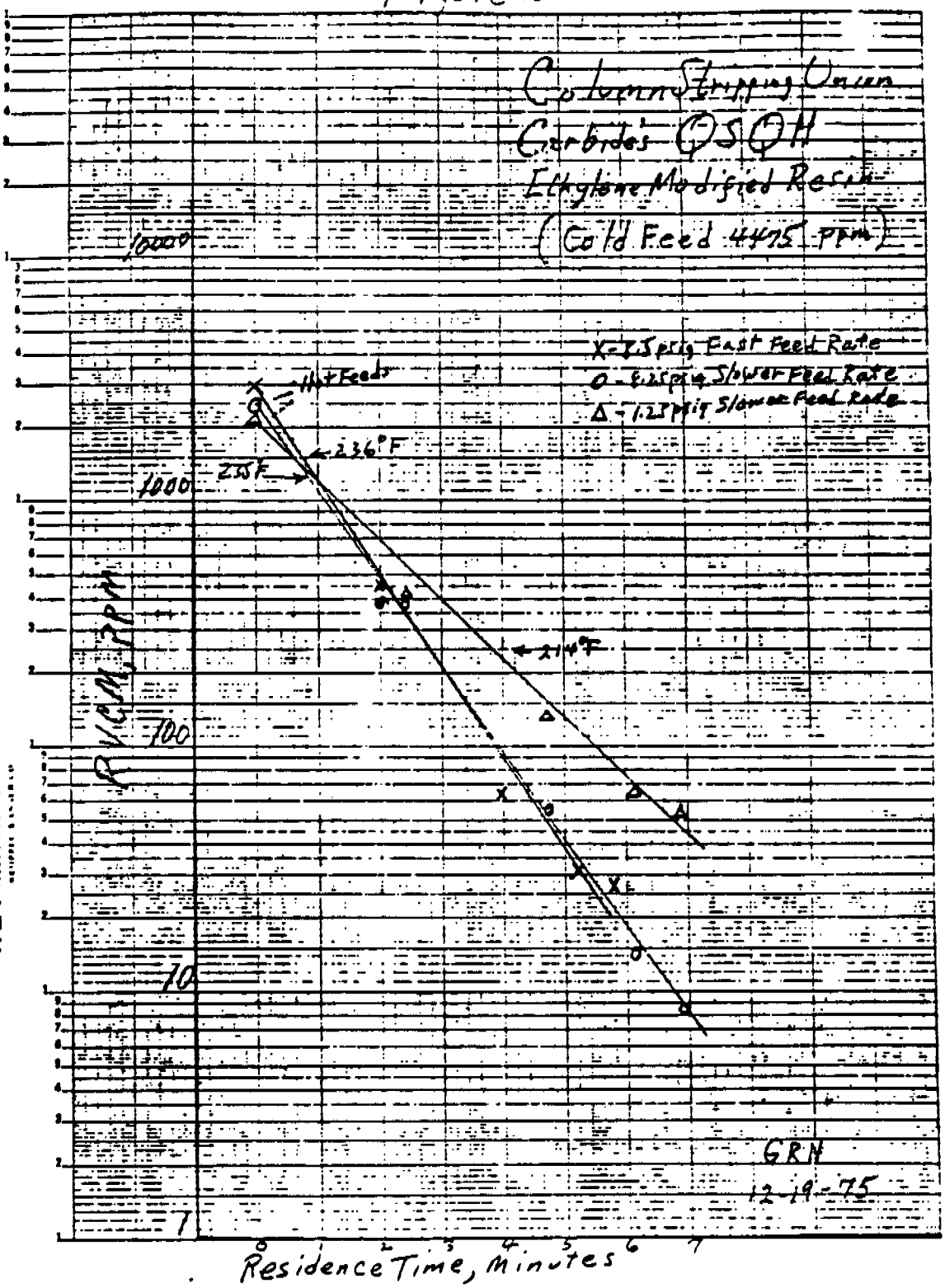


Figure 2A



106

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DOCUMENT

Bates number 049135 – 049157 has been skipped

102

Q. How are vinyl chloride vapors removed from autoclave before entr

A. Autoclave is filled with 130°F water to displace vinyl chloride vapc to the gas holder.

Q. What is the operating pressure of the gas h

A. The gas holder operates at 22-inches H_2O gas holder (Type C). 102 a

Q. How long does it take to fill autoclave with water to displace vinyl chloride vapors? Where does the water go?

A. It takes 12 minutes to fill autoclave and 15 minutes to empty. Water is not re-used -- it goes to the waste treatment area.

Q. What type of water is used to fill autoclaves?

A. Raw, lake water is used.

Q. What is stated capacity of plant?

A. Annual production capacity of plant is 125 MM pounds.

Q. After maintenance finish cleaning autoclave, how is it pressure tested?

A. Again, autoclave is filled with water and hydrostatically tested.