Serial No. KN-71-2

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

"3,10"-Dichloroquinacridone

Period Covered June 1970 - January 1971

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DATE: 2/11/71

KN-71-2
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NEWARK PLANT

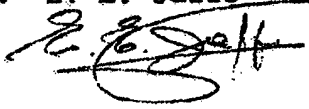
PIGMENT COLOR RESEARCH REPORT

TITLE: "3,10"-Dichloroquinacridone

PERIOD COVERED: June, 1970 to January, 1971

SUBMITTED BY: L J Pepoy Date Submitted: 1/13/71

Approved by: E. E. Jaffe Date Released: 2/11/71



ABSTRACT

Conditions have been found for the preparation of "3,10"-Cl_2DQA in 95% yield based on succinylsuccinate ester (SSE). Further refinement of the data may be desirable to arrive at the lowest concentration of acid catalyst consistent with high yield of "3,10"-Cl_2DQA.

The oxidation of "3,10"-Cl_2DQA to "3,10"-Cl_2QA has been accomplished with a spectral purity of 96% from laboratory-prepared, dry 3,10-Cl_2DQA However, a modification of the procedure is necessary to achieve the same degree of oxidation with Semi-Works (SW-70-00111) prepared "3,10"-Cl_2DQA due to lower quality "3,10"-Cl_2DQA which resulted from operational difficulties.

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I. Introduction

This report is a summary of the effort, directed toward finding conditions to maximize the yield and quality of "3,10"-dichlorodihydroquinacridone(3,10-Cl_2DQA) and its oxidation product, "3,10"-dichloroquinacridone (3,10-Cl_2QA).

II. Period Covered

June 1970 - January 1971

III. Patent Status

No patent applications have been filed

IV. Summary and Conclusions

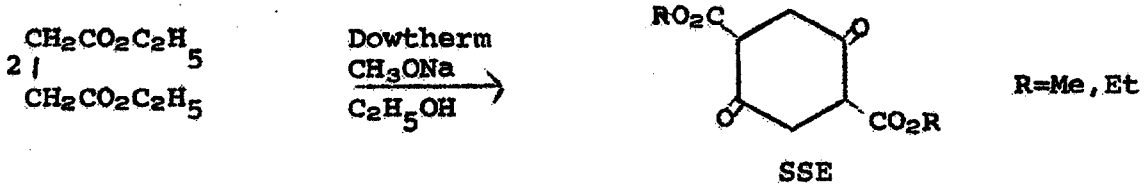
Conditions have been found for the preparation of "3,10"-Cl_2DQA in 95% yield based on succinylsuccinate ester (SSE). Further refinement of the data may be desirable to arrive at the lowest concentration of acid catalyst consistent with high yield of "3,10"-Cl_2DQA.

The oxidation of "3,10"-Cl_2DQA to "3,10"-Cl_2QA has been accomplished with a spectral purity of 96% from laboratory-prepared, dry 3,10-Cl_2DQA. However, a modification of the procedure is necessary to achieve the same degree of oxidation with Semi-Works (SW-70-00111) prepared "3,10"-Cl_2DQA due to lower quality "3,10"-Cl_2DQA which resulted from operational difficulties.

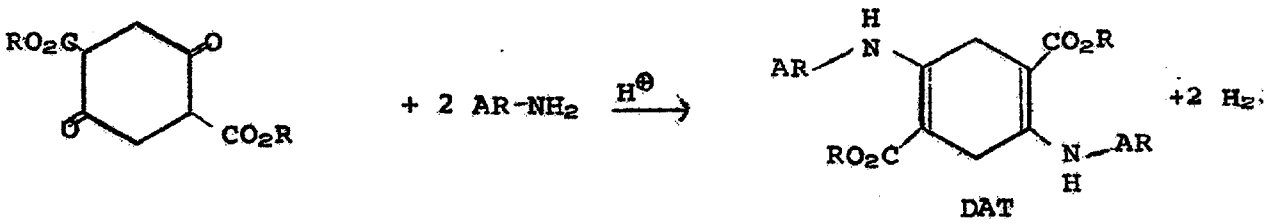
V. Discussion

1. Preparation of "3,10"-Dichlorodihydroquinacridone

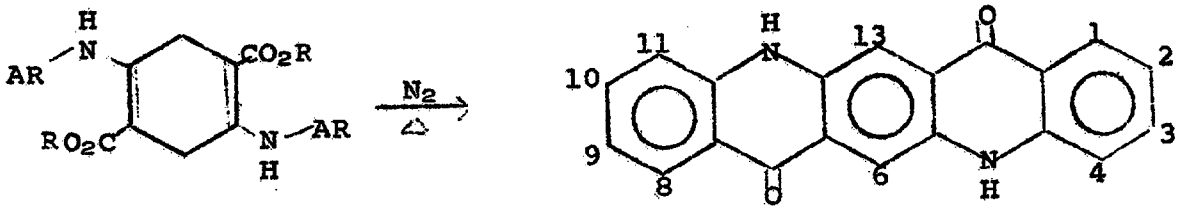
The preparation of a dihydroquinacridone involves the following three reactions:



SSE



DAT

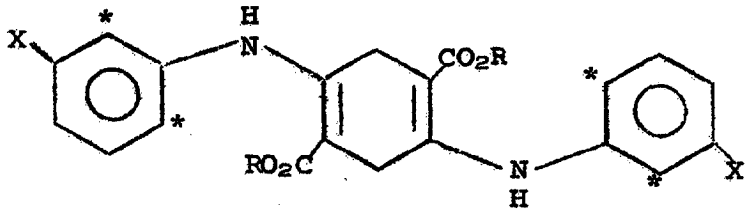


QA

For the problem at hand we were concerned only with the second and third reactions. The first reaction has reached the stage of being routine in the plant and as a consequence, in the laboratory we used isolated mixed ester (Et, Me) SSE.

The second reaction involves the acid-catalyzed condensation of SSE and two moles of an aromatic amine. The reaction is driven to completion by removal of product water under vacuum during the condensation stage and provides the dianilinodihydroterephthalate (DAT).

The cyclization of the DAT to the quinacridone (QA) is effected by the Conrad-Limpach reaction in boiling Dowtherm. It is at this stage that isomers would result if a substituted aniline were the amine used. Thus, an ortho-substituted aniline would give a 4,11-disubstituted DQA while a para-substituted aniline would provide the 2,9-isomer. The problem of obtaining a mixture of isomers occurs when one employs a meta-substituted aniline. If we refer to the following structure, we can see that ring closure can occur



at the positions marked by asterisks. Thus, we obtain a mixture of 1,8- 1,10-, and 3,10-disubstituted isomers. The significance of this mixture will be referred to later.

We ran various combinations of batch concentrations for both the condensation and the pyrolysis. The use of a 20% excess of m-chloroaniline to SSE and batch concentrations of 288% for condensation and pyrolysis gave 94-95% yields ex SSE of good quality "3,10"-Cl_2DQA(1941-57,-63) (See Experimental for details).

2. Oxidation of "3,10"-Dichlorodihydroquinacridone

As a class, the DQA's are colorless substances. The pale pink color which one observes is thought to be due to small quantities of QA derived from oxidation of DQA. Thus, to realize the color of the QA, the DQA must be oxidized to the QA a reaction which can be accomplished with various oxidizing agents. Du Pont procedures make use of Sitol, the sodium salt of m-nitrobenzenesulfonic acid, in a water-alcohol-caustic medium.

Infra-red spectroscopy was used for the preliminary evaluation of completeness of oxidation. As the efficiency of the oxidation

improves, there is a characteristic change in the shape of the N-H stretch region and a disappearance of an absorption band in the $1500cm^{-1}$ (6.65μ) region attributed to the methylene group of the DQA. A more precise and quantitative measure of the oxidation was carried out spectrophotometrically on sulfuric acid solutions of "3,10"-Cl_2DQA and "3,10"-Cl_2QA.

Various ratios of methanol (or ethanol)-sodium (or potassium) hydroxide-water were used. For legal and inventory reasons we preferred to use methanol instead of ethanol. In the past, potassium hydroxide has given more complete oxidation of some DQA's than has sodium hydroxide presumably because the potassium salt of the DQA is more soluble in the reaction medium. However, with "3,10"-Cl_2DQA the reverse has been found to be the case (1941-28,-30-49,-71). Possibly the potassium salt is more easily hydrolyzed back to the Cl_2DQA than its sodium salt.

Another point of interest that was evident from the early attempts at oxidation was the fact that the presence of large quantities of water were deleterious to the reaction. Thus, the oxidation had to be limited to the more costly, but necessary, region of high alcohol content in the alcohol-caustic-water ternary system (See experimental section for successful oxidation procedures)

Earlier in the report (p. 3) we mentioned that the preparation of 3,10-Cl_2DQA gave a mixture of isomers. This isomer mixture causes a problem with solvent bleed for this pigment. Past experience (KN-60-18) has shown that when the QA is substituted in the 4,11-positions (and presumably the 1,8 positions) solubility of the pigment increases. This may be due to steric interference of intermolecular hydrogen bonding between N-H and O=C< groups. The bleed can be eliminated by extracting the pigment with boiling dimethylformamide. However, this course is unacceptable from an economic and operational point of view.

Some bleed could be tolerated. An example is RT-787-D, "Monastral" Scarlet. In fact, Orange RK, a notorious bleeder might even be acceptable in thermoplastic acrylic lacquer. Thus, we attempted to produce "3,10"-Cl_2QA with a solvent bleed approaching RT-787-D. As a screening test for bleed we followed TF-7201-8 method and settled on three solvent systems: 1) 2B alcohol; 2)T-37767 lacquer thinner; and 3) 45:45:10 blend of xylene/T-37767/Butyl Cellosolve (1941-10).

At first we attempted to eliminate the most soluble (1,8) isomer by extraction of 3,10-Cl_2DQA with methanolic potassium hydroxide (1941-4C) and then oxidation (1941-4D). However, this scheme did not eliminate the bleed. Extraction of "3,10"-Cl_2QA with methanol-sodium hydroxide-water (1941-47) gave a product with less bleed than Orange RK, but again an extra step would be required in the plant. Conditions were found (1941-44C,-51C,-51D) that gave 94-96% spectral purity "3,10"-Cl_2QA which gave solvent bleeds intermediate between RT-787-D and Orange RK either by methanol washing (and hydrolysis) of the "3,10"-Cl_2QA disodium salt (1941-52) or partial acid (HOAc) hydrolysis of the salt (1941-55B). The best test for acceptable or unacceptable

bleed is determined in an actual paint system using the overstripe bleed test. Samples have been prepared (1941-65A-D,-66A,B,-74A,B) which will be submitted for outdoor exposure and the bleed test.

3. Semi-Works Run

During the week of December 14, 1970 a run (SW-70-00111) was made to prepare "3,10"-Cl_2DQA. The trial was fraught with difficulties which contributed to poor quality "3,10"-Cl_2DQA and possibly a low yield.

A sample of the Semi-Works - prepared SSE was condensed with m-chloroaniline and pyrolyzed in the laboratory to give a 93.2% yield (ex SSE) of good quality "3,10"-Cl_2DQA (1941-68). In the Semi Works (SW) a leak developed, due to metal fatigue, during the distillation which extended the time for this step and the solution transfer to the overhead tank, thus keeping the Cl_2DAT at elevated temperatures for an additional eight hours. Such treatment is known to degrade the DAT. Thus, when SW-prepared 3,3'-Cl_2DAT was pyrolyzed in the lab (1941-70B), only a 69.8% yield of Cl_2DQA was realized.

During the pyrolysis in the SW, operational difficulties in maintaining good boil-up were encountered. A constant rate of distillate removal could not be maintained. These two difficulties are known to give poor quality DQA and a low yield. Semi Works material was judged to be inferior to laboratory Cl_2DQA based on color and the prolonged washing cycle of the presscake.

The low quality of the SW "3,10"-Cl_2DQA required a modification of the oxidation procedure which appears to give as good results as obtained with laboratory - prepared "3,10"-Cl_2DQA.

VI. Experimental

Preparation of "3,10"-Dichlorodihydroquinacridone (1941-63)

To a 1 l four-neck flask equipped with a mechanical stirrer, thermometer, addition funnel, and a Vigreaux column connected to a vacuum distillation receiver was added 47g (0.194 mol) Et, Me SSE, 59.4g(0.465mol) m-chloroaniline (MCA), 102.5ml Dowtherm A(DT), and 2.14ml N-methylaniline (NMA) (288% concentration). Then 0.5ml trifluoroacetic acid (TFA) is added and the vacuum applied immediately. A vacuum of 20-30 torr is applied,the temperature brought to 90-95°C, and maintained in this range for 1 hour.

The vacuum is brought to 8-10 torr, the heat input increased, and fresh Dowtherm added as Dowtherm, excess MCA, TFA, and NMA are removed. Distillation is continued until the distillate contains less than 0.05% MCA (1941-64).

The vacuum is broken and the system is placed under a nitrogen atmosphere. For pyrolysis at 288% concentration, 66.5ml Dowtherm is added to the DAT, the temperature raised to 145°C, and the solution (ca.250ml) transferred to a heated addition funnel for pyrolysis.

The pyrolysis apparatus consists of a 5 l. four-neck flask equipped with a mechanical stirrer, the above mentioned addition funnel (under nitrogen), a thermometer, a nitrogen inlet tube, and a

Vigreaux column. The Cl_2DAT-DT solution is drip added in 90 min. into 147.5ml DT (1941-56) or into 340ml DT (1941-63) in the 5 l flask while maintaining maximum boil-up and removing 83.5ml or 169 ml respectively of DT plus alcohols.

After the addition is completed, the mixture is stirred under reflux for 1/4-1/2 hr., then cooled under nitrogen below 100°C, the solid filtered off and washed DT free with methanol, and dried. Yield: 91-95%.

Below are listed some data for the preparation of "3,10"-Cl_2DQA.

	Batch Concentration Based on unsubstituted DQA (Cl_2DQA)		ml TFA		
Ref.	Cond.	Pyrol.	47g SSE(NMA)	%Yield	Comments
1941-3-1	216(263)	108(132)	1 (no)	96.7	
-3-2	" "	" "	" "	93.1	
-15	288(351)	179(208)	" "	94.4	
-50	" "	" "	" "	90.4	3 hr DAT addition
-39	" "	" "	" "	89.4	
-40	" "	" "	" "	91.4	more DT in flask
-41	" "	" "	" "	93.2	2 hr DAT addition
-33	" "	216(263)	" "	90.8	2 hr DAT addition
-43	" "	" "	" "	91.6	
-16	" "	288(351)	" "	88.6	
-48	" "	" "	" "	91.7	3 hr DAT addition
-56	" "	" "	" (yes)	90.9*	
-57	" "	" "	" (no)	94.1*	large batch
-61	" "	" "	0.22(yes)	91.8	large batch
-62	" "	" "	" "	90.0	
-63	" "	" "	0.5 "	95.3*	SW method
-67	" "	" "	" "	89.4	hold DAT for 6 hrs.at 140°C SW method
-76	" "	" "	0.37 "	90.3	acceptable amt. of TFA, SW method

* NMA presence seems to lower the yield somewhat. A larger amount of catalyst seems to counteract this effect.

Oxidation of "3,10"-Dichlorodihydroquinacridone

It will be noted that the oxidation procedure requires a reflux period to form the salt of the Cl_2DQA. The reflux step seems to be necessary to improve the spectral purity of the product. Plant amounts for DQA oxidation (68 tank) are included for comparison. The value of 12 g "3,10"-Cl_2DQA (1941/73A) corresponds to the through-put equivalent to that of unsubstituted DQA produced in the plant, if the methanol used for washing of the product is excluded.

	1941-51C (D)	Plant	1941-73A(SW)
DQA	-	2100 lbs.	-
"3,10"-Cl_2DQA	6g (11.8g)	-	12g.
methanol	107.4ml	1260 gal.	111.1 ml
water	5 ml	1070 gal.	2 ml
sodium hydroxide	10g	75 gal.	10g
Sitol	6g(11.8g)	76 gal.	12 g
water	-	166 gal.	-
	Reflux 3-4 hours		
water	-	500 gal.	-
work up	100ml MeOH		1 l MeOH
Spectral Purity	94.7(94.1)		

The work-up procedure can consist of hydrolyzing the Cl_2QA salt with methanol (larger amount needed for SW material to minimize bleed) or with acetic acid (about 75% of the calculated amount of acid to neutralize the caustic is required). Solvent bleed and spectral purity of the methanol hydrolyzed material are slightly superior to the acid-hydrolyzed pigment.