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NEWPORT PLANT
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SUBJECT: 2,9-DIMETHYL QUINACRIDONE - TFA CATALYSIS

PERIOD COVERED: OCTOBER, 1966 to SEPTEMBER, 1967

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ABSTRACT

2,9-dimethyl DQA was produced in the plant at 70% of theory by a TFA catalyzed process at a 179% batch size. The 2,9 Me_2DQA quality was borderline because of the instability of Me_2DAT at the 170°C. Dowtherm solution temperature. Oxidation variables were developed so that any quality of Me_2DQA can be oxidized to good Me_2QA.

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I. INTRODUCTION AND OBJECTIVE

Production found the PTSA process for Me_2DQA to be poorly operable. It was used for making batches 8000 through 8017. The oxidation of many of these batches proceeded only with difficulty. Due to the poor quality of the Me_2DQA and the high caustic concentration, the oxidation would stop at the Na_2Me_2QA stage. When this occurs, some of the Me_2DQA never oxidizes and remains as a diluent in the final product after hydrolysis. In addition, the PTSA process lends itself to distillation system pluggage problems because of the high (7/1) PT/SSE ratio. Also the neutralization and removal of PTSA after the PT condensation proved difficult due to the insolubility of the 2,9 Me_2DAT. It was the object of this study to develop a workable TFA process which would eliminate the problems of the PTSA process and would produce readily oxidizable Me_2DQA. The TFA approach has the advantages of (1) a low (3/1) PT/SSE ratio and (2) easily removing the TFA catalyst by distillation.

II. SUMMARY AND CONCLUSIONS

1. The 70% Me_2DQA goal yield by the 179% TFA process was demonstrated in the May, 1967 campaign. This is an improvement over the PTSA process.

2. The Me_2DQA plant quality is borderline. The problem appears to be in Me_2DAT stability in Dowtherm at 170°C., a problem common to both processes.

3. Me_2DQA oxidizability depends on purity. By varying conditions (seed and NaOH concentrations), any quality Me_2DQA can be oxidized.

4. HT drowned Me_2QA has been demonstrated to be the preferred seed for the oxidation of Me_2DQA. Dispersion mill powder (gamma or beta) can also be used.

5. The oxidizability of severely degraded Me_2DQA can be improved to a passable level by extracting with 5% NaOH/MeOH. This treatment has no effect on borderline material.

6. Batch size cannot be increased by the existing process because of the low solubility of Me_2DAT.

III. PATENT STATUS

A patent proposal covering the use of seed to make the oxidation go to completion has been written. The details of this technique are covered in discussion section F-2.

The use of TFA is covered by 1572-K, allowed 10/18/67.

IV. SUGGESTIONS FOR FUTURE WORK

The need for additional work on the dimethyl-TFA process is discussed in the body of this report. Several of these items are currently active.

1. Low Temperature Me_2DAT Solution

Changing to a TFA catalyst for the FT condensation eliminated many of the shortcomings of the PTSA catalyzed process. The instability of Me_2DAT at the 170°C. solution temperature in Dowtherm of the mixed methyl-ethyl ester results in low and erratic Me_2DQA quality. To achieve lower operating temperatures, mixed esters of Me_2DAT were suggested by W. S. Sturve. The solution temperature of Me_2DAT ($n\text{-}Bu_2$) (98°C.) and Me_2DAT (Et/Bu) (90°C.) appear very promising.

2. Me_2DQA Quality

To avoid the need of determining the quality (oxidizability) of Me_2DQA by a series of laboratory oxidations, a direct analysis is required.

3. "Sitol" Concentration

The amount of "Sitol" used in the present oxidation is excessive. Additional work to establish the optimum amount vs. the variable Me_2DQA quality is required.

4. Other Desirable Analytical Procedures

a. Improved Me_2QA standard for purity determination.

b. A quantitative procedure for determining Me_2DQA in Me_2QA.

5. Verify Possible Polymorphic Nature of Me_2DQA

V. DISCUSSION OF RESULTS

Results will be discussed in the order in which they occur in the synthesis.

A. SSE

No work was done on SSE. This is a well established process developed in the unsubstituted quinacridone studies.

B. PT Condensation and Distillation

In this reaction, two moles of p-toluidine (PT) are condensed with one mole of the methyl/ethyl ester of succinyl succinic acid (SSE) in the presence of trifluoroacetic acid (TFA). A third mole of PT is present during the condensation and is removed with the TFA by vacuum distillation at the completion of the 30-minute condensation.

The laboratory condensation is normally run at 85-90°C. (plant 87-93°C.). Increasing the condensation temperature to 110°C. had no adverse effects on yield or quality. There is some indication that the higher temperature gives a higher yield - 71% vs. 68%.

The effect of varying the PT and TFA concentrations were also studied. The normal 1 mole excess of PT was varied from 0.4 moles to 1.3 moles (216% batch size) without affecting 2,9 Me_2DQA yield or quality. Similarly, doubling the TFA catalyst was without effect.

A study was made of the effect on stability of refluxing Me_2DAT/Dowtherm in the presence of free PT and TFA at a pressure of 25 mm of Hg. Refluxing was maintained for periods up to 150 minutes at pot temperatures ranging from 125°C. to 135°C. In no case was DPU formed in subsequent laboratory (high boil-up) pyrolyses nor were any unusual difficulties encountered in oxidizing this material. Increasing the PT excess from one mole to six moles and with either TFA or PTSA as catalyst gave similar results. The absence of DPU formation under these conditions was attributed to the temperature being too low for the secondary DPU reaction to occur. The experiment was repeated using a 60 minute reflux, a 150°C. pot temperature and either TFA or PTSA as catalyst. Only the PTSA catalyzed material produced DPU in the pyrolysis. Oxidation proceeded normally.

At the completion of the condensation, the excess PT and the TFA are removed by vacuum distillation. During this distillation, the pot temperature is allowed to rise to a maximum of 150°C. at a pressure of 25 mm of Hg. Under these conditions, part of the Me_2DAT is out of solution. This explains why yield samples taken at this stage of plant operation are generally low. Another result of having the Me_2DAT out of solution is that it can occlude PT. The presence of PT in the Me_2DAT during pyrolysis could be responsible for the poor quality of plant Me_2DQA. To check this out, a sample of Me_2DAT/Dowtherm,

B. PT Condensation and Distillation (Continued)

that had been distilled to the normal 0.05% PT, was dissolved, cooled to 150°C. and redistilled. The Dowtherm distillate contained 0.095% PT indicating that it may be occuluded in the Me_2DAT. By laboratory pyrolysis and oxidation, the re-distilled material was slightly purer than the "as is" plant distilled Me_2DQA based on oxidizability. An attempt to duplicate this in the plant was unsuccessful. Considerable degradation took place during the extended processing and the oxidizability of the resulting Me_2DQA was very poor.

In the May, 1967 plant campaign, it was necessary to replace most of the TFA in the recycled PT for each batch. Laboratory syntheses did not show up this problem since the PT-TFA distillate was never recycled. To check out the loss in the laboratory, a distillation pot was charged with Dowtherm, TFA-PT salt, and PT. The water cooled condenser was maintained at 50-54°C. to duplicate plant conditions. Distillation was carried out at a maximum pot temperature of 150°C. and a pressure of 25 mm of Hg. At the completion of the distillation, 88% of the TFA was in the distillate. None was found in either the distillation pot or the cold trap. hence, it does not appear that the high condenser temperature is responsible for the TFA loss in the plant. The problem is probably associated with the plant equipment

C. Pyrolysis

In order to run a pyrolysis, it is necessary to have the Me_2DAT completely in solution. Otherwise, some of the Me_2DAT that was out of solution would plate out on the equipment causing pluggage. Solution of the Me_2DAT in Dowtherm is accomplished by heating to 170°C. and holding at that temperature until it enters the pyrolysis tank. During this long hold at high temperatures, degradation of Me_2DAT occurs. This was demonstrated in the laboratory by holding the Me_2DAT in Dowtherm for 24 hrs. at various temperatures before running a normal 90 minute high boil-up laboratory pyrolysis. The difference in yield between these samples and one pyrolyzed without holding was taken as a measure of the degradation. Results were as follows:

	150°C.	160°C.	170°C.	180°C.
Me_2DAT	-17.4%	-20.6%	-11.2%	-19.4%
DAT	- 4.7%	- 5.3%	- 5.9%	- 9.2%

C. Pyrolysis (Continued)

From these data, it appears that Me_2DAT is less stable than unsubstituted DAT. In spite of the yield loss due to degradation, all samples oxidized readily. This is attributed to the large boil-up in laboratory pyrolysis avoiding by-product formation.

The effect of boil-up rate was demonstrated by reducing the boil-up rate to one-half of normal (see KN-67-11 for details) and then oxidizing the resultant Me_2DQA. The normal boil-up gave easily oxidized Me_2DQA, while the reduced boil-up produced "grape juice" in the oxidation step, that is, it hung up as Na_2Me_2QA.

Early in the study of the Me_2DQA-TFA process, an attempt was made to determine the effect of small amounts of PT and TFA being carried over into pyrolysis. During the pyrolysis of the sample containing PT, a slight oily film formed on the side of the flask. The sample containing the PT-TFA salt not only had the oily film, but also appeared dirty. The Me_2DQA yields and the oxidation of these samples were normal. This again points up the fact a high boil-up will prevent a degradation of the Me_2DQA quality.

D. Me_2DQA Purification

The present plant pyrolysis boil-up is not sufficient to overcome the effects of prior degradations on Me_2DQA quality. For this reason, a means of purifying Me_2DQA is sometimes needed. A pure product, as judged by oxidizability, can be obtained by converting Me_2DQA to the sodium salt in strong alcoholic caustic and then precipitating the Me_2DQA with H_2SO_4. This is similar to the method used to convert alpha DQA to beta DQA except a higher NaOH concentration is needed. Unlike DQA, Me_2DQA does not undergo a phase change under these conditions. A procedure of this type is not practical in the plant.

The present means of cleaning up Me_2DQA after pyrolysis is to wash it on a Nutsche with MeOH until essentially free of Dowtherm. The Dowtherm contains the impurities. Since the impurities are largely insoluble in MeOH, it serves no useful purpose to wash beyond this point. However, poor Me_2DQA is still far from being free of impurities at this point. One or more of these impurities acts to inhibit oxidation. Additional impurities can be removed by washing on the

D. Me_2DQA Purification

Nutsche with a 10-90 mixture of 50% NaOH and MeOH. When this was done with fair quality Me_2DQA from batch 8021, a dark filtrate was removed. Additional washings with MeOH were made until the filtrate was colorless. This material oxidized no better than the control. Apparently Me_2DQA of at least fair quality cannot be helped by this technique. Since an improvement is obtained when the Me_2DQA is purified by precipitating from strongly alkaline MeOH, some of the impurities must be occluded by the Me_2DQA crystals. This experiment was repeated using poor quality Me_2DQA (batch 8026). The Me_2DQA was washed three time with 50% NaOH/MeOH (10/90). Only the first wash gave a dark filtrate. The oxidation (no seed) of this material gave a mixture of Na_2Me_2QA and Me_2QA crystals. The unwashed control formed "grape juice" (Na_2Me_2QA). This improvement in the oxidizability of poor quality Me_2DQA was demonstrated in the September, 1967 campaign on batches 8027 and 8028. Cleaning the crystal surfaces of these two batches of Me_2DQA made it possible to oxidize with only 5% HT Me_2QA seed. Laboratory results indicated that 8027 would have required 15% seed without the alkaline wash.

E. Me_2DQA Crystal Phase

Some work has been done to determine if Me_2DQA exists in more than one phase. The normal crystal form has been designated beta phase since it is isomorphic with beta phase Me_2QA. The Newark group has an x-ray pattern of what is supposed to be a mixture of alpha and beta Me_2DQA. However, no one has been able to substantiate this by making a pure alpha phase. An attempt to do this by the method used for converting alpha DQA to beta DQA was unsuccessful. Next, refluxing in solvents was tried. DMF and Dowtherm both increased crystallinity and possibly made a change in crystal habit. Phase was not affected. This study is continuing as time permits.

F. Oxidation

1. General

When this study was started, Me_2DQA had been made in the plant by the PTSA route. In the oxidation of the last five batches made using PTSA, there was considerable difficulty in hydrolyzing the Na_2Me_2QA to Me_2QA. At the time, it was thought that a TFA process would yield a cleaner Me_2DQA which would be easier to oxidize. The oxidation process used at that time reduced to a laboratory scale is as follows:

F. Oxidation (Continued)

1. General (Continued)

	Gms.	Ml.	Moles
(1) Charge a 1 liter, 4-neck, r.b. flask equipped with agitation, reflux condenser, thermometer and dropping funnel with:			
2,9-Me_2DQA	40.0	-	0.12
MeOH	251.0	322	7.86
(2) Add 50% NaOH slowly keeping temperature below 60°C.	180.0	118	2.25
(3) Stir 30 min. at 55-60°C.			
(4) Add "Sitol"	40.0	-	0.18
(5) Heat to 75-80 in 30 min.			
(6) Add MeOH in 5-10 min. maintaining temperature at 75-80°C.	218.3	280	6.82
(7) Stir 2 hrs. after slurry turns red at 75-80°C.			
(8) Filter hot			
(9) Wash BY - with hot water			
(10) Dry at 80°C.			
(11) Goal yield	39.8		0.94

All of the previously discussed experiments under condensation and pyrolysis were oxidized by this method. On heating to 75-80°C. (step 4) all went into the "grape-juice" stage. This occurs when the Na_2Me_2QA comes out of solution as blue plates rather than hydrolyzing to Me_2QA. The time required for the second methanol (step 6) to hydrolyze the Na_2Me_2QA varied from 50 minutes to over 4 hours. No conclusions could be drawn from the oxidations since the hydrolyses times did not correlate with the variables studied. However, when the same sample of Me_2DQA was oxidized, there was very little difference in hydrolysis time. Two samples required 100 minutes and the third, 115 minutes. Goal yields also had very little meaning as unreacted Me_2DQA will be recovered with the Me_2QA.

F. Oxidation (Continued)

1. General (Continued)

In plant operation, MeOH contains about 3% water while laboratory MeOH is essentially anhydrous. To determine if this would be a problem, laboratory oxidations were run with MeOH containing 3 and 5% water. There were no differences noted between the oxidations with wet MeOH and the anhydrous control.

The rate of NaOH addition (step 2) was thought to be critical in the conversion of Me_2DQA to its soda salt. A slow addition was supposedly needed for a complete conversion. In this experiment, no quality differences were noted between dumping the 50% NaOH solution in as rapidly as possible and adding in 45 minutes. The only difference noted at the end of the addition was that of temperature--63°C. vs. 57°C. for caustic added in 30 minutes.

A study was made to determine if Me_2DQA that did not get converted to the sodium salt could act as an inhibitor for the oxidation reaction. This was done by splitting the addition of Me_2DQA. 2-1/2% and 25% portions were added after the "Sitol" (step 4), and 2-1/2% was added after the second MeOH (step 6). Where the second addition of Me_2DQA was added after the "Sitol", it apparently immediately converted to the sodium salt. Hydrolysis of Na_2Me_2QA took place in 45 minutes at both Me_2DQA levels. Where the Me_2DQA was added after the Na_2Me_2QA was already formed, hydrolysis took 175 minutes. Although considerably longer than the previous two, it was not considered an abnormal hydrolysis with this lot of Me_2DQA.

2. Seeding

Having to go through the "grape juice" stage in an oxidation is highly undesirable since there is no guarantee that the Na_2Me_2QA can be hydrolyzed in a manner that will allow the reaction to go to completion. In the initial attempt at seeding, premilled, partly oxidized Me_2DQA was used as the seed. At 10% and 25% premilled Me_2DQA, the oxidation (the addition of "Sitol" to the hydrolysis of Na_2Me_2QA) required 240 minutes and 225 minutes respectively. Although premilled Me_2DQA oxidizes rapidly by itself, it does not act as a seed for the normal particle size Me_2DQA.

Beta and gamma dispersion milled QA mill powders were also investigated as seed at a 10% toner level (67% mill powder) based on the weight of Me_2DQA. These oxidations went directly to Me_2QA without going through the "grape juice" stage. Seeding with mill powder also affected the crystal phase. The unseeded oxidation gave a mixture of alpha and beta Me_2QA. With seed, only beta Me_2QA was formed. Another advantage of the rapid oxidation rate

F. Oxidation (Continued)

2. Seeding (Continued)

was the possibility of eliminating the second MeOH which was used to aid in the hydrolysis without stopping the oxidation. Working with a different lot of Me_2DQA, 1% and 5% (toner basis) seed levels were investigated. Only the 5% beta or gamma QA mill powder was effective. However, at this reduced seed level, a mixture of alpha and beta Me_2QA was obtained.

At this point in the study, there was some question as to whether the small particle size QA was seeding the oxidation or the large quantity of $Al_2(SO_4)_3$ was producing local areas of acid which hydrolyzed the Na_2Me_2QA to Me_2QA. The following results were obtained:

Seed	Oxidation Rate	α/β**	IR (Me_2DQA)
None	200'*	0.624	Excellent
$Al_2(SO_4)_3$	155'*	0.118	Good +
γ QA mill powder	70'	0.056	Good

(*) Went through "grape juice" stage

(**) Ratio of 7.4°/5.6° 2θ x-ray peaks

These results indicate that $Al_2(SO_4)_3$ has some effect in depressing the formation of alpha phase Me_2QA. However, its effect on the hydrolysis of Na_2Me_2QA was negligible. Hence, it is the small particle size QA that is seeding the reaction.

Dispersion mill powder contains about 14.9% toner. The remainder is $Al_2(SO_4)_3$ which is awkward to handle. One possible means of eliminating this problem would be to use extracted and washed dispersion milled QA press-cake. This was tried at both a 5 and a 10% dispersion milled QA level without success. Both samples went through the "grape juice" stage. The failure was attributed to particle growth during the extraction so that the QA particles were too large to act as seed.

Since it was necessary to use mill powder to seed the reaction, the possible problem of high water soluble salts was investigated. A series of simulated oxidations were run in which the "Sitol" and Me_2DQA were omitted. This was done in order to see the effect of the aluminum salt and caustic at the reaction temperatures and concentrations. The control, as expected, formed a clear,

F. Oxidation (Continued)

2. Seeding (Continued)

colorless solution. When $Al_2(SO_4)_3$ was added after the NaOH addition, an insoluble slurry was formed and remained during the remainder of the reaction conditions. However, when the second MeOH was replaced by water, practically all of the aluminum salt was in solution--probably as the aluminate ion. By using water in place of the second MeOH, it should be possible to wash the Me_2QA to a low water soluble salt level.

A series was run in which the dispersion milled gamma QA mill powder was varied from 2% to 5% on a toner basis. Unexpectedly, all of the samples went through the "grape juice" stage. Since the 5% level was previously shown to be satisfactory with another lot of Me_2DQA, this experiment pointed up the importance of determining the proper seed level for each lot of Me_2DQA. In the March, 1967 dimethyl campaign, this technique was used with each lot of Me_2DQA. The following tabulates the use of seed in this campaign:

September, 1966 Campaign

Lot	Laboratory Test	Level Used in Plant	IR	% Me_2QA*
8018	7% seed	10%	Good	94.4%
8019	10% seed	10%	Good	87.6%
8020	7% seed	7 + 3%	Good-	96.1%

(*) 5120-22A used as standard.

Batch 8018 used 10% seed in the plant rather than the 7% found needed in the laboratory because the latter appeared borderline. It was decided to go with 7% seed in the plant with batch 8020, since 5% seed gave "grape juice" in the laboratory. However, the plant batch gave "grape juice". It was saved by adding an additional 3% seed. The reason for the difference between the laboratory and plant run was never determined. It was suspected that 8020 may have contained more NaOH than it should have. Another possibility is that the laboratory washing of the test sample was more effective than the normal plant washing.

To eliminate the large amount of $Al_2(SO_4)_3$ diluent associated with the beta and gamma QA mill powders, the work started by W. A. West on HT drowned Me_2QA as a seed for the oxidation was reactivated. The quantity of HT-Me_2QA needed to seed the reaction varied with the quality of the

F. Oxidation (Continued)

2. Seeding (Continued)

Me_2DQA. Many of the batches of Me_2DQA tested could be oxidized with as little as 2-1/2% seed. The seed was added as a dry powder. It was effective because of its very small particle size. X-ray evidence indicates that HT-Me_2QA is an effective means of suppressing the alpha phase.

As a result of the work on seeding, the oxidation process was modified to the following:

	Gms.	Ml.	Moles
(1) Charge a 1 liter, 4-neck, r.b. flask equipped with agitation, reflux condenser, thermometer and dropping funnel with:			
2,9-Me_2DQA	40.0	-	0.12
MeOH	251.0	322	7.86
(2) Add 50% NaOH slowly keeping temperature below 60°C.	180.0	118	2.25
(3) Stir 30 min. at 55-60°C.			
(4) Add HT-Me_2QA seed (2-1/2%)	1.0	--	0.003
(5) Add "Sitol" (dry)	40.0	-	0.18
(6) Heat to 75°C. in 30 min.			
(7) Stir 1 hr. at 75-80°C.			
(8) Add water	280.0	280	15.56
(9) Stir 30 min. at 75-80°C.			
(10) Filter hot			
(11) Wash BY - with hot water			
(12) Dry at 80°C.			
(13) Goal Yield	39.8	-	0.12

3. MeOH Concentration

In some cases, regardless of the seed concentration, a few crystals of Na_2Me_2QA would not hydrolyze until water was added in step 8. Prior to the addition of the water, the oxidation was so thick that there was very little if any agitation. Increasing the MeOH concentration by as little as 5% appeared to have eliminated the Na_2Me_2QA

F. Oxidation (Continued)

3. MeOH Concentration (Continued)

problem. The oxidation slurry was still very heavy, but generally stirrable. Increasing the MeOH concentration in excess of 50% resulted in the hydrolysis of some Na_2Me_2DQA. This could be detected in the final product by IR as Me_2DQA. To prevent the undesired hydrolysis from occurring and yet still have an oxidation that goes to completion before adding water in step 8, the MeOH in step 1 was increased 10% to 354 ml. (276.1 gms.).

4. Aqueous "Sitol"

The addition of dry "Sitol" (sodium salt of m-nitrobenzene sulfonic acid) is a hazard because of a possible dust or MeOH explosion in the chute. Hence, it was highly desirable to convert the oxidation process to aqueous "Sitol". There was some question as to whether this could be done, since the presence of water was thought to hydrolyze Na_2Me_2DQA back to Me_2DQA. The resulting Me_2DQA will not oxidize. This was the reason that the original oxidation process used 97% MeOH and dry "Sitol".

To determine the tolerance of the oxidation for water, a ladder series was run. The water was added right after the "Sitol" in step 5. Expressed as a "Sitol" solution concentration, the following results were obtained:

"Sitol" Solution	Me_2QA Purity by IR
100% (no water)	Excellent
67%	Excellent
50%	Good +
40%	Good
36%	Good
33%	Good -
31%	Fair
29%	Poor

Based on these results, it should be possible to use a 36% "Sitol" solution without the final product containing an excessive amount of Me_2DQA. The plant uses a 43% "Sitol" solution which is well within the process limits.

F. Oxidation (Continued)

4. Aqueous "Sitol" (Continued)

For laboratory studies, it is not practical to use aquous 'Sitol". At room temperature, a 43% aqueous "Sitol" is more like a presscake than a solution. For this reason, it is handled hot in the plant. The same effect is obtained in the laboratory by adding dry "Sitol" and an equivalent amount of water. Hence, in step 5, 40.0 gms. of "Sitol" are washed into the oxidation flask with 60 ml. of water. This modification was checked out using batches 8018, 8019 and 8020 of Me_2DQA. All gave good quality Me_2QA by IR.

The amount of "Sitol" used is far in excess of that required on a moler basis to oxidize Me_2DQA. A ladder series was run in which aqueous "Sitol" was varied from a 3.5% excess to a 78% excess. The normal excess is 52%. The 3.5% excess of "Sitol" when run with 2-1/2 HT Me_2QA seed gave excellent Me_2QA by IR. Increasing the excess to 28 to 52% gave good Me_2QA while a 78% excess gave only fair Me_2QA. Hence, it would be desirable to reduce the "Sitol" concentration for improvements in both quality and economy. Similar results were obtained in the absence of seed.

An attempt to confirm this reaction with a 3% aqueous "Sitol" excess was unsuccessful. Additional work will be needed to establish a safe "Sitol" level. Because a lower "Sitol" level also means less water in the oxidation, it will be necessary to reduce the amount of 50% NaOH added to maintain the same caustic concentration. Due to a lack of time, this phase of the dimethyl work is currently inactive.

5. NaOH Concentration

A study was undertaken on the effect of NaOH concentration, since it plays a most important part in the oxidation of Me_2DQA. In the absence of NaOH, a "Sitol" oxidation does not take place. With insufficient NaOH, part of the Me_2DQA is not oxidized. This was demonstrated by a ladder series in which the NaOH concentration was reduced. 2-1/2% HT Me_2QA was used as seed and dry "Sitol" was the oxidant.

NaOH	Me_2QA Quality (IR)
19.6%	Excellent
17.8%	Good +
15.9%	Good
14.0%	Fair
12.6%	Poor

F. Oxidation (Continued)

5. NaOH Concentration (Continued)

Increasing the NaOH concentration beyond an optimum level will result in "grape juice" (Na_2Me_2QA). When this occurs, the final product will be loaded with unoxidized Me_2DQA. How this can occur can be better understood by examining the reversible reactions involved in the oxidation.

$$Me_2DQA \rightleftharpoons Na_2Me_2DQA\ (Soln.) \rightleftharpoons Na_2Me_2DQA\ (Solid)$$

$$\downarrow (o)$$

$$Na_2Me_2QA\ (Soln.) \rightleftharpoons Na_2Me_2QA\ (Solid)$$

$$\uparrow\downarrow$$

$$Me_2QA\ (Soln.) \rightleftharpoons Me_2QA\ (Solid)$$

A large NaOH excess is needed to shift the equilibrium to form Na_2Me_2DQA as completely as possible. Too large an excess results in large blue crystals of Na_2Me_2QA coming out of solution. When this occurs, the oxidation does not go to completion. In the presence of seed, Me_2QA comes out of solution and the reaction goes essentially to completion at the higher NaOH concentration. The amount of seed necessary for this to occur increases directly with the NaOH concentration. The NaOH concentration needed for a good oxidation depends upon the purity of the Me_2DQA. This will be discussed under Na_2DQA purity.

In a series using aqueous "Sitol" and 2-1/2% seed, the optimum NaOH concentration is seen to be a range for fair quality Me_2DQA.

NaOH	Me_2QA Quality (IR)
17.3%	Fair
17.9%	Good-
18.4%	Good-
18.9%	Good
19.4%	Good
19.6%	Good
20.4%	Good
21.3%	Poor

At the 21.3% concentration, the oxidation hung up as a mixture of Me_2QA and Na_2Me_2QA. Hydrolysis to Me_2QA was completed after adding water (step 8). The optimum NaOH concentration with 2-1/2% seed lies between 18.9% and 20.4%.

F. Oxidation (Continued)

5. NaOH Concentration (Continued)

By reducing the NaOH concentration, it is possible to oxidize Me_2DQA without seed. This is demonstrated in the following series:

NaOH	Me_2QA Quality (IR)
16.0%	Poor
16.7%	Fair
17.3%	Good-
17.9%	Good
18.5%	Good
19.1%	Good+
19.7%	Excellent
20.2%	Poor
20.6%	"Grape-juice"
21.2%	"Grape-juice"

The optimum NaOH concentration for the oxidation run without seed is 17.3% to 19.7%. The spread remains essentially unchanged. Only the concentration is changed by using seed. All of the preceding data were obtained using Me_2DQA from batch 8018.

6. Laboratory Oxidation

Based on the results of all the oxidation studies, the following is the currently used oxidation formula:

		Gms.	Ml.	Moles
(1)	Charge a 1 liter, 4-neck, r.b. flask equipped with agitation, reflux condenser, thermometer and dropping funnel with:			
	2,9-Me_2DQA	40.0	-	0.12
	MeOH	280.4	354	8.76
(2)	Add 50% NaOH slowly keeping temperature below 60°C.			
	Normal caustic	216.0	142	2.70
	Low caustic	200.0	131	2.50
	Low, low caustic	184.0	121	2.30
(3)	Stir 30 min. at 55-60°C.			
(4)	Add HT-Me_2QA seed			
	0%	0.0	-	0.00
	2-1/2%	1.0	-	0.003
	5%	2.0	-	0.006
	7-1/2%	3.0	-	0.009
	10%	4.0	-	0.012

F. Oxidation (Continued)

6. Laboratory Oxidation (Continued)

		Gms.	Ml.	Moles
(5)	Add "Sitol" (dry)	36.0	-	2.67
(6)	Add water	48.0	48	2.67
(7)	Heat to 75°C. in 30 min.			
(8)	Stir 1 hr. at 75-80°C.			
(9)	Add water	280.0	280	15.56
(10)	Stir 30 min. at 75-80°C.			
(11)	Filter hot - recycle bleed			
(12)	Wash BY - with hot water			
(13)	Dry at 80°C.			
(14)	Goal yield: 0% seed	39.8	-	0.12
	2-1/2% seed	40.8	-	0.12
	5% seed	41.8	-	0.12
	7-1/2% seed	42.8	-	0.13
	10% seed	43.8	-	0.13

The reaction in a good oxidation is usually complete by the time the reaction reaches 75°C. (step 7). This is easily determined under the microscope (oil immersion lens) by the absence of blue crystals of Na_2Me_2QA.

A starting series for testing the quality of plant Me_2DQA consists of the following:

	HT-Me_2QA Seed	50% NaOH
(a)	0%	low
(b)	2-1/2%	normal
(c)	5%	normal
(d)	5%	low

If all of these end up looking like grape-juice in step 8, higher quantities of seed and/or lower quantities of NaOH must be tried. Depending on the quality of the Me_2DQA, it will generally take between one and three sets of four oxidations to determine plant oxidation conditions.

F. Oxidation (Continued)

7. Me_2DQA Purity

The ease of oxidation of Me_2DQA depends upon its purity. As purity decreases, the NaOH concentration must be decreased and the seed concentration increased in order to have the oxidation go to completion. This is why each batch of Me_2DQA made in the plant was checked in the laboratory to determine NaOH concentration and seed level before the plant oxidation was run. Where possible, the NaOH level was reduced so that not more than 5% HT Me_2QA seed was needed.

The effect of the Me_2DQA impurity was demonstrated in the laboratory by carrying out a normal oxidation except for omitting the "Sitol". This amounts to reprecipitating the Me_2DQA. The filtrate was extracted with xylene to recover the impurity. This material represented 0.4% of the starting material. When it was dissolved and charged into an oxidation (step 1), the reaction did not go beyond the "grape-juice" stage. This same lot of Me_2DQA without the extra added impurity readily oxidizes without seed.

Similarily, a very poor lot of Me_2DQA was made easily oxidizable without seed. As was done before, the oxidation was run in the absence of "Sitol". The purified Me_2DQA was then isolated and dried. The original Me_2DQA required 10% HT Me_2QA to oxidize while the purified material oxidized readily without seed.

G. Plant Use of HT Me_2QA Seed

May, 1967 Campaign

Lot	HT Me_2QA Seed		NaOH Conc.	IR (DQA)	% Me_2QA*
	Lab	Plant			
8021	2.5%	2.5%	19.8%	Excellent	100.2%
8022	2.5%	2.5% + 2.5%	19.8%	Poor	92.6%
8023	2.5-5.0%	5%	19.8%	Good	103.7%
8024	2.5-5.0%	5%	19.8%	Good	102.0%
8025	5.0%	5%	18.9%	Good	99.8%
8026	9.0%	1% + 8%	18.9%	Poor	90.0%

(*) Standard

G. Plant Use of HT Me_2QA Seed (Continued)

Where the laboratory tests indicated borderline quality, the higher amount of seed was used in the plant. Batch 8022 plant quality was apparently somewhat worse than the laboratory tests had indicated. The second addition of seed did not appear to have helped the situation. Batch 8026 Me_2DQA was of very poor quality. By mistake, only 1% seed was initially added. It was partially recovered by adding the other 8% seed. The other four oxidations behaved as expected based on laboratoey oxidations.

H. Determination of Me_2DQA in Me_2QA by IR

All attempts to quantitatively measure the Me_2DQA in Me_2QA by IR have been unsuccessful. However, by the following procedure, an approximate measure of the Me_2QA quality can be determined. A small sample of the Me_2QA to be tested is ground into Nujol with a spatula. For good grinding, the mix should be viscous. The sample is then fluidized by the dropwise addition of more Nujol while mixing with the spatula. This is continued until the dispersion has the approximate viscosity of Nujol itself.

The instrument, a Perkin-Elmer double beam IR, is turned on and warmed up in the normal manner. Settings are as follows:

Resolution	927
Response	1
Gain	5
Speed	4
Suppression	6

Nujol is placed between two NaCl plates (part #027-1182) in the reference beam. Set the instrument to 6.197μ . Place the Me_2QA/Nujol dispersion between two other NaCl plates in the sample beam. Adjust the sample thickness so that absorbence (optical density) at 6.197μ lies between 0.6 and 0.8. Then set the instrument at 5.8μ and scan to 7.0μ . The relative quality of the Me_2QA is obtained by comparing the spectrum with the spectra that follow. Me_2DQA absorbs at 6.58μ .

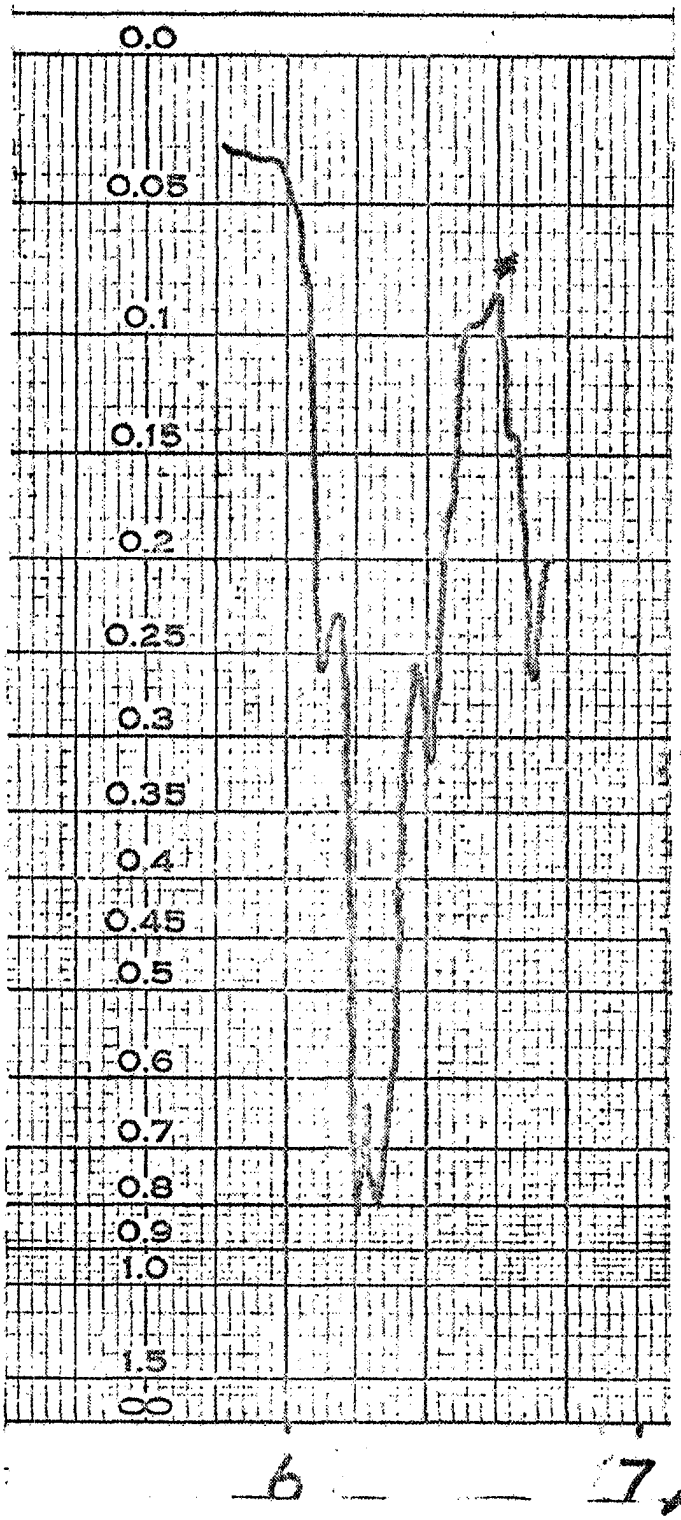
IV. REFERENCES

Additional data may be found in the following references:

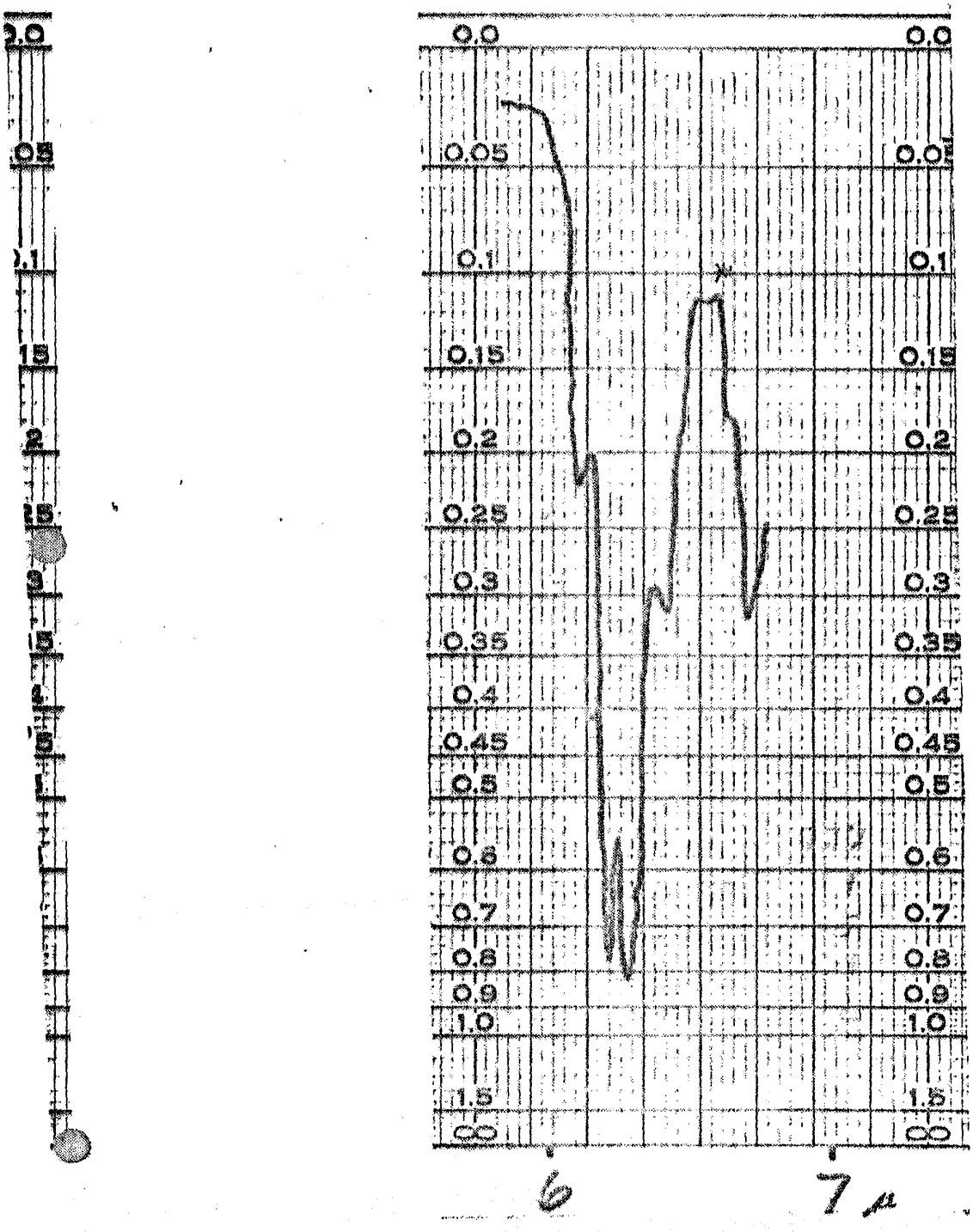
1. PT Condensation and Distillation

5120-2 - Vary PT concentration from 80% to 110%-216% batch size.

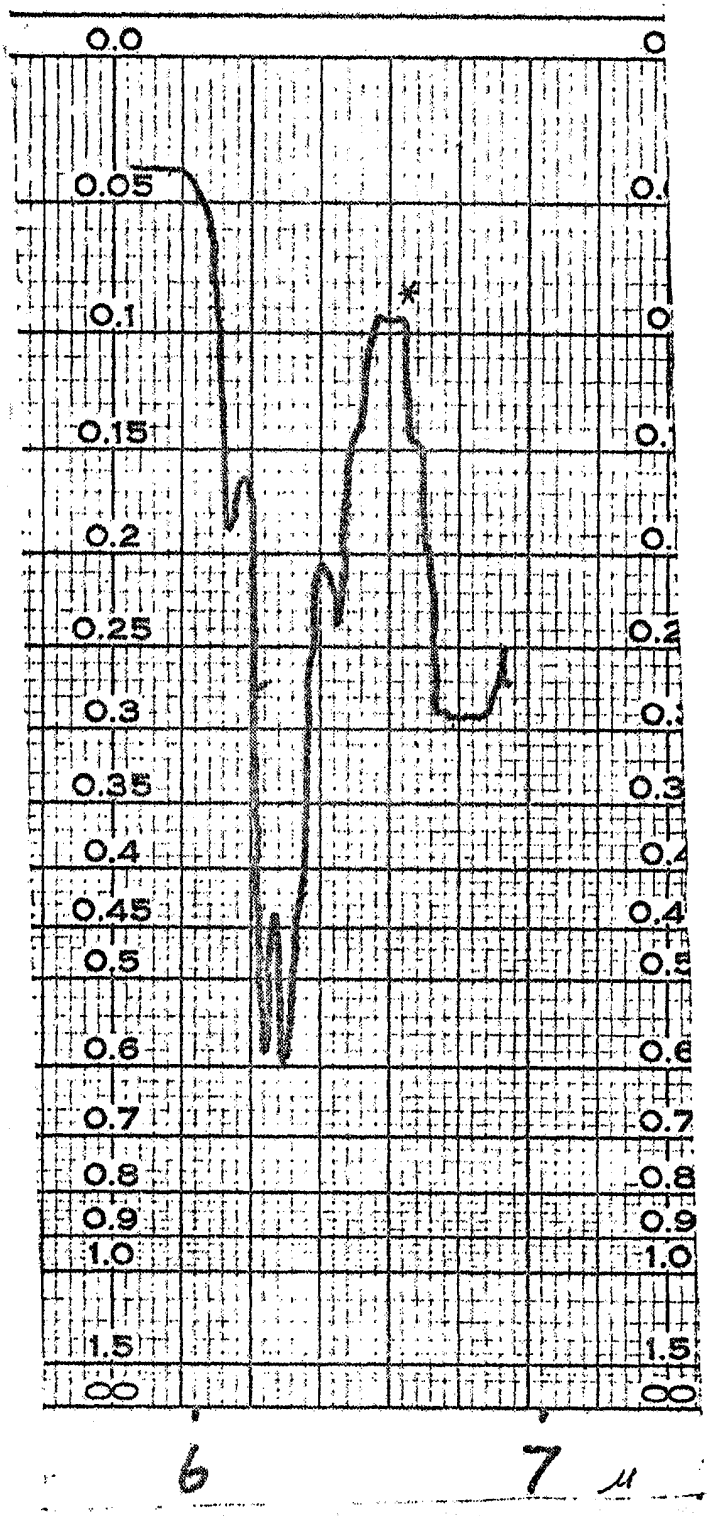
EXCELLENT



6007



G 225



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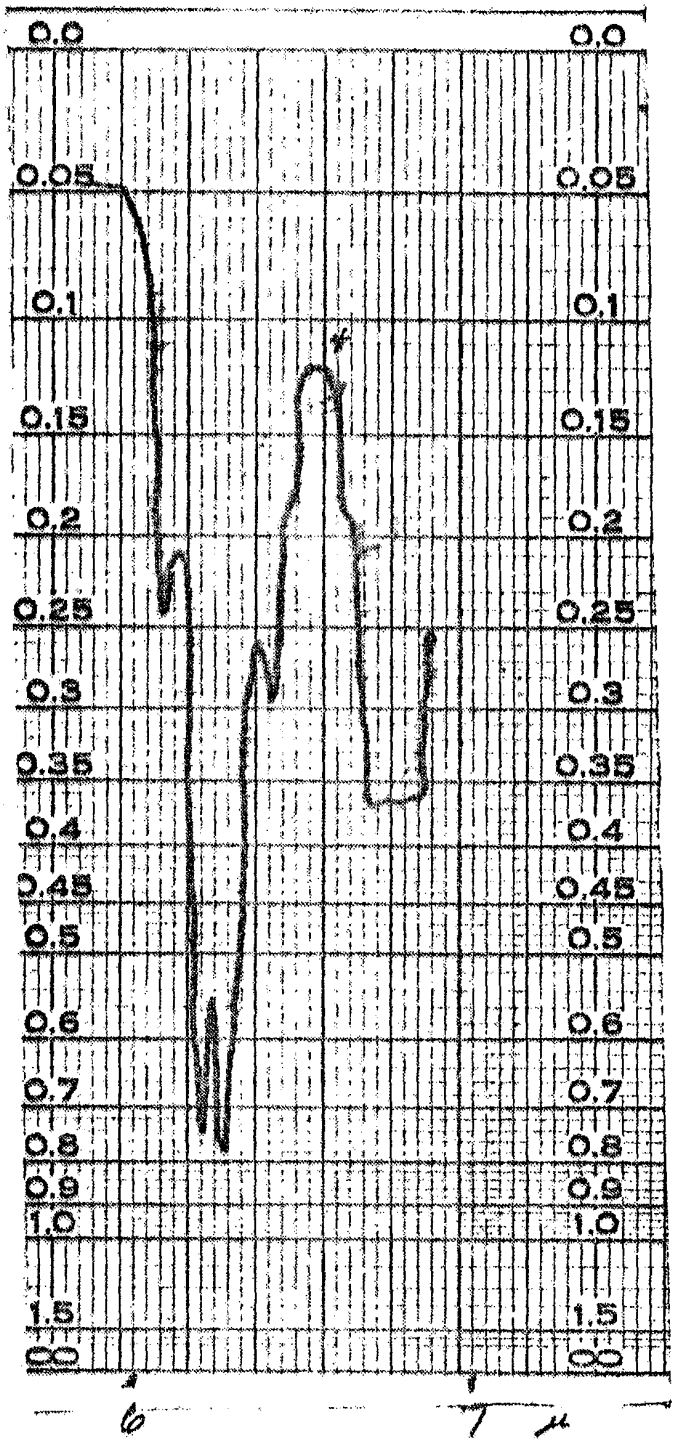
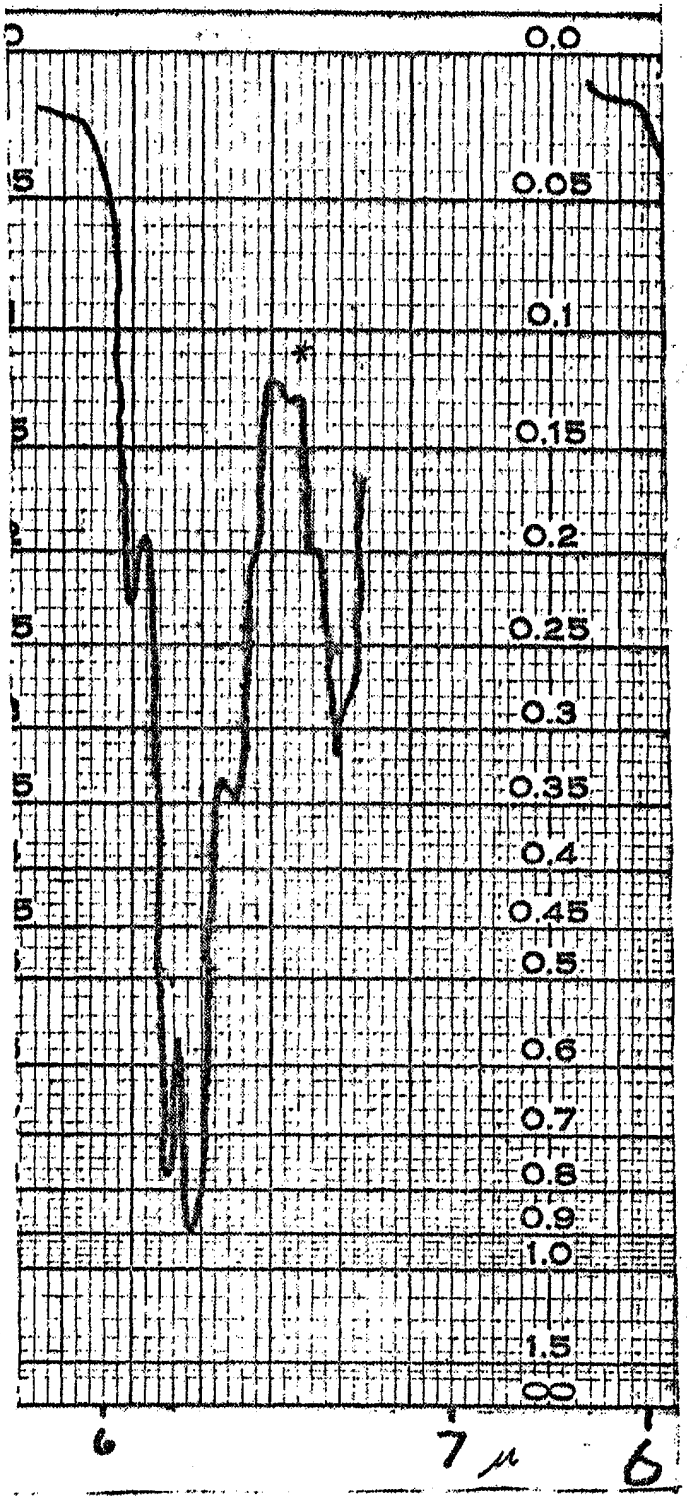
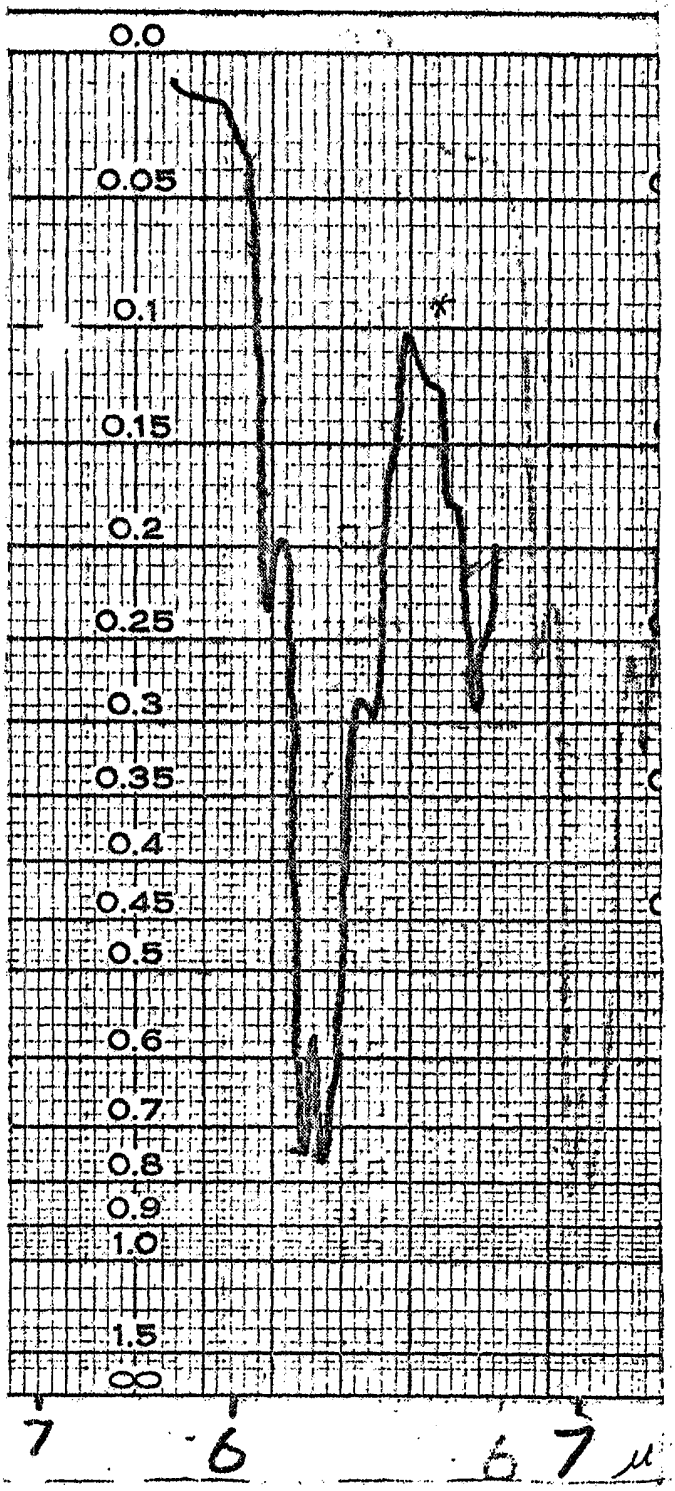


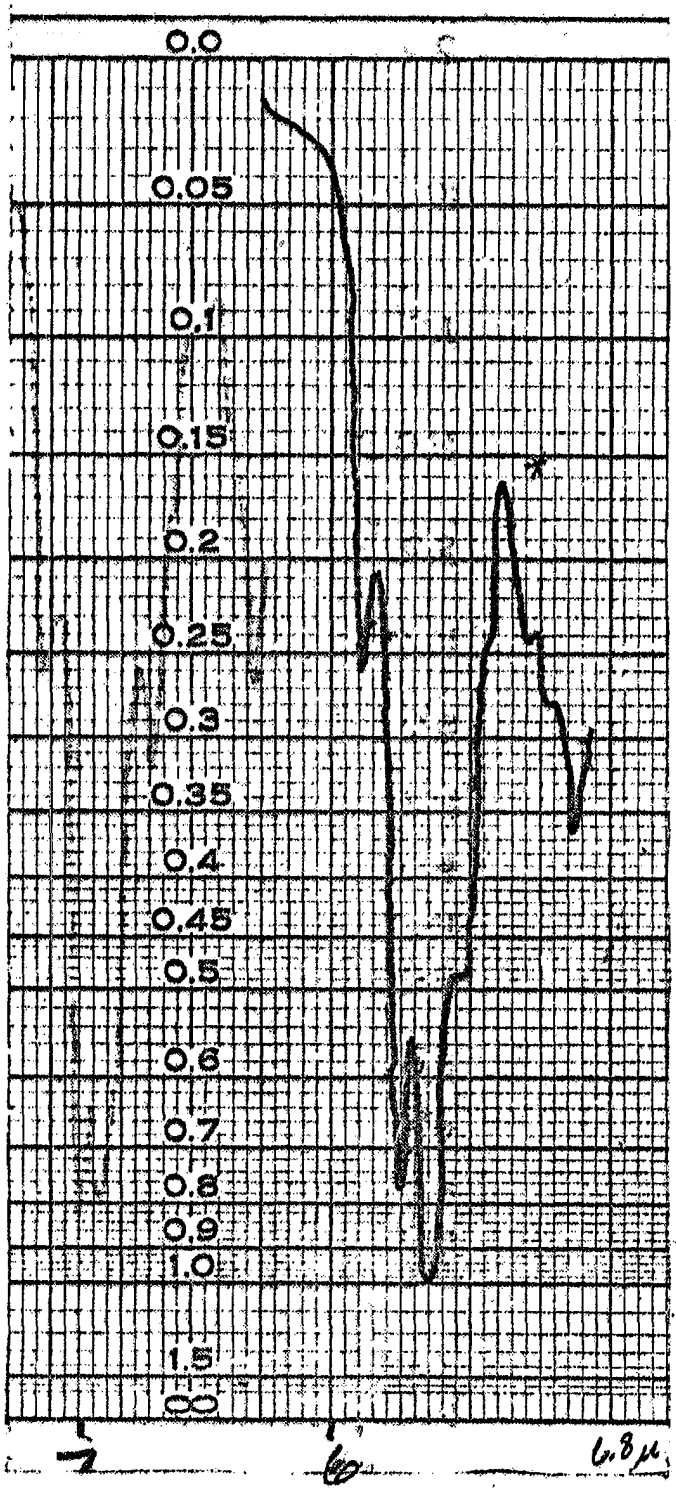
FAIR



POOR



VERY POOR



1. PT Condensation and Distillation (Continued)

5120-3 - 85-90°C. vs. 105-110°C. condensation temperature and doubling TFA catalyst.

6 - 0-150' reflux after condensation (3/1 PT/SSE); 60' reflux (7/1 PT/SSE); PTSA catalyst, 60' reflux.

7 - 60' reflux (7/1 PT/SSE) - TFA vs. PTSA

44 - Attempted oxidation of precipitated Me_2DQA

79 - Redistillation of plant Me_2DAT

96 - Plant TFA loss

2. 2. Pyrolysis

5120-83 - Contaminate pyrolysis feed with PT and TFA. Me_2DAT stability.

85 - Reduced laboratory pyrolysis boil-up.

3. Me_2DQA Purification

5120-98 - Wash fair Me_2DQA with 5% NaOH/MeOH

99 - Wash poor Me_2DQA with 5% NaOH/MeOH

4. Me_2DQA Crystal Phase

5120-39 - Recrystallize Me_2DQA from NaOH/MeOH.

51 - Reflux Me_2DQA in DMF and Dowtherm.

5. Oxidation of Me_2DQA

a. General

5120-8 -Oxidation of experiments 1-7

9 -Reproducibility of laboratory oxidation

10 -3-5% water in MeOH

11 -50% NaOH addition rate

12 -Contamination of oxidation with Me_2DQA after "Sitol" addition.

13 - Water in oxidation

14 - Oxidizability of Me_2DQA batch 8006

15 - Water in oxidation

5. Oxidation of Me_2DQA (Continued)

b. Seeding

5120-17 - Beta QA mill powder with premilled Me_2DQA

18 - Gamma QA millpowder with premilled Me_2DQA

19 - Seeding with beta QA millpowder, gamma QA millpowder, and premilled Me_2DQA

20 - Co-oxidize Me_2DQA and alpha DQA.

21 - 1% + 5% beta and gamma QA millpowder levels

22 - Co-oxidize Me_2DQA and beta DQA.

23 - Water soluble salts from $Al_2(SO_4)_3$

24 - $Al_2(SO_4)_3$ as seed

25 - Extracted Dispersion Milled beta and gamma QA presscake as seed.

26 - Millpowder concentration.

27 - Gamma QA millpowder level.

30 - Gamma QA millpowder required to oxidize Me_2DQA batch 8018

31 - Gamma QA millpowder required to oxidize Me_2DQA batch 8019

32 - Gamma QA millpowder required to oxidize Me_2DQA batch 8020

35 - HT Me_2QA level

36 - " "

40 - 2-1/2% HT Me_2QA at increased MeOH.

49 - Laboratory HT drowning of Me_2QA

52 - Evaluation of 5120-49

68 - " " plant HT Me_2QA

70 - " " " " "

71 - Oxidation conditions for Me_2DQA batch 8021

72 - " " " " " 8022

5. Oxidation of Me_2DQA (Continued)

b. Seeding (Continued)

5120-73 - Oxidation conditions for Me_2DQA batch 8023

74 - " " " " " 8024

75 - " " " " " 8025

76 - " " " " " 8026

c. MeOH Concentration

5120-37 - Increased MeOH

38 - " "

d. Aqueous "Sitol"

5120-41 - 0-67% water

45 - 67-111% water

46 - Oxidize Me_2DQA batches 8018, 8019 and 8020 with aqueous "Sitol"

55 - Aqueous "Sitol" addition temperature

63 - Aqueous "Sitol" concentration (68-116%)

66 - " " " (68-116%)

97 - 68% aqueous "Sitol" ±20% Me_2DQA

e. NaOH Concentration

5120-47 - Concentration reduced from 100% to 56%

48 - Add aqueous "Sitol" at reflux (NaOH 100-120%)

53 - Aqueous "Sitol" (NaOH 100-140%)

54 - Dry "Sitol", no seed (NaOH 56-100%)

57 - Aqueous "Sitol" (NaOH 100-120%)

58 - " " , no seed (NaOH 89-111%)

59 - Good quality Me_2DQA (NaOH 89-111%)

60 - Aqueous "Sitol", no seed (NaOH 100-122%)

62 - " " " " (NaOH 122-144%)

64 - Aqueous "Sitol", 11% NaOH - ±20% Me_2DQA

5. Oxidation of Me_2DQA (Continued)

   f. Me_2DQA Purity

      5120-86 - Oxidation of re-precipitated Me_2DQA

6. XOR-179 Closing Report - Attached

7. XOR-181 Closing Report - Attached

E. I. DU PONT DE NEMOURS & COMPANY

CC: W. S. Struve/
A. A. Brizzolara - Newark
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Newport, Delaware
August 10, 1967

547 ORGANIC COLORS - NEWPORT

XCR-179 - CLOSING REPORT

TITLE: Plant Synthesis - 2,9 Dimethyl QA

BACKGROUND: Research has shown in the laboratory that the use of TFA, rather than PTSA, as a condensation catalyst allows a reduction in the TD/SSE mole ratio from 7/1 to 3/1. A reduction in the amount of TD used will speed the recovery of TD and may ease some of the plugging problems encountered earlier. Use of TFA also eliminates the PTSA neutralization step previously partially responsible for poor yield, quality and operability. Research has also shown that the problems associated with the oxidation can be overcome by using dispersion milled gamma QA mill powder as seed.

OBJECTIVE: Synthesize 2,9-dimethyl DQA using TFA as the condensation catalyst and oxidize it to 2,9-dimethyl QA using dispersion milled gamma QA mill powder as seed.

CONCLUSIONS:

1. Yields were low for several reasons:
   a. Two of the three lots had low SSE yields.
   b. Major loss due to an inoperable Shriver. This necessitated using the leaf filters. One of the leaf filters was subsequently found to be bleeding badly to the sewer.
2. The dimethyl DQA TFA process is operable.
3. Satisfactory oxidations were obtained by using 10% dispersion milled gamma QA mill powder as seed. Laboratory tests demonstrated that the oxidations would not have gone without the seed.

CONCLUSIONS: (Continued)

4. The Shriver became inoperable probably because it was already partially plugged (QAQ from beta oxidations) when the dimethyl campaign began. Because of this, pressing was so slow that the dimethyl QA slurry cooled and set up.

5. Normal dispersion millings with QA gave products yellow vs. standard. This necessitated using increased quantities of dimethyl QA to get standard color. The problem appears to be incomplete solid solution.

RESULTS: The following in process yields were obtained:

Sample	Step	Method	8018	8019	8020
[illegible]/DP	After filtration	IR	68%	63%	73%
Me$_2$DAT/DT/pX	After condensation	Distillation and pyrolysis	54%	47%	62%
Me$_2$DAT/DE	After distillation	Pyrolysis	59%	(1)	(1)
Me$_2$DAT/DT	Start of transfer	Pyrolysis	50%	46%	63%
Me$_2$DAT/DC	End of transfer	Pyrolysis	60%	(1)	(1)
Me$_2$DAT/DP	End of pyrolysis	65 tank	25%	58%	71%
Me$_2$DAT/Me CP	68 tank	Chapman	63%	50%	54%
Me QA/Me QA(2)	End of oxidation	Chapman	51%	49%	74%

(1) Sample not taken.

(2) Contained 130# QA seed.

These data indicate that part of the yield loss occurred in the DAT recrystallization of batches 8018 and 8019. The volume of 8019 at this point was approximately 80% of the other two. No conclusions could be drawn from the in-process samples that were laboratory finished. The reason for this is not clearly understood, but appears to relate to [illegible]y of the DAT sample and to a lesser extent, tank levels.

Product losses for the run can be disbursed as follows:

RESULTS:

Synthesis	549#	
Samples	30#	
Spill (8019)	30#	
Filter and Drying	1056#	
Rework Lot	400#	
Total Losses	2065#	
QA Packed out	3300#	
Expected QA Production	5365#	(based on 71.7% yield)
Theoretical QA Production	7486#	

Investigation subsequent to the run has brought out that one leaf filter was bleeding badly, and it may not have always been backed up by the other leaf filter. This could help explain the disastrous loss between oxidation and packout. Unfortunately, no samples were taken of the leaf wash water to the sewer, so that no concrete sewer losses can be ascertained.

No major operating problems were encountered during the campaign. The only problem was a partially plugged condenser during the distillation of batch 8019. This occurred when the cooling Dowtherm got below the normal 48-52°C. The process itself gave no problems.

In the laboratory, it was found that 10% dispersion milled gamma QA mill powder was needed for batches 8018 and 8019 oxidations to go to completion. Batch 8020 required only 7% dispersion milled gamma QA mill powder to go to completion. However, in the plant, a sample of batch 8020 taken when 68-1 reached reflux, was in the "grape juice" stage. This batch was recovered by the addition of 3% mill powder. The percent assay QA for these batches was: 8018 - 94.4%; 8019 - 87.6%; 8020 - 96.1% (vs. 93.0-93.4% std.).

Because of the large amount of NaOH and "Sitol" used in the oxidation, the salt content of the final slurry is very high. Hence, when the temperature drops much below 60°C., the slurry sets up solid. The partial blockage of the Sharples slowed down the pressing to the point where the slurry could cool down enough to set up. At that point, the press was shut down and washed. The filterability of the oxidation slurry when diluted was reconfirmed on a laboratory pressure filter. Hence, the pressing problem does not relate to the dimethyl QA particle size.

Process data sheets are attached.

RESULTS: (Continued)

The first 7 mill charges used 85.5# dimethyl QA (100% basis) vs. a normal charge of 80.0#. This was done because the product was running on the yellow side in previous campaigns. As the product was still yellow, the dimethyl QA charge was increased to 90.0# (100% basis). A satisfactory product was obtained after this change. The following tabulates Newport quality results on each mill charge:

Lot From	To	MT	Str.		Mill Hrs.	100% Me_2QA
147		L^{99} Y^{29}	83	Y^{5} I^{5}	8-1/2	85.5#
148		L^{11} Y^{15}	96	Y^{29} I^{11}	"	"
149		D^{29} B^{20}	96	Y^{15} I^{11}	"	"
150	151	D^{29} B^{20}	92	Y^{29} I^{15}	"	"
152	153	D^{15} B^{15}	95	Y^{25} I^{15}	"	"
154	155	D^{29} B^{15}	91	B^{20} D^{15}	8	90.0#
156		D^{25} B^{20}	100	B^{25} D^{11}	"	"
157		D^{99} B^{99}	92	B^{25} D^{20}	"	"
158	160	D^{29} B^{29}	97	Y^{5} D^{8}	"	"
161		D^{29} B^{29}	92	B^{11} D^{18}	7	"
162	163	D^{99} B^{99}	90	B^{15} D^{25}	"	"
164	166	D^{99} B^{99}	97	B^{15} D^{15}	"	"
167	169	D^{99} B^{99}	87	B^{15} D^{15}	"	"
170	172	D^{29} B^{29}	90	B^{15} D^{20}	8-1/2	"
173, 174,	176	D^{25} B^{25}	93	B^{11} D^{7}	5-1/2	"
177		D^{15} I^{20}	90	Y^{10} I^{7}	"	"
178 and 179		L^{7} Y^{10}	99	B^{15} D^{11}	"	"

The reason for the yellowness is believed to be due to incomplete solid solution formation in the acid extraction. It should be possible to correct this situation by changing the acid concentration and/or contact time. The following tabulates Newport rubouts of mill charge mixes to be extracted and Newark alkyd plant tests of the extractions vs. [illegible]-D std.

RESULTS: (Continued)

Lot	Mill Charge	Rubout MT	Rubout Str.	Rubout XT	Alkyd MT	Alkyd Str.	Alkyd XT
407	147, 148, 154, 156, 158, 159, 160, 162, 163, 167, 168, 172, 173	D^{20}	92	B^6	B^5 I^2	100	B^8 D^4
410	149, 150, 151, 152, 164, 165, 169, 170, 175, 176, 177	D^{29}	93	Y^1	B^4	100	B^4
411	153, 155, 157, 161, 163, 166, 168, 169, 174, 178	D^{29}	92	B^{10}	B^{10} I^{10}	102	B^{18}

All three lots were OK to ship.

2,9 DiMe QA Plant Cycle Times

The following is a summary of the cycle times experienced during the recent 2,9 DiMethyl QA plant run. Lost time is not shown.

Cycle and Batch	Actual Time	Theoretical Time	Plant Std.	Comments
DES/SSE				
8018	36	12	13	24 hr. lag between DES and SSE
8019	19	12	13	Lost 5 hrs. dissolving solids.
8020	12	12	13	Good run
DD Condensation/Distillation (SSE transfer to final level adjustment)				
8018	10	7	6	Lost 2 hrs. fixing rotameters and finding DT line
8019	13	7	6	Erratic distillation (line pluggage ?)
8020	8	7	6	Good run
Pyrazole (Start of transfer to final cool-down)				
8018	18	11	11	10-hr. transfer
8019	15	11	11	10-hr. transfer - lost 2 hrs.
8020	12	11	11	8-hr. transfer

Cycle and Batch	Actual Time	Theoretical Time	Plant Std.	Comments
Nutsche Filtration				
8018	16	10	11	
8019	10	10	11	(Nutshce used as hold tank
8020	10	10	11	(because of long press (cycles
Oxidation				
8018	15	10	12(8)	Lost time getting sample results
8019	10-1/2	10	12	
8020	16	10	12	Insufficient seed - lost 6 hrs.
Freezing				
8018	7	3	3	(Blinded Shriver - all batches
8019	13	3	3	(dumped to leaf filters at (end of times shown
8020	9	3	3	

CLOSING REPORT WRITTEN BY: R. A. Johnson
R. A. Johnson

APPROVED BY: H. H. Gyorgy
H. H. Gyorgy
Research Supervisor

/lmj

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J. J. Adams -
C. F. Wood (5) - "
F. N. Odell - "
J. C. Chaney - "
R. H. MacAllister - "
L. S. Millelot - "
R. H.Wetzel - "
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Newport, Delaware
October 3, 1957

547 ORGANIC COLORS - NEWPORT

XOR-181 - CLOSING REPORT

TITLE: Plant Synthesis - 2,9 Dimethyl QA

BACKGROUND: TFA, rather than PTSA, was shown to be a suitable catalyst for the p-toluidine (PT)-SSE condensation in the laboratory and the plant (XOR-179). The more soluble and active TFA permits a reduction in TD/SSE ratio from 7/1 to 3/1, reducing pluggage problems and the catalyst neutralization step which previously resulted in reduced yield and quality. Further, laboratory study on the oxidation has shown that the voluminous 7-10% gamma (as millpowder) seed can be replaced by 2.5% HT drowned dimethyl QA.

Dimethyl DQA, tested in the laboratory, showed instantaneous hydrolysis from Na_2Me_2QA to Me_2QA with this seed. It was further found that a small reduction in NaOH concentration eliminates the need of seed in this oxidation using normal Me_2DQA. Modifications of the ratio of ingredients now permits use of "Sitol" solution; with the elimination of seed, no dry solids need be added to the tank. This eliminates extensive equipment requirements which would be required for safe solids addition.

OBJECTIVE: Synthesize 2,9 dimethyl QA at the 179% batch size using TFA as the condensation catalyst; 2.5% HT drowned 2,9-dimethyl QA as seed, and, if possible, no seed in the oxidation.

CONCLUSIONS:

1. The laboratory 70% goal yield for Me_2DQA was demonstrated in the plant.
2. The oxidation yield is essentially quantitiative.
3. Dry 2,9 dimethyl QA yield is dependent on recovery efficiency which in this six batch campaign was 90% versus 86% for β-QA.
4. Me_2DQA quality was poor. This appears to relate to Me_2DAT degradation during processing.
5. Because of quality deficiencies, it was not possible to oxidize Me_2DQA without seed.
6. Some operating problems were encountered in this run.
   a. Disappearance of TFA and TD.
   b. A need to modify the TFA/TD distillation to better remove TD.
   c. Filtration losses.
   d. Maintain batch identity to establish batchwise yields.
7. The first two batches of β-QA coming out of the Me_2QA campaign were poor in yield and fluorescence. Due to other operating changes on these batches, the degree to which this degradation was due to the 2,9 Me_2QA run cannot be established.

RESULTS: The following yield data were obtained:

Yield %	8021	8022	8023	8024	8025	8026
63 - SSP	70	66	76	75	77	77
62 - DAT						
IR	62	59	66	60	59	53
Pyr.	58	58	63	55	-	-
77 - Pyr.	-	73	-	-	65	57
65 - TDA	72	72	99?	68	77	58
68 - DQA	71	61	82	66	68	56
QA	74	91?	81	70	74	58
Dry QA	52	62	65	71	45	70

RESULTS: (Continued)

The low 62 DAT yields vs. 77 pyrolysis yields indicate non-uniformity of the 62 tank sample. The non-uniformity results from part of the Me_2DAT being out of solution at the 120-50°C. tank temperature. It is believed that the Me_2DAT comes out on the side of the tank rather than as a slurry; hence, a weak sample is obtained..

An excellent material balance was obtained on this run.

Material Balance Lbs.

	8021	8022	8023	8024	8025	8026
Me_2DQA						
65 Tk.	1472	1472	(?)	1394	1566	1182
68 Tk.	1451	1249	1666	1349	1395	1140
Seed	37	37	83	68	78	109
Total	1488	1286	1749	1417	1473	1249
Me_2QA						
68 Tk.	1533	(?)	1737	1486	1572	1280
Leaf filter	0	0	0	600	0	222
Spray Drier	1100	1300	1400	900	1000	1300
Total	1100	1300	1400	1500	1000	1522
Loss	-388	+ 14	-349	+ 83	- 473	+242
Cumulative	-388	-374	-723	-640	-1113	-871
Tar - 74 Still						
Calculated	163	163	163(?)	241	69	453
Cumulative	163	326	489	730	799	1252
Found	-	-	-	1080	-	1430

The overall Me_2DQA yield was 67%. Batch 8026 was considerably lower in DQA yield probably due to degradation of the Me_2DAT during re-distillation of the TD. Excluding this, the first five batches average 70%. This compares favorably with a laboratory yield of 70±2%. The yields check out well with the tars found in 74 still.

The oxidation yield for Me_2DQA to Me_2QA in 68 tank was 103% for the five batches for which data are available. This corresponds to a 99.5% laboratory yield and is within expected sampling/analytical accuracy.

RESULTS: (Continued)

A 90% yield was obtained across the filters and drier. Pigment was found in the filtrate storage tanks. No quantitative measure is possible, since these tanks are fed continuously to methanol recovery and the solids are sewered.

Based on storage tank measurements, the yield from DES to dry Me_2QA was 61%. This excludes the added seed.

The only presently available measure of Me_2DQA quality is its ease of oxidation. Good quality Me_2DQA oxidizes readily at high NaOH levels and without seed. Poor quality Me_2DQA requires seed and/or reduced NaOH levels to be oxidized. Yield is not affected.

The Me_2DQA quality in this campaign was poorer than the previous one in March (XOR-179). The oxidation conditions required were as follows:

	8021	8022	8023	8024	8025	8026
NaOH level (lbs./gal.)	0.166	0.166	0.166	0.156	0.156	1.56
% HP Me_2QA seed	2.5	2.5	5.0	5.0	5.0	9.0

The product quality was as follows:

QA - IR	Good	Poor	Good	Good	Good	Poor
% QA (Std. 5119-71B)	100	93	104	102	100	90

Based on these data, four of the six QA batches were of excellent quality. The other two could be consumed by blending. The poor quality of 8022 probably relates to 15% of the Me_2DQA remaining on the Nutsche. This resulted in a 15% NaOH excess. By an error in calculation, only 10% of the seed required for 8026 was added initially. Particle growth of the Na_2QA made the subsequent addition of the remainder of the seed result in borderline quality - Me_2DQA in the product.

One problem encountered in this campaign was the disappearance of TFA. It was necessary to make an addition of virgin TFA for each 62 tank condensation --

	TFA	
8021	10#	Initial charge
8022	8#	
8023	10#	
8024	6#	
8025	9#	
8026	10#	Initial charge

On batch 8026, virgin TD and TFA were used in an attempt to improve quality. There was no evidence that any of the lost TFA was hung up in the 62 system as the TD salt. Further studies will be needed to solve this problem

Another problem involves the removal of TD by vacuum distillation after the condensation. Normal procedure is to distill until there is 0.05% or less TD in the column bottoms. Since Me_2DAT will come out of solution at the 150°C. 62 tk. temperature, it is possible that some TD is trapped. This trapped TD could then be available to cause trouble in the subsequent pyrolysis. An attempt was made on 8026 to overcome this problem by heating 62 tank to 170°C. at the end of the distillation to put everything into solution, cooling back to 150°C., and redistilling. Additional TD was removed by this technique. However, the extra heating was apparently more harmful than allowing some of the TD to remain. The Me_2DQA (8026) was the poorest made as measured by ease of oxidation. It was necessary to use 9% seed to make the oxidation reaction go to completion.

There were no filtration problems in this campaign. The problem of the Shriver being plugged in the March campaign was overcome by preheating the Shriver to 60°C. and maintaining the Me_2QA slurry at 62-8°C. These steps were necessary to keep the salts in the Me_2QA slurry in solution. It was the precipitation of these salts combined with a partially QAQ blinded cloth that blinded the Shriver in the first campaign.

The post Me_2QA performance was as follows:

	9578	9579	9580	9581	9582
63-SSE	37(?)	72	72	74	76
62-DAT	58	74	76	80	-
65-DQA	51	60	72	92(?)	74
Fluorescence	34P	55P	118G	124G	118G

The first two batches subsequent to this campaign were poor in yield and in quality while the next three were excellent. The first batch had previously drummed out SSE added which apparently had degraded. The second batch showed an unexplained degradation in pyrolysis. There was no firm relationship of either to the Me_2QA campaign.

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