FOR COMPANY USE ONLY

DATE

PROCESS FILE

TEST AUTHORIZATION NO. TA-C- 74-1001 11-5-74

OFFICIAL PRODUCT NAME t-Amylanthraquinone (t-AAQ) PROCESS FILE

PRODUCT CODE NO. 050-816-2000 POUNDS PRODUCT PROPOSED 9,000

AREA "Ponsol" BUILDING NAME "Ponsol" Int.

TITLE Amylanthraquinone - Modified Drowning & Neutralization Procedure

PREPARED BY: D. M. Crouse RESPONSIBLE FOR TEST AND TEST CONCLUSION: D. S. James

PURPOSE OF TEST: To improve the AAQ yield by improving the recovery of AAQ/TCB solution through the wash steps.

The goal is to increase the TCB recovery from 67.8% to 81% which could increase the yield to 81%.

DURATION OF TEST: Eighteen (18) charges.

STANDARD INVOLVED: TMR-C-71-61, dated 8-16-72, TA-C-74-565, dated 8-7-74, TA-C-73-683, dated 8-7-74, TA-C-74-471, dated 8-7-74.

ANALYTICAL CONTROL: ☒ No change ☐ Change described under Test Details

TECHNICAL BASIS FOR CHANGE: See attached.

TEST DETAILS:
(Include Safety and Waste Disposal)

See attached.

SAFETY: The first neutralization should be monitored by supervision to make sure no problems of overheating are encountered. None are expected (see Technical Basis).

WASTE DISPOSAL: No change in the nature of the waste products is anticipated. A successful test will reduce the waste load substantially.

DISTRIBUTION:

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S. C. Doberstein	T. E. Lewis	Group File (2)
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APPROVED BY:

James E. Kirby 11/14/74 CHIEF SUPVR., OPERATIONS DATE

Arthur F. Burk 11/12/74 CH. SUPVR., TECH. OR PLT. ASSIST. DATE

DATE

SUPERINTENDENT, ANALYTICAL (When Required) DATE

SUPERINTENDENT, DYE QUALITY CONTROL (When Req'd) DATE

AUTHORIZED BY:

SUPERINTENDENT, MANUFACTURING (Or Delegates) DATE

SUPERINTENDENT, TECHNICAL (If Any) DATE

MU-1752-B-R6

WF

DUP050467718

TECHNICAL BASIS FOR CHANGE:

Low yields in the AAQ process were traced to poor recoveries through the wash steps (see Test Conclusion 73-683, dated 8-7-74). The cause of poor recoveries is probably due to emulsions and slow settling rates leaving an interfacial layer that is cut to the ditch containing AAQ in trichlorobenzene. Laboratory study of settling rates suggested some improvements in the work up procedure may reduce this possibility.

Settling Rates

The settling rates of a plant sample taken during the final wash were obtained as a function of the following variables:

- temperature,
- agitation time before allowing to settle and,
- additives (NaCl, Na_2SO_4, "Alkanol" surface active agent).

The final wash is a water wash after neutralization and has caused settling problems in the past. The experiments, done in triplicate, took 50cc of the AAQ/TCB solution and 50cc of the aqueous layer, agitated for a specified time and at a given temperature (5 min., 80°C. for the control) and then the settling time could be observed in a 100cc graduated cylinder. Reproducibility was good.

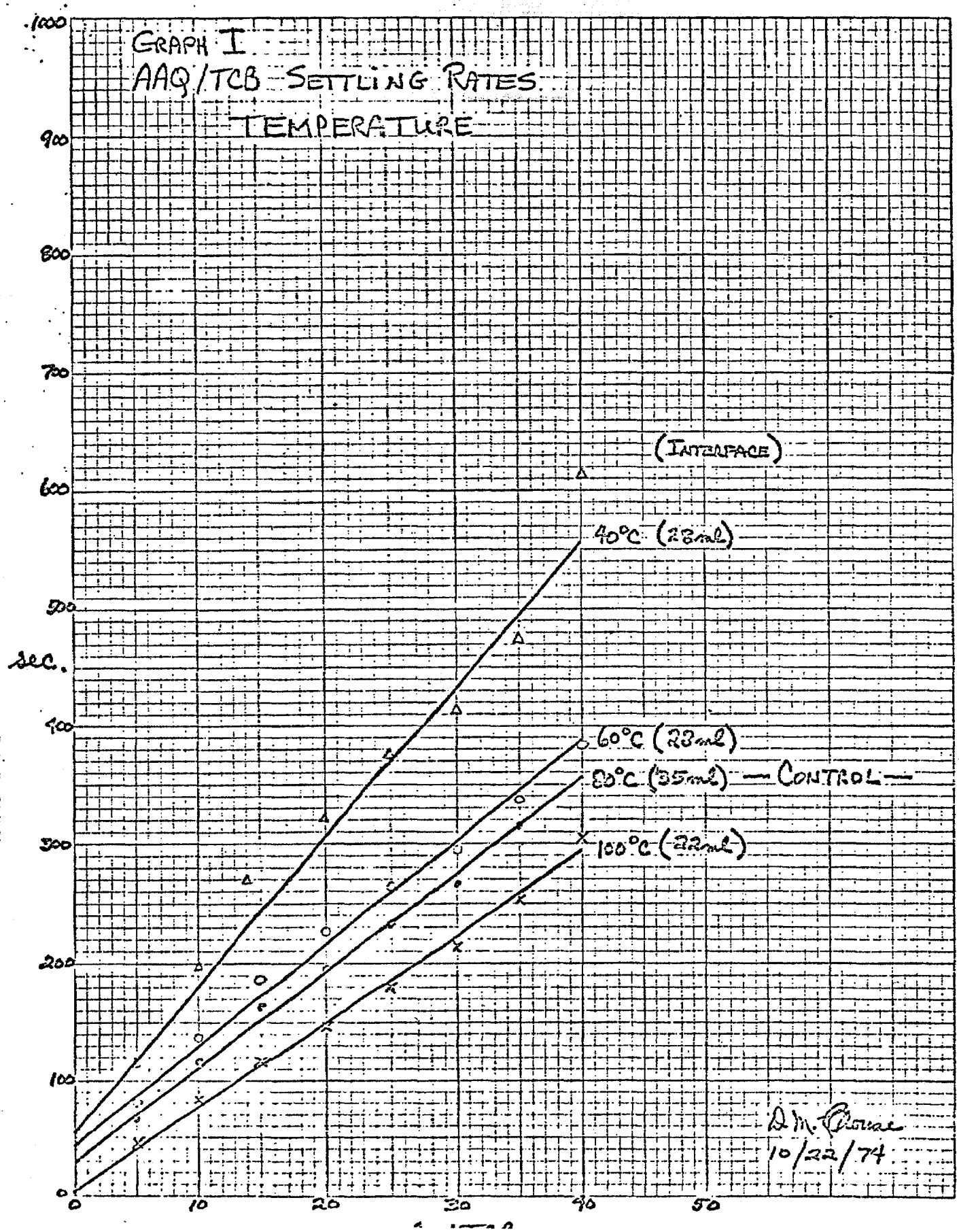
The following results were obtained (OCNB-2839-100).

(a) Temperature - Increasing temperature increased the settling rate (Graph I). The process specifies 55-60°C. which appears to be a minimum. As the TCB layer settled out a large interface layer (emulsion) was observed. This was observed at all temperatures.

(b) Agitation - Increasing the agitation time decreased the settling rate (Graph II) and also increased the volume of the interface layer.

(c) Additives - Experiments with additives to break the emulsion and increase settling rates indicate up to 6% salt* (NaCl or Na_2SO_4) will substantially reduce settling times (by 70%) and eliminate the interface layer (Graph III). The surfactant "Alkanol" 1009 reduced settling time but did not eliminate the interface.

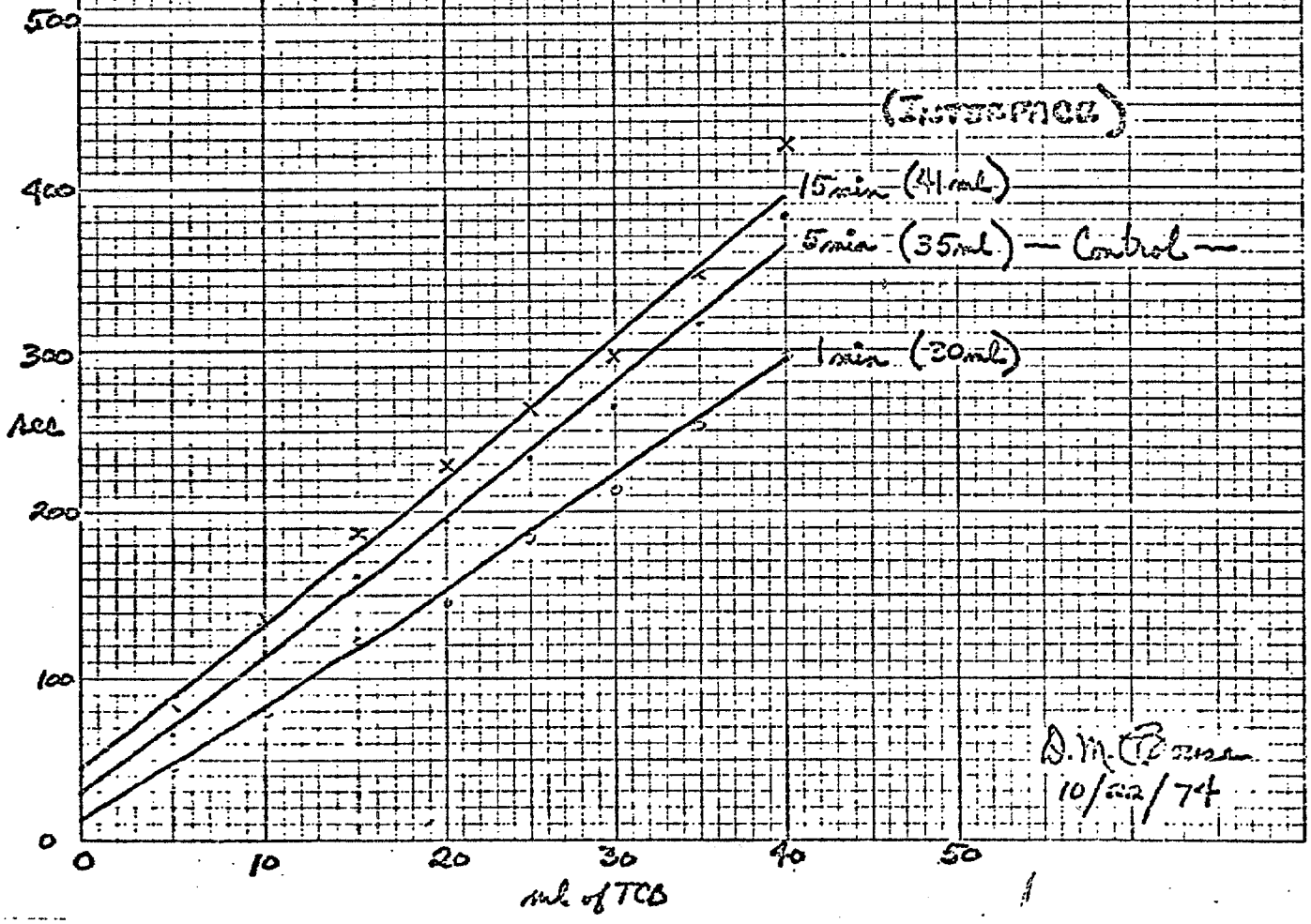
*Weight % salt in the aqueous phase.



GRAPH II

AAQ/TCB SETTLING RATES

AGITATION



D. M. Brown
10/22/74

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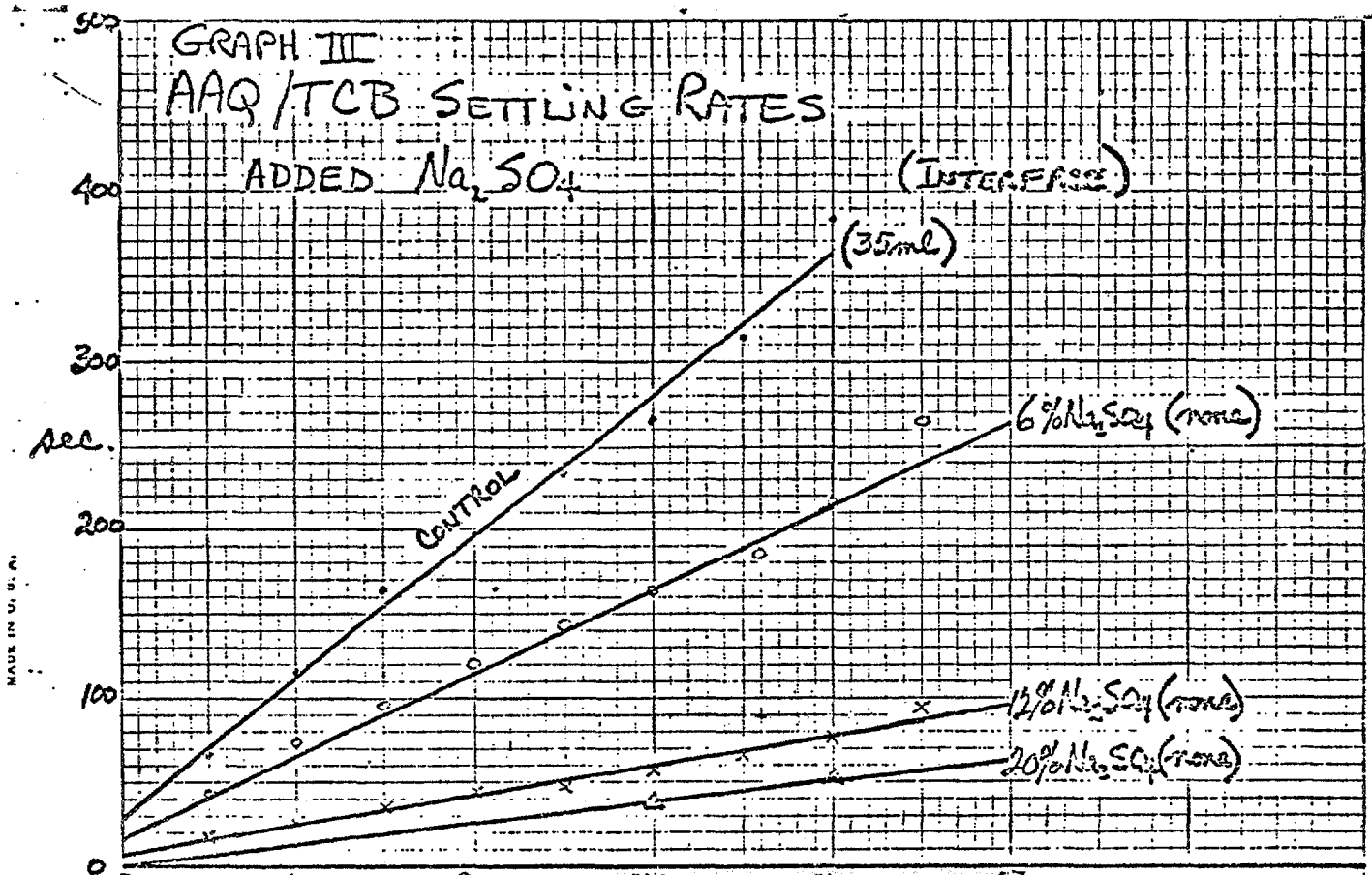

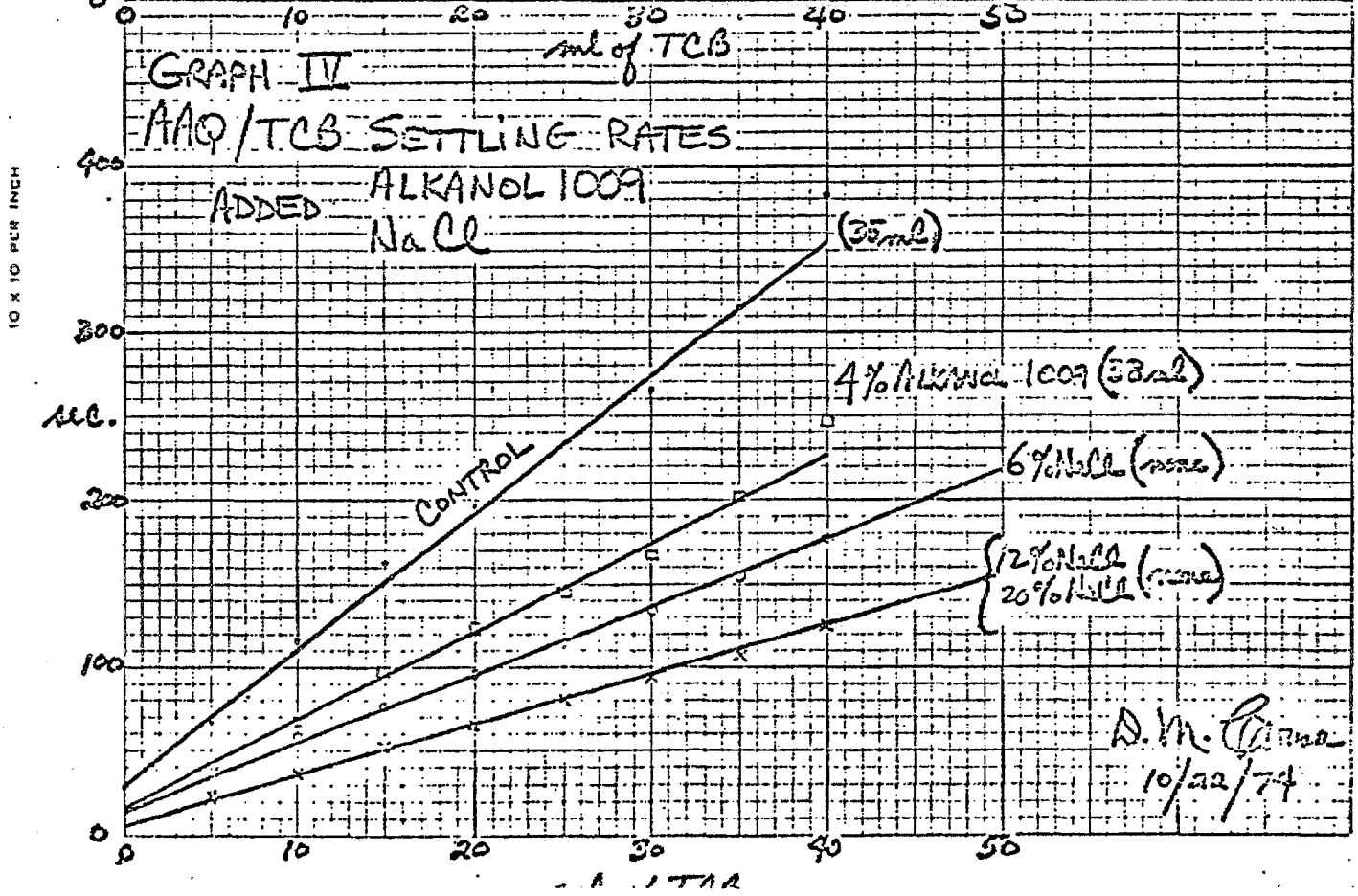

D. M. [illegible]
10/22/74

MADE IN U.S.A.

10 X 10 PER INCH

DUP050467722

Washing & Neutralization Procedure

The drowning, washing and neutralization procedure was modified using the following guidelines

(1) The salt content, Na_2SO_4, will not drop below the 3-5% range.

(2) The temperature will be 75-80°C. during the settling period.

(3) Agitation time is a minimum.

(4) Settling time is a maximum.

To do this the water washes after cutting the mother liquor were deleted. Neutralization at this stage will consume more caustic but make more emulsion breaking agent, sodium sulfate. It will also generate more heat. Laboratory experiments in a Dewar flask gave a temperature rise of about 15°C. when neutralizing 17% sulfuric acid with 30% caustic. This should be easily controlled in the plant. Using the modified procedure (Table I) a slight improvement in yield was noted. The laboratory, however, has higher recoveries than the plant presumably because settling times are less and visual observation of the separation is possible. The amount of tar seems to depend on how much water is transferred to the distillation (more water means more salts).

An estimated material balance through the washing steps in T-7 and T-19 has been made in the Appendix A. The concentrations of sodium sulfate were defined. A comparison of the changes made in this test are shown in Table II. The recovery and yield is the goal based on laboratory experience.

Technical Basis for Change (Cont'd)

TABLE I

AAQ using Modified Work Up Procedure - Laboratory

	Current Work-up Procedures	Test Authorization Work-up Procedure	
OCNB-2868	122	125	127
Reactants			
ABBA, g	406	406	406
, % solids	12	12	12
, % AI	9.8	9.8	9.8
Oleum, g	475	475	475
, %	7.5	7.5	9.0
Product			
Distillation			
H_2O, g	0	29	20
TCB, g	303	303	298
AAQ, g	32	33	34
Tar, g	7	30	17
Total, g	342	395	369
Sulfur, ppm	-	nil	nil
TCB Recovery*, %	85	85	84
AAQ Yield**, %	76	78	81

* Theory 357g

** Purity 88% and theory 37g

Technical Basis for Change (Cont'd)

TABLE II

Comparison of Present & Proposed Work Up Procedure

Drowning, T-7	Present Process	Proposed Process
Drowning, T-7		**Drowning, T-7**
Wt. H_2O, lbs.	25,000	25,000
Temp., ° C.	55 - 60	75 - 80
Agitation, hr.	2	1
Settling, hr.	1	2 - 3
Washing, T-19		**Cut, T-19**
Wt. H_2O, lbs.	About 10,000	None
Temp., ° C.	55 - 60	75 - 80
Agitation, hr.	¼	None
Settling, hr.	1	1 - 2
Neutralization, T-19		**Neutralization, T-19**
Wt. H_2O, lbs.	10,000	12,000
Temp., ° C.	55 - 60	75 - 80
Agitation, hr.	¼	¼
Settling, hr.	2	2 - 3
Wt. NaOH, lbs.	100	3,000
Washing		**Washing, T-19**
Wt. H_2O lbs.	10,000	7,000
Temp., ° C.	55 - 60	75 - 80
Agitation, hr.	¼	¼
Settling, hr.	2	2 - 4
Overall time, hr.	8 3/4	8 3/4 - 12 3/4
Estimated Recovery & Yield		
TCB Recovery, lbs./lot	6,321	7,800
, %	67.8*	81**
AAQ Yield, lbs./lot	1,508	1,800
, (100%) lbs./lot	1,211	1,553
, %	60.0*	81**
Total, lbs./lot	7,829	9,600

* TCB Theory 9,329 lbs., AAQ (100%) theory, 2015 lbs. see Appendix TC-73-683.

**TCB Theory 9,600 lbs., AAQ (100%) theory, 750 x 0.85 x 3 = 1,913 lbs. See Appendix A "Drowning" this test.

TEST DETAILS:

Drowning

1. Charge 20,000 - 25,000 lbs. of process water to T-7.

   If the coil is not available 20,000 lbs. of water should be charged in Step (1) to assure the temperature rises above 55°C.

   25,000 lbs. is preferred. Max. Temp. of process water - 35°C.

2. With agitation on blow the charge from K-7 to T-7.

   K-7 should not be above 95°C.

3. Agitate the charge in T-7 for 0.5-1.25 hrs. at 55-90°C. Preferred range is 75-80°C.

   If temperature is below 55°C. steam should be passed through the coil to heat the charge or injected directly into the mass.

   Emulsions are likely to occur at temperatures below 55°C.

   Temperatures above 90°C. could lead to a fume condition.

4. After 1 hr. agitation, stop the agitation and allow the charge to settle 2-3 hours before draining the water layer to the ditch from the top side outlet.

   This leaves about 935 gal. in T-7 of which about 353 gal. is AAQ/TCB solution.

   Sample the water layer for product by dropping a small amount of water layer sample into a large quantity of tap water and look for small droplets of product at the bottom. If too much water layer sample is added the sample will be too dark to detect product.

5. After the water layer is ditched the TCB product layer is ready for transfer to the washing vessel.

6. Pump the charge from T-7 to T-19.

7. Hold the charge in T-19 and repeat the drowning procedure until three (3) charges have accumulated in T-19.

Neutralization

8. When three charges are in T-19 heat to 75-80°C., without agitation, and let settle for 1-2 hrs.

9. Transfer the water layer to the ditch from the bottom side outlet of the upper set.

   This leaves about 1723 gal. in T-19 of which about 1059 gal. is AAQ/TCB solution.

   Check for the presence of product before ditching.

10. Add 12,000 lbs. of 55-60°C process water.

    Temperature should be 55-65°C. after addition.

11. Turn on agitator and with temperature less than 65°C. neutralize the charge to a pH between 7.0 and 9.0.

    Maximum temperature 90°C.
    Approximately 3,000 lbs. 30% NaOH needed.

12. Adjust temperature to 55-80°C. and agitate for additional 5-15 min., then allow the charge to settle at 55-80°C. for 2-3 hours. Preferred temperature 75-80°C.

13. Transfer the water layer to the ditch as described in Step 9 above.

Washing

14. Add 5M-15M lbs. of 75-80°C. water to T-19 and agitate for 5-15 min., then allow the charge to settle at 55-80°C. for 2-4 hours. Preferred amount of water, 7M lbs. and settling time 3 hr., and temperature 75-80°C.

15. Transfer the water layer to the ditch leaving the minimum amount of water with the charge.

    The minimum water will probably be by cutting from the top-side outlet of the lower set leaving about 1084 gal. in T-19 of which less than 1050 gal. is AAQ/TCB solution. The sodium sulphate concentration should be 3-5% in the aqueous phase.

16. If necessary to reduce the salt content add 5-15M lbs. of 75-80°C. water, preferably 7M lbs., without agitation and allow to settle 1-3 hrs. followed by transferring the water layer to the ditch as in Step 15. DO NOT AGITATE.

17. Charge is ready for transfer to S-9.

APPENDIX A

Assumptions:

(1) T-7 & T-19 hold 33.4 gal./vertical in. of liquid (dia. 97").

(2) Side outlet height from base of tank.

Outlet No.	T-7		T-19	
	Inches	Gal.	Inches	Gal.*
1	15	501	15.9	530
2	19	635	24.2	807
3	23	768	32.5	1084
4	28	935	51.6	1723
5	-		60.3	2012
6	-		68.7	2265

*Actually measured

(3) Density

	Lbs./Gal.
9.0% Oleum	15.5
17.4% Sulfuric Acid	9.34
Water	8.34
AAQ/TCB	11.2
30% NaOH	11.07
7.5% Na_2SO_4	9.2 est

Drowning, T-7

4,000 ABBA/TCB was 800 lbs. ABBA (20% solids) or 750 lbs. AAQ

5140 9% Oleum x 102% H_2SO_4 = 5243 lbs. H_2SO_4 (100%)

Volume organic:

4,000 - 50 lb. H_2O = 3950 lbs./11.2 = 353 gal.

Concentration aqueous

25,000 lbs. H_2O + 5140 lbs. Oleum + 50 Lbs. = 30,190 total lbs.

5243/30,190 x 100% = 17.4% sulfuric acid

Volume aqueous

30,190/9.34 = 3232 gal.

Cut at 935 gal. (28" outlet)

Therefore transfer to T-19

353 gal. AAQ/TCB

935-353 = 582 gal. 17.4% H_2SO_4

Neutralization T-19

Combine 3 charges and cut at 1723 gal.

Have in T-19

3 x 353 = 1059 gal. AAQ/TCB

1723-1059 = 679 gal. 17.4% H_2SO_4

Caustic needed

679 gal. x 9.34 lb./gal. x 17.4%/98 lbs./mole x 2 eq./mole ÷ 100

= 22.52 eq. of acid

22.52 eq. x 40 lb./eq. ÷ 30%

= 3003 lbs. 30% NaOH

Concentration of Na_2SO_4 in Aqueous Phase

H_2SO_4 at start 679 x 9.34	= 6342 lbs.
H_2O added	= 12000 lbs.
Caustic added	= 3003 lbs.
	21345 lbs.

$\frac{22.52}{2}$ moles x 142 lbs./mole = 1599 lbs. Na_2SO_4

1599/21345 = 7.5% Na_2SO_4

Wash T-19

Cut at 1723 gal.

Assume 10% AAQ/TCB lost

Have in T-19

1059 x 90% = 953 gal. AAQ/TCB

1723-953 = 770 gal. 7.5% Na_2SO_4

Concentration Na_2SO_4

770 Gal. x 9.2 = 7084 lbs. 7.5% Na_2SO_4
(531 lbs. 100% Na_2SO_4)

H_2O added = 7000 lbs.
14084 lbs.

531/14084 x 100% = 3.8% Na_2SO_4

Transfer to S-9

Cut at 1084 gal.

Assume 10% AAQ/TCB lost

Have in S-9

953 x 90% = 858 gal. AAQ/TCB (9,610 lbs.)

1084-858 = 226 gal. 3.8% Na_2SO_4

est. 226 x 9.2 x 3.8% = 79 lbs. Na_2SO_4

Optional Dilution and Cut

Add 10,000 lbs. H_2O = 1200 gal.

226 x 9.2/(10,000 + 226 x 9.2) x 79 = 14 lbs. Na_2SO_4