

STATUS REPORT

SUSPENSION VINYL RESINS RESIDUAL VINYL CHLORIDE IN QSAN HOMOPOLYMER AS FUNCTION OF STRIPPING CONDITIONS

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Date: June 28, 1974

Supervisors: Dr. J. C. Chaty
Mr. R. L. Frantz

Project No. 216B10
File: 19631

SUMMARY

Because of potential pressure by OSHA and EPA to reduce residual vinyl chloride monomer in resin distributed to processors, a study was undertaken to determine the effects of vacuum stripping conditions on the residual VCl in the general purpose homopolymer QSAN. In brief, the most significant variable was shown to be stripping temperature. At 90°C stripping temperature, all samples, regardless of time, studied amount of vacuum (as long as one exists), or particle size, the residual VCl was 70 ppm or less. Moreover, three of the four samples stripped at 90°C contained 10 ppm or less VCl for an average of 20 ppm. Current production resin (QSAN) being stripped at 70°C and 15 inches of vacuum contains an average of 275 ppm VCl. An increase from 70 to 80°C in stripping temperature should lower the residual VCl to 100 ppm or less. This increase was made on the North and East lines on June 14, 1974 based on these results and recommendations.

A multiple regression analysis was also run on the data. It confirmed the eyeball analysis of the graphed data but also provided the following results: (1) for each 10°C increase in stripping temperature the residual monomer decreased by 550 ppm, (2) for each .25 hour of exposure time the monomer decreased by 160 ppm, and (3) for each 5 inches of vacuum the monomer content decreased 260 ppm. The temperature accounted for 65% of the variability.

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DISCUSSION

Figure VI shows the apparatus used in this experiment. Normal production homopolymer (165 micron QSAN) and a pilot plant sample of 100 micron size QSAN were evaluated in this series of tests. The samples were taken as slurry samples out of the blowdown tank immediately after venting the high pressure residual monomer to the recovery system. The procedure used for stripping the slurry samples is contained in the Appendix.

The first test proved unreliable (Table I) because of the procedure of drying the stripped resin overnight in the oven. Even the unstripped sample analyzed as "nil" after being in the oven overnight. Thus the procedure was changed to delete the oven drying and simply run residual VCl on the decanted wet cake (running total solids on each sample to allow calculations on a resin basis).

Table II shows the results of the second test which utilized the procedure of the first test sans the oven drying. Figures I, II, and III show the results of residual VCl versus the stripping conditions. Only stripping temperature showed a significant trend in affecting the residual VCl in the resin.

Table III shows the result of the third test which varied only time and temperature at 15 inches of vacuum on each sample. The vacuum decreased to 9 inches at 90°C because of boiling. Figures IV and V show the plots of the residual VCl versus temperature and time. Here again with as little as 15 minutes exposure time, temperature was the controlling factor.

A multiple regression analysis was run on the data using midpoints of the following: 50°C stripping temperature, 22 inches of vacuum, and about 40 minutes of exposure time. The resulting equation relating the residual monomer to the stripping conditions is as follows:

$\text{ppm VCl} = 1634 - 228 (\text{time}) - 1641 (\text{temp}) - 361 (\text{VAC})$, where time is + 20 minutes, or about 10 ppm/minute, temp is plus or minus 30°C or about 55 ppm/°C, and VAc is plus or minus 7 inches or about 51 ppm/inch of vacuum in the range of the experimental conditions (20° - 90°C, 15 minutes - 1 hour, and 15 - 29 inches of vacuum).

CONCLUSIONS AND RECOMMENDATIONS

From these brief, but consistent, experiments, it is concluded that stripping temperature is the most important variable in the reduction of residual vinyl chloride in QSAN homopolymer. It is recommended that the stripping temperature be gradually increased in production equipment to reduce residual VCl (which is subsequently recovered) while, at the same time, monitoring potentially affected resin characteristics such as heat stability, dryblend time, contamination, and fisheyes.

Adolph A. Peterson

Notebook Reference: Process Studies
Notebook No. 9114 4 - DER, pp 29 - 37

Appendix: Three tables
Six figures
Two procedures

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TABLE I
OVEN DRIED SAMPLES OF VACUUM
STRIPPED PRODUCTION QSAN

<u>Sample Number</u>	<u>Stripping time (Minutes)</u>	<u>Temperature (°C)</u>	<u>Vacuum (inch Hg)</u>	<u>Residual VCl (ppm)</u>
1	15	27	26.9	Nil
2	60	25	28.7	39
3	15	50	24.2	10
4	60	50	26.0	Nil
7	15	22	15.0	22
8	60	22	15.0	12
9	15	50	15.0	23
10	60	50	15.0	Nil
11	15	80	15.0	Nil
12	60	80	15.0	Nil
unstripped	-	-	-	Nil

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TABLE II

FIRST VALID TEST OF RESIDUAL VCI
AS FUNCTION OF STRIPPING CONDITIONS

Ab Aug 1-760 - (H₂O) (from H₂/in)

<i>Bulky</i>	Sample Number	Stripping time (Minutes)	<i>P⁰</i> mHg	Temperature (°C)	Vacuum (inch Hg)	<i>Ab</i> Residual VCI (ppm)	<i>water</i> Temp, °C
<i>Prob</i> yes	1	60	15.477	18	29.3	2269	18.4
NO	2	15	18.65	22	28.5	3381	32.2
NO	3	15	21.068	23	15.0	3245	81.5
NO	4	60	22.377	24	15.0	3193	81.5
NO	5	15	107.20	53	15.0	2672	81.5
<i>Prob</i> yes	6	15	75.65	46	26.6	1603	48.2
NO	7	60	71.88	45	15.0	1803	81.5
<i>Prob</i> yes	8	15	35.51	80	15.0	124	81.5
NO	9	60	64.8	43	26.0	1357	57.5
NO	10	60	149.38	60	15.0	163	81.5
Unstripped sample of 165 micron QSAN						3398	

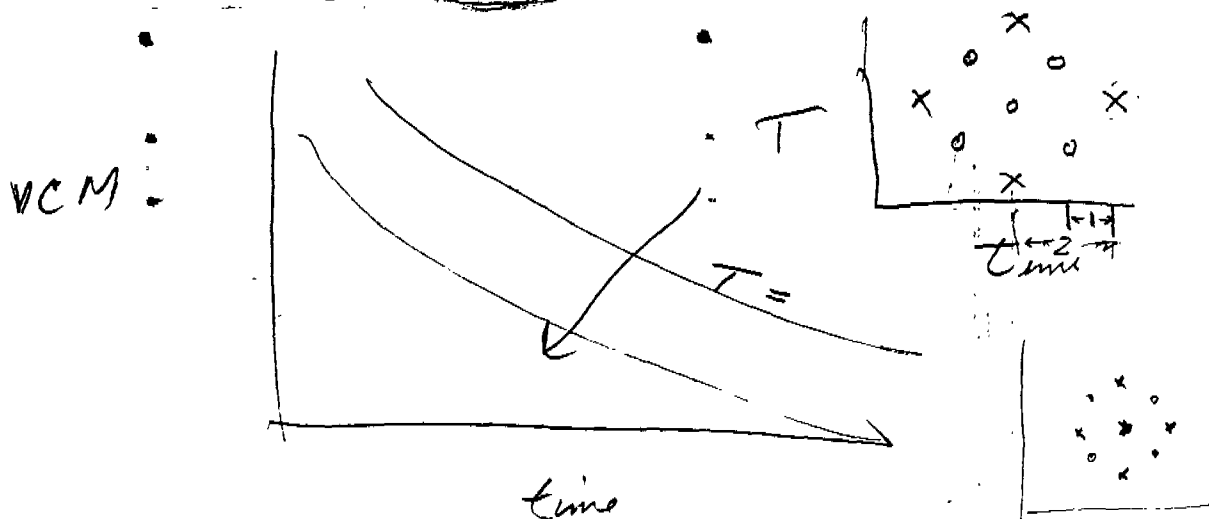
<i>Bulky</i>	Sample Number	Stripping time (Minutes)	<i>P⁰</i> mHg	Temperature (°C)	Vacuum (inch Hg)	Residual VCI (ppm)
<i>Prob</i> yes	1A	60	15.477	18	29.3	2234
NO	2A	15	18.65	22	28.5	3475
<i>NO</i>	3A	15	25.209	26	15.0	4177
NO	4A	60	26.739	27	15.0	3765
NO	5A	15	97.2	51	15.0	2524
<i>Prob</i> yes	6A	15	75.65	46	26.6	1389
NO	7A	60	124.82	57	15.0	1652
<i>Prob</i> yes	8A	15	35.51	80	15.0	69
yes	9A	60	107.2	53	26.0	1041
<i>Prob</i> yes	10A	60	355.1	80	15.0	138
Unstripped sample of 100 micron QSAN						4446

TABLE III

SECOND VALID TEST OF RESIDUAL VCI
AS FUNCTION OF STRIPPING CONDITIONS

<i>Residual VCI</i>	Sample Number	Stripping time (Minutes)	<i>pH</i> pH	Temperature (°C)	Vacuum (inch Hg)	<i>ppm</i> Residual VCI (ppm)	<i>water</i> 100 e. H. obs. ppm
<i>no</i>	1	60	149.38	60	15	1161	81-82
<i>no</i>	2	15	149.38	60	15	2021	00
<i>no</i>	3	60	289.1	75	15	218	00
<i>yes</i>	4	60	525.76	90	9	2	90.3
<i>yes</i>	5	15	525.76	90	9	62	00
<i>no</i>	6	15	289.1	75	15	305	81-82
Unstripped sample of 100 micron QSAN						5100	

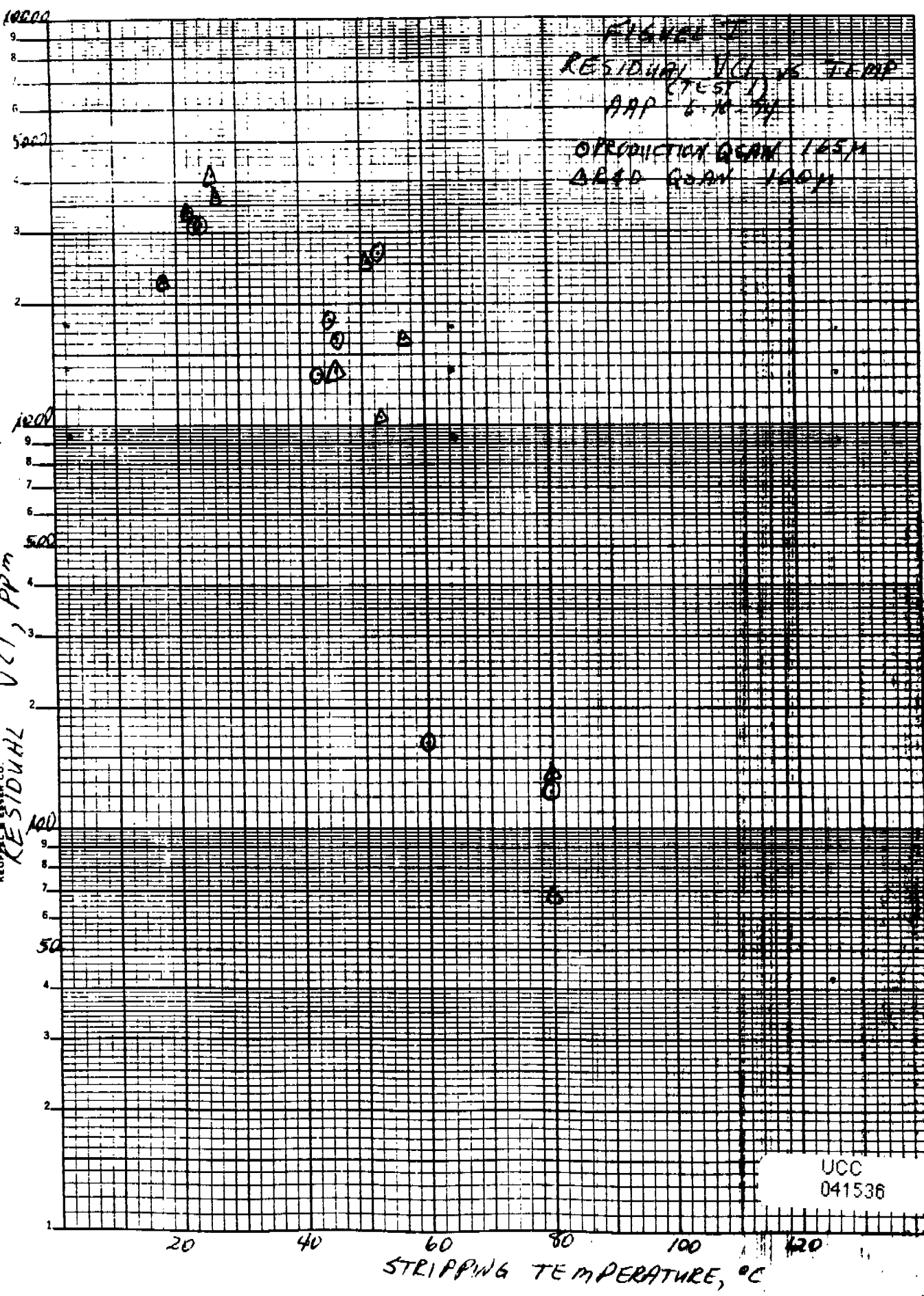
<i>yes</i>	1A	60	525.76	90	9	10
<i>yes</i>	2A	15	525.76	90	9	trace
<i>no</i>	3A	15	289.1	75	15	304
<i>no</i>	4A	60	289.1	75	15	199
<i>no</i>	5A	60	149.38	60	15	2075
<i>no</i>	6A	15	149.38	60	15	2084
Unstripped sample of 165 micron QSAN						5068



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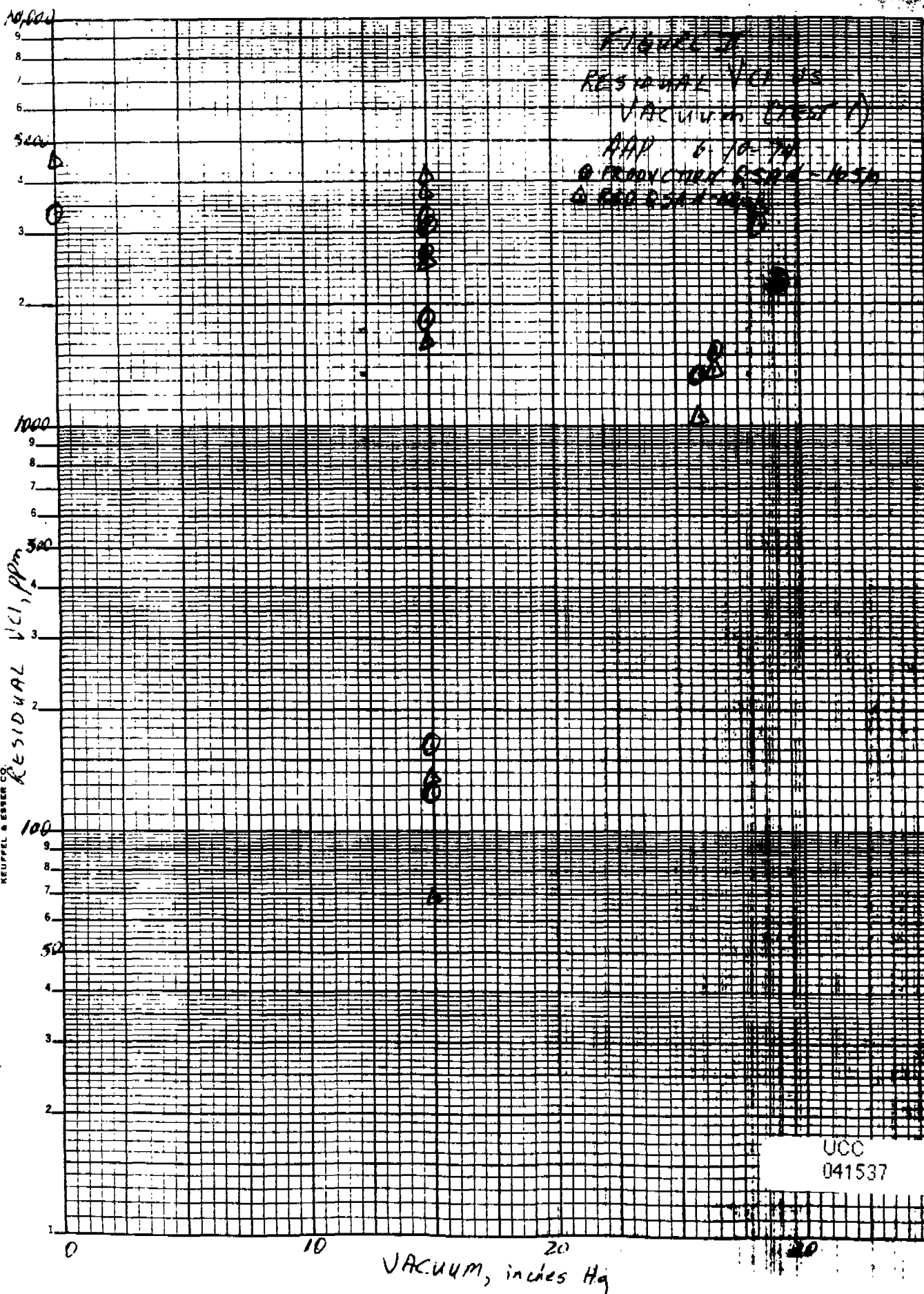
K^oE SEMI-LOGARITHMIC 4 54 3
 3 CYCLES X 70 DIVISIONS
 KEUFFEL & ESSER CO. MADE IN U.S.A.

RESIDUAL VCI, PPM



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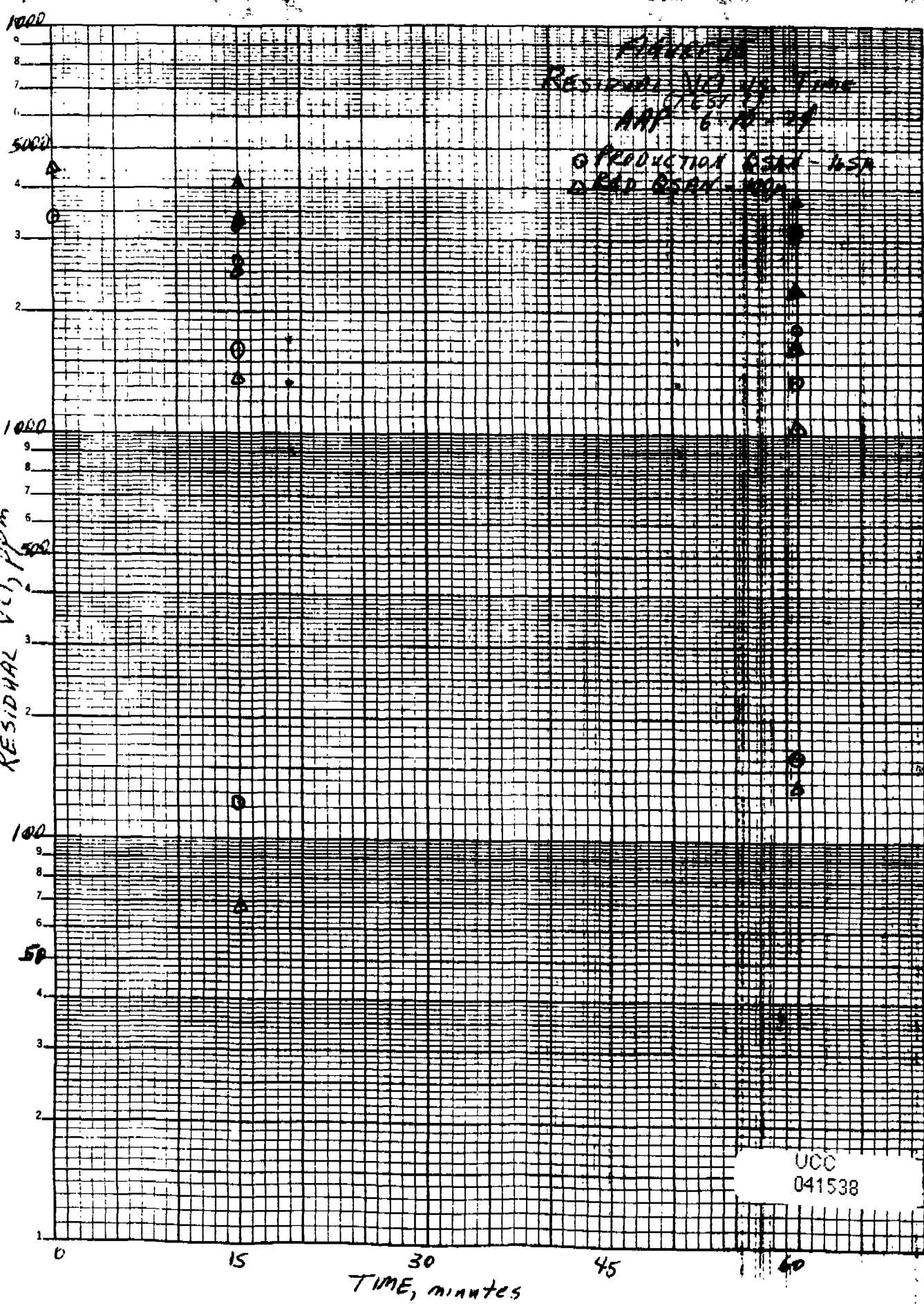
K-E SEMI-LOGARITHMIC 46 5493
 NEUFEL & ESSER CO. MADE IN U.S.A.



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K.E. SEMI-LOGARITHMIC 46 5493
 3 CYCLES X 70 DIVISIONS
 KEUFFEL & ESSER CO. MADE IN U.S.A.

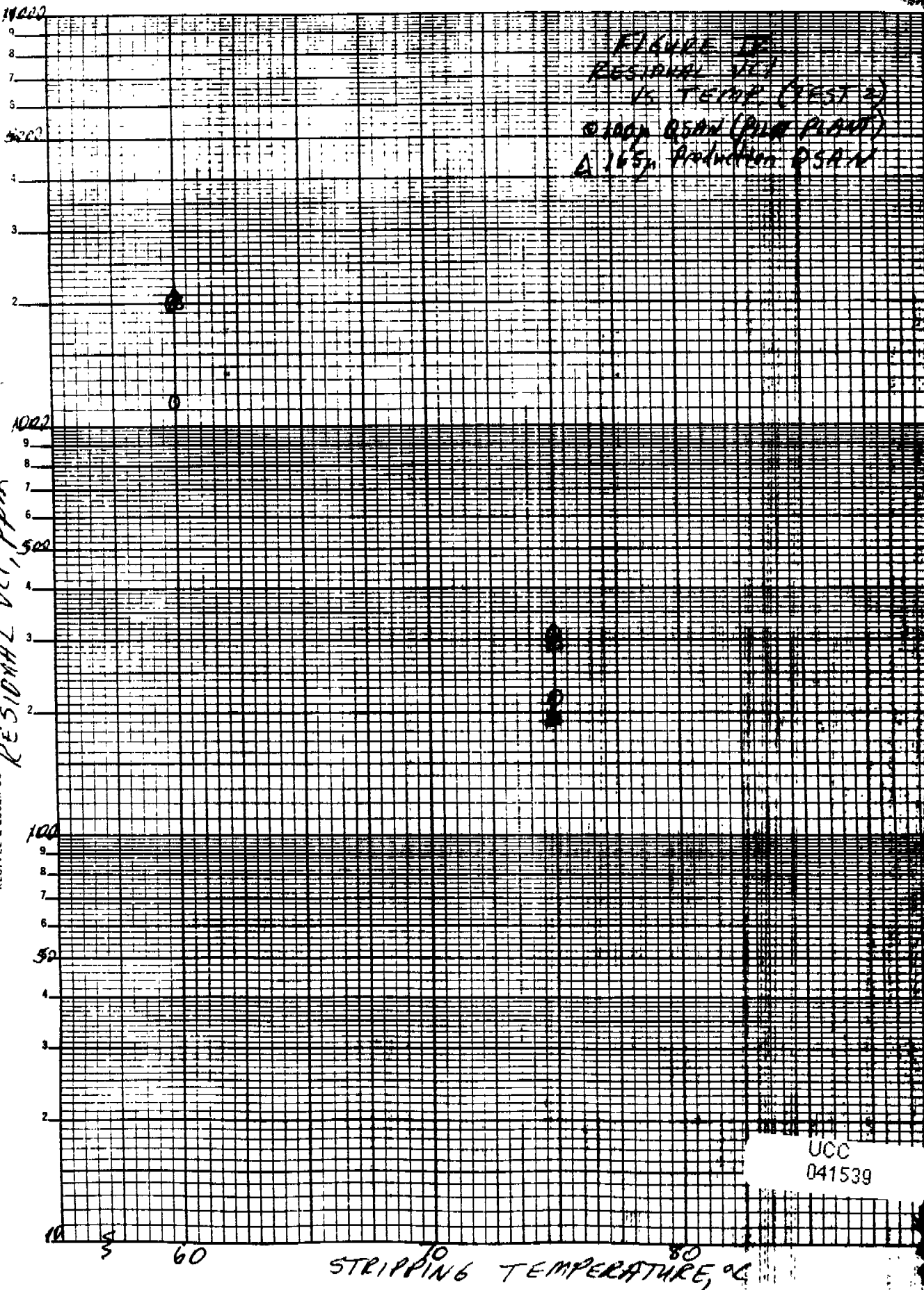
RESIDUAL VCL, ppm



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K-E SEMI-LOGARITHMIC 46 5493
MADE IN U.S.A.
KEUFFEL & ESSER CO.

RESIDUAL VCI, ppm



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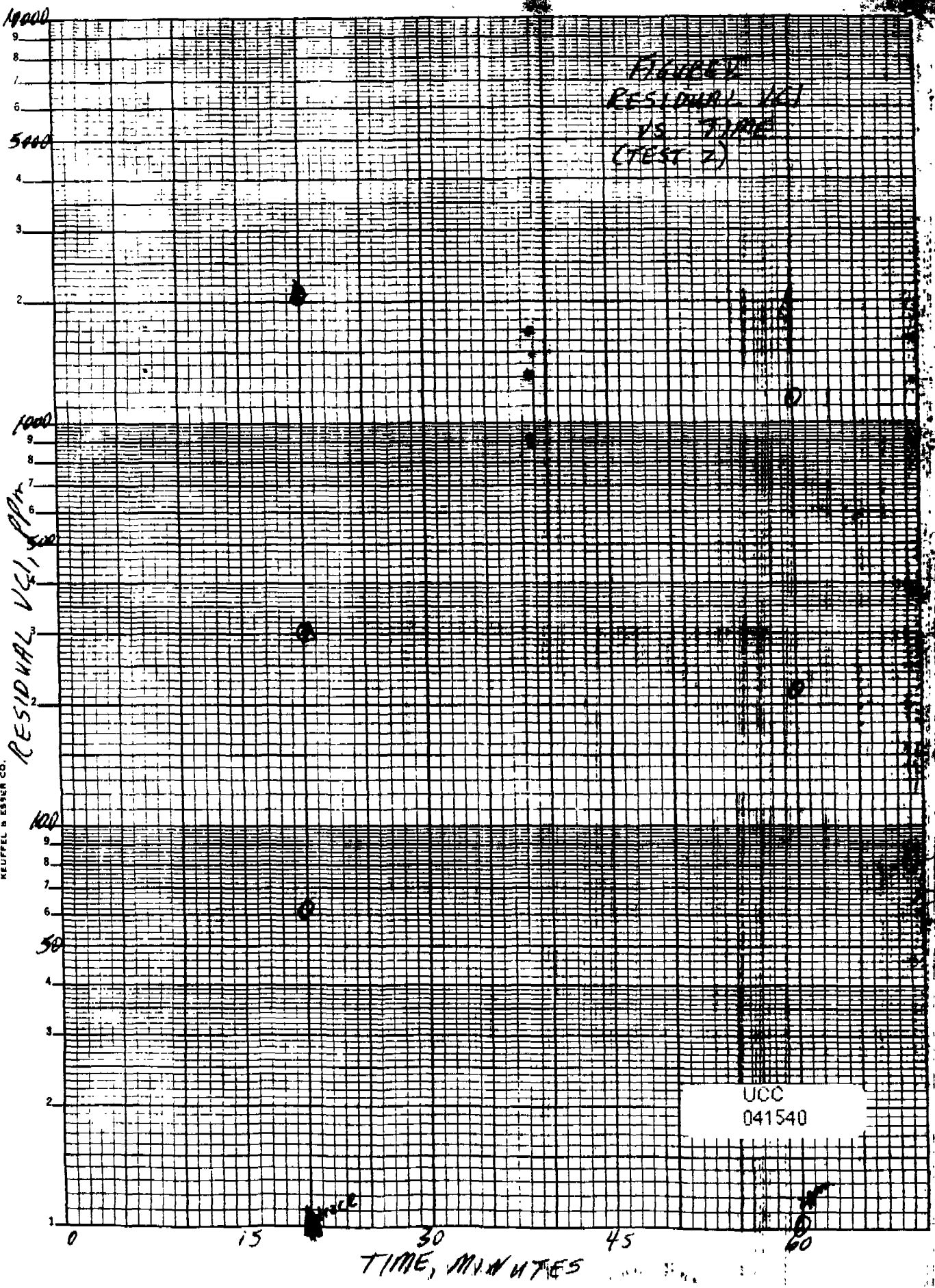
K-E SEMI-LOGARITHMIC 46 5493
3 CYCLES X 70 DIVISIONS, MIN IN U.S.
KEUFFEL & ESSER CO.

10000

5000

1000

100



RESIDUAL VOLTAGE
VS. TIME
(TEST 2)

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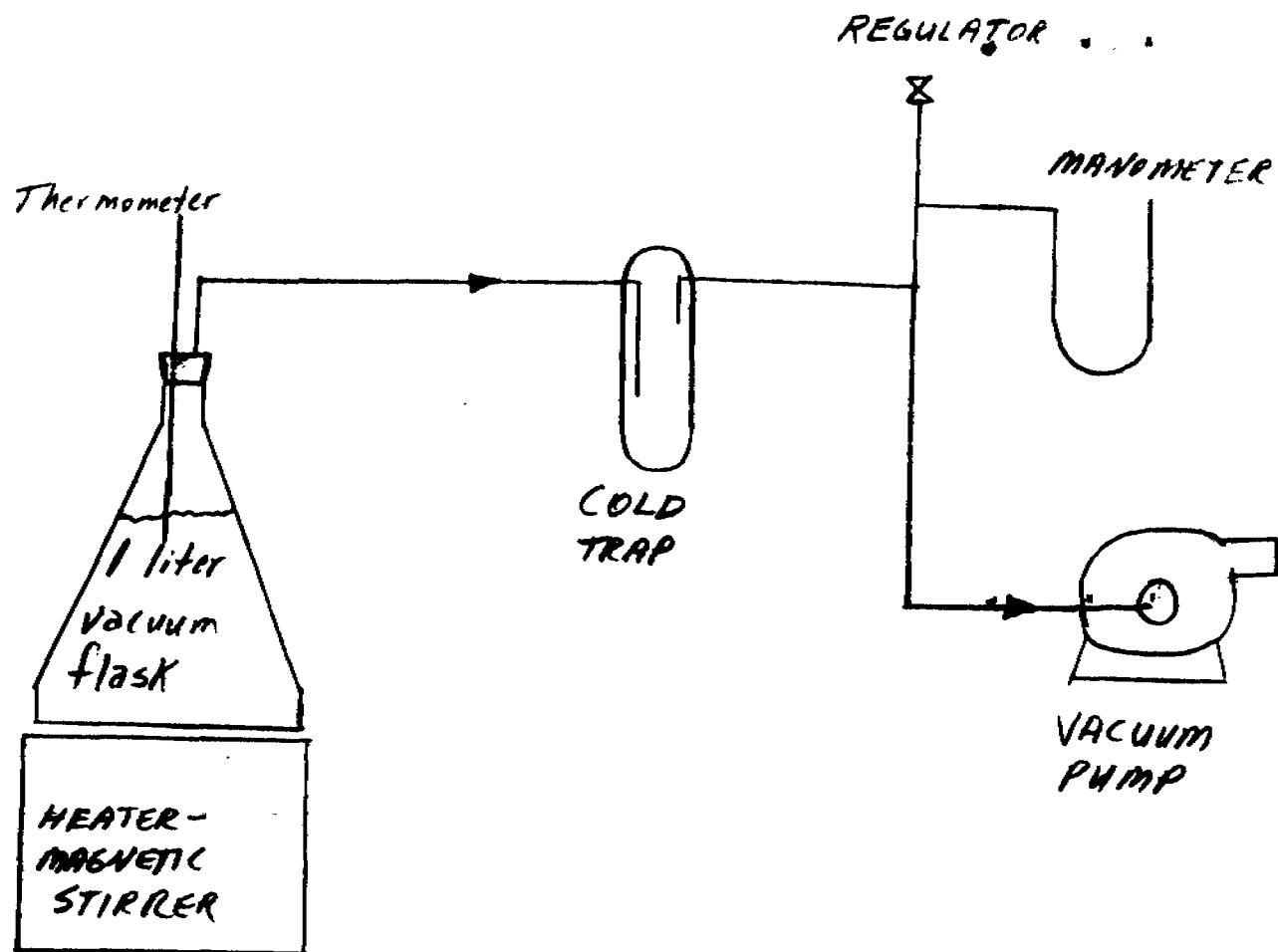


FIGURE VI - APPARATUS . . .
FOR STRIPPING STUDY

EXPERIMENT TO DETERMINE OPTIMUM STRIPPING
CONDITIONS TO REDUCE VCI RETAINED IN THE RESIN

A. A. Peterson

5-29-74

On Thursday, May 30, we plan to make the following experiment on normal production

Q5AN: 1) Sample the #1 BDT of the production unit after it has been vented to the 3 psig vent header. The fresh air mask should be utilized during sampling to minimize exposure to VCI. Take a 5 gallon sample from the BDT pump discharge. This sample should be tightly closed to minimize further loss of VCI and to minimize exposure.

2) Take the sample to the lab for stripping tests.

3) Use the following equipment for stripping tests: Vacuum pump, 1 liter round bottom flask, trap flask to prevent entrainment carryover, vacuum gauge for round bottom flask, heating mantle for round bottom flask, thermometer to measure temperature in round bottom flask, necessary tubing and support equipment. Use the laboratory notebook entitled Process Studies to record the data.

4) Each time a sample is removed from the 5 gallon drum, be sure to shake to insure a fairly constant slurry concentration for each sample to be stripped.

5) Each sample of slurry to be stripped should be approximately 0.5 liter.

6) Place the 0.5 liter sample into the round bottom flask and stopper with a three hole stopper to permit evacuation, temperature measurement, and vacuum readings.

7) Perform the stripping at the following sets of conditions (one sample for each)

a) Room temperature for 15 minutes at the boiling point

b) Room temperature for 1 hour at the boiling point

c) 50 ° C for 15 minutes at the boiling point

d) ~~50 ° C for 15 minutes~~ 50 ° C for 1 hour at the boiling point

e) 80 ° C. for 15 minutes at the boiling point

f) 80 ° C. for 1 hour at the boiling point

g) Repeat a thru f at 15 inches of vacuum if this is less than the boiling point

8) Dry each sample (approximately 200 gms of dry resin) at ~~50~~ 40 ° C overnight in the oven

9) Deliver each sample to Bob Arnold for analysis of VCI content.

We will use this or a modified procedure on several batches of resin made in the pilot plant in which we will vary resin particle size and porosity to determine the effects of the variables on the effectiveness of resin stripping.

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CONTINUED STRIPPING STUDIES, SUSPENSION RESINS

Dan O'Daniel
J. C. Chaty

As can be seen from the attached graphs, the most significant variable affecting residual VCI in the previous study appears to be the temperature. I propose the following more detailed study to pinpoint the effect:

SAMPLE	Production QSAN	PILOT PLANT 100 micron QSAN
TEMP	60, 75, 90 °C	60, 75, 90°C
VACUUM	15 inches Hg	15 inches Hg
TIME	15, 60 minutes	15, 60 minutes

This will be six samples plus the unstripped sample for each type of a total of 14 samples to be submitted to the lab. We will begin this work on Tuesday, June 11.

Adolph

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M. E. EISENHOUR

CHEMICALS AND PLASTICS

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

TO (NAME) Mr. J. C. Akins
COMPANY Mr. M. E. Eisenhour
LOCATION Mr. R. L. Frantz
Mr. G. T. Pyle
Mr. R. W. Sesler
COPY TO Mr. O. A. Shelton
Mr. G. F. Tacquard

DATE May 14, 1974

SUBJECT Reduction of Residual
VCM in Suspension Resin

Attached is the program based on objectives agreed to in the meeting held on May 9, 1974 on the above subject.

The objectives of the program are as follows:

- I. The overall objective is to reduce the residual VCM to the minimum achievable with present equipment and recipes without loss of production.

Specific Objectives:

- A. To determine the VCM levels as related to process variables and pertinent resin properties.
- B. To determine the function of temperature on residual VCM in resin which has been blended.
- C. To determine the effect of blending on stratification of resin.

The program lists the steps, the initials of the person accountable, and a completion date. With the exception of Mr. Akins, the program has been discussed with the person accountable and has his understanding and acceptance. In general, a two-week program is planned with data on products made during that period. The program can be extended to include additional products if needed.

F. L. Johnson
F. L. Johnson

R. M. Arnold
R. M. Arnold

FLJ/st

Attachments

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I. Overall Objective

Reduce the VCM in the suspension resin to minimum level achievable with present equipment and recipes without loss of production.

How

1. Achieve maximum vacuum stripping capability with equipment available (OAS, 5/9/74)
2. Achieve consistent stripping conditions from shift to shift (OAS, 5/17/74)
3. Operate dryers at maximum outlet temperature as consistently as possible (GTP, 5/10/74)
4. Use bins with blending nozzles whenever available and blend for two hours at maximum air flow (GTP, 5/17/74)
5. Measure and record air flow to blenders (GTP, 5/17/74)

A. Specific Program Objective

Determine the VCM levels in the resin as related to process variables and pertinent resin properties in keeping with overall objective above.

How

1. Record process variables
 - a. Put in necessary instruments to measure vacuum at vacuum strippers (OAS, 5/17/74)
 - b. Record stripping conditions and vacuum obtained on log sheet as each autoclave is stripped (OAS, 5/17/74)
 - c. Record dryer outlet temperatures hourly on log sheets next to bin being filled (GTP, 5/17/74)
2. Determine VCI levels in resin on
 - (a) at least 50% of blends (RMA 5/20 - 6/3/74)
 - (1) boxes
 - (2) each compartment on HC's
 - (b) retain samples in capped glass bottles until program complete (RMA, 5/20 - 6/3/74)

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3. Accumulate data as indicated on attached data sheet for each resin type (FLJ, 6/7/74)
4. Data will include particle size and dryblend from quality control analysis. Dryblend data will be run once/shift per resin type on single bin - no composites. (JCA, 5/20 - 6/3/74)
5. Determine correlation of VCI with process variables and/or resin properties (FLJ, RMA, 6/10/74)

B. Specific Program Objective

Determine the function of temperature on residual VCM in resin which has been blended.

How

1. Use bins (604, 605) in Bldg. 178 where heated air is available (GTP, 5/20/74)
2. Install instrumentation to measure air flow to bins in Bldg. 178 (GTP, 5/20/74)
3. Check air volumes to bins to determine if equal (and record) during test (RMA, 5/20 -)
4. Blend for 4 hours - sample initially and hourly. Determine residual VCM (RMA, 6/7/74)
5. To determine effect of temperature directly - run one bin without heated air and second with heated air (RMA, 6/17/74)
6. Review and report results (FLJ, RMA, 6/10/74)

C. Specific Program Objective

Determine the effect of blending on stratification of resin.

How

1. Determine if stratification occurs by running screen analysis on "beginning, middle, and end" samples taken as van box is loaded. (RMA, 6/7/74)
2. Review and report results (FLJ, RMA 6/10/74)

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