KN-70-4 AQUEOUS OXIDATION OF DQA TO QA WITH PHASE CONTROL By: J. Jackson 1/68 - 1/69

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MU-1780 (Rev. 3/78)

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KN-70-4 #15

# NEWARK PLANT
# PIGMENT COLOR RESEARCH REPORT

## AQUEOUS OXIDATION OF DQA TO QA WITH PHASE CONTROL

Period Covered January, 1968 - January, 1969(Part time)

FILE: 223.91

DATE: 2/17/70

NJ 14071

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

FINAL REPORT

**SUBJECT:** AQUEOUS OXIDATION OF DQA TO QA WITH PHASE CONTROL

**PERIOD COVERED:** JANUARY, 1968 - JANUARY, 1969 - Part Time

**SUBMITTED BY:** Julius Jackson JULIUS JACKSON **DATE SUBMITTED:** 1/15/70

**APPROVED BY:** J.D. Struve **DATE RELEASED:**

**ABSTRACT**

The feasibility of oxidizing 6,13-dihydroquinacridone to α or β phase QA in an aqueous system, not involving additional organic solvents, has been demonstrated. A novel system of regenerative catalysts involving $Fe^{++}/Fe^{+++}$ ion and the sodium salt of 2-anthraquinone sulfonic acid was developed. In the event a shortage of oxidation capacity arises, this system should be considered because of its lower ingredient costs and higher kettle capacity.

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## I. INTRODUCTION

The knowledge that DQA can be oxidized to QA utilizing air as the oxidant has been available for some time. Various workers have demonstrated the feasibility of this operation using suspensions high in organic solvents.

1. Klein and Cooper, Ref. 5, demonstrated the feasibility of air oxidation of DQA to QA using a polycyclic aromatic quinone/air/tetramethyl sulfone system. This work has led to the issuance of U.S. 3,475,436.

2. Griswold, Ref. 6, demonstrated the use of 2-anthraquinone sulfonic acid as a catalyst for the oxidation of DQA to QA with air or hydrogen peroxide in a mixture of $NaOH/H_2O$/methanol.

3. Kolski, Ref. 7, studied the dry oxidation of DQA to QA by heating in air or oxygen. This work is being extended by others.

4. West, Ref. 8, demonstrated the oxidation of DQA to QA using 2-chloroanthraquinone as a catalyst with air in a $NaOH/H_2O$/methanol system and attempted to oxidize DQA to QA, utilizing a $KOH/H_2O$ system and the sodium salt of 2-anthraquinone sulfonic acid.

None of these workers demonstrated air oxidation with control of phase in a strictly aqueous system with less than stoichiometric quantities of the anthraquinone. For further details concerning the prior art see CP-92, Air Oxidation of DQA, Ref. 9.

Initial work in this report was directed at making QA of any phase, since it was thought that current HT acid drowning studies would make it possible to convert to either βQA or γQA in a subsequent size reduction and drowning operation.

After the initiation of the work, it was found possible to direct the operations to yield either βQA or γQA by seeding operations, which could be of interest in the manufacture of QA by our standard processes.

## II. SUMMARY AND CONCLUSIONS

1. Methods of oxidizing 6,13-dihydroquinacridone to QA in an aqueous solution were successfully developed on a laboratory scale.

2. The manufacture of γQA or βQA phases can be made at will.

3. Semi-Works development of the β process was satisfactory. More work would be required on the Semi-Works γQA process.

4. The methods are more economic than our presently used Sitol oxidation.

5. Exterior exposure of β phase pigment made by dispersion milling of air-oxidized β crude are being obtained in Series 68450. At six months exposure, the products were satisfactory.

6. Substituted DQA's exhibiting high solubility in NaOH or KOH can probably be oxidized by these techniques.

7. The work was discontinued in view of the presently large oxidation kettle capacity at Newport and the progress shown by studies on the direct dry air oxidation of DQA to QA.

## III. PATENT STUDIES

The basic processes developed in the body of this report are believed to be new and novel. A patent memorandum CP-92 (11/14/68) has been written and is awaiting action by the Patent Group.

## IV. EXPERIMENTAL DETAIL

### Typical Processes

### Type I - Preparation of βQA in Absence of $Fe^{++}$ Catalyst

Ref. 1803-34B

90 grs. α-DQA (.285 moles) made as per U.S. 2,821,529
into 200 cc $H_2O$
containing 2 cc Dowanol EB (1)
1.5 cc Surfynol 485 (2)
1.0 cc Emcol P10-59 (3)
stir 5 min.
add under reflux - good agitation
50% NaOH 214 cc (107 gr. NaOH = 2.67 moles)
wash in with 15 cc $H_2O$.
Heat to 105-110°.
Hold at 105-110° for 30 minutes.
Add 2.5 gr. β-sodium anthraquinone monosulfonate (AQS) or "silver" salt.
turn on air
hold at 105-110° under reflux for 5 hrs.
wash down walls of flask with 40 cc $H_2O$ every hour.
Dilute to 6 l $H_2O$
heat to boil
filter wash negative to BY
dry.
Yield 88 grs.
Infrared - Nujol Rub - No absorption 6.6; 14.37 microns - no DQA.
Crystal phase - beta
% QA 96.3 - sulfuric acid

(1) Dow Chemical Co. Ethylene glycol butyl ether

(2) Airco Chemical Co. Ethoxylated acetylenic glycol

(3) Witco Chemical isopropylamine salt dodecyl benzene sulfonic acid

Comments - Type I

Role of Surfactants

Since α-DQA is not readily wet by water, it was found beneficial to include surface active agents to assist in this operation. Dowanol EB and Surfynol 485 are a highly effective combination and did not interfere with the oxidation mechanism.

The low solubility and extremely poor wetting characteristics of the QA generated by aeration mechanism created the formation of a thick, extremely stable difficultly stirrable foam. The addition of Emcol P10-59 overcame this problem and aided in the lowering of viscosity of the system.

Alkali Use

Lesser amounts tend to give lower levels of oxidation. Large excess over the theoretical equivalent to form $Na_2DQA$ has been used. KOH may be substituted for NaOH, KOH use tends to slow rate of oxidation and results in formation of some quinacridone-quinone.

Study of DQA Purity

Several samples of DQA were worked with.

| Lots # | Fluorescence Value |
|---|---|
| 5230 | 91 |
| 9623-3 | 92 |
| 9622 | 106 |
| Feb. 68 shipment | 124 |

A marked increase in difficulty of oxidation has been observed with purer DQA (despite the fact that such DQA particles appear to be smaller). Influences on the ease of formation of $Na_2DQA$ may be a factor although this could not be substantiated by microscopic examination.

Reaction Mechanisms

The following reaction mechanisms were examined and are commented on.

1. $\alpha DQA + H_2O + NaOH + Air + AQS^* \xrightarrow{\Delta}$ αQA (very slow rate)
2. $\beta DQA + H_2O + NaOH + Air + AQS^* \xrightarrow{\Delta}$ γQA (slow rate)
3. $Na_2DQA + H_2O + NaOH + Air \xrightarrow{\Delta}$ βQA (v slow rate)
4. $Na_2DQA + Air \xrightarrow{\Delta}$ $Na_2QA$ (v slow rate)
5. $Na_2DQA$ in solution + AQS* in solution → βQA + $Na_2$anthrahydroquinone (very fast rate)

At this point in the study, the optimum mechanism seemed to involve the formation of the $Na_2DQA$ salt - its solution and oxidation.

1. $\alpha DQA + H_2O + 2NaOH$ $Na_2DQA$ solid $\rightleftharpoons$ $Na_2DQA$ (solution)

2. $Na_2DQA$ (solution + AQS*(solution) $\longrightarrow$ $\beta QA$ + $Na_2$anthrahydroquinone (solution)

3. $Na_2$anthrahydroquinone-sulfonate + $H_2O$ + Air $\longrightarrow$ anthraquinone sulfonate + NaOH

*AQS - β sodium salt anthraquinone monosulfonic acid.

## Ingredient Ratios

Since rapid oxidation (which always seems accompanied by formation of the purest βQA) is essential, a study of the DQA/$H_2O$/NaOH ratio was undertaken, on the basis of finding the point of (1) maximum solubility of $Na_2DQA$ coupled with sufficiently high alkalinity to prevent hydrolysis. This is complicated by the extremely low solubility of the sodium salt of β sulfonic acid-anthraquinone in strongly alkaline solutions. Disulfonic acid salts are even less desirable from this point of view. Other anthraquinones have been found less desirable than the mono acid salt.

## Temperature

High temperatures seem essential to accomplished the oxidation (possibly because of maximizing the solubility of $Na_2DQA$ and AQS). This, of course, lowers the solubility of $O_2$ in the reaction mass. This high temperature tends to promote recrystallization of the $Na_2DQA$ and particle size growth as the reaction progresses. Studies involving the addition of water after partial oxidation to increase the solubility of the $Na_2DQA$ component, and better dispersion of the air bubbles were made to increase the rate of the reaction and minimize recrystallization effects. Attempts to lower the temperature to prevent hydrolysis of $Na_2DQA$ prior to oxidation resulted in very low oxidation rates.

## Cost Reduction

This study was then continued in an attempt to determine:

1. Minimum amounts of AQS.
2. Most suitable oxidant.
3. Optimum conditions for scale up.

1. Despite the theoretical possibility of the anthraquinone to be reduced by interaction with the DQA and reoxidized by air, a significant quantity is needed by this reaction. We have studied the range .03 moles per mole DQA to 0.18 moles/mole. Secondary reactions leading to the formation of such compounds as anthrone and anthranol its enol form, and oxanthrone from the anthrahydroquinone probably account for the need to use more than trace quantities of anthraquinone sulfonic acid salt.

The most reproducible process at this period was achieved with higher levels of AQS, but intermediate levels of .034 moles/mole DQA seemed feasible. The high cost of this compound necessitates a minimum use.

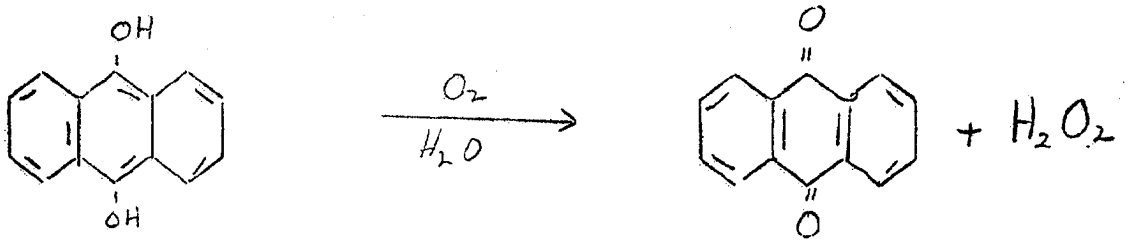
2. This reaction seems to involve three basic requirements in addition to economics.

a. Oxidation potential of the quinone hydroquinone system.
b. Solubility and chemical stability in the aqueous alkali solution of the quinone.
c. Ease of oxidation of the reduced hydroquinone by $O_2$.

We have studied anthraquinone, β-carboxylanthraquinone-hydroquinone, 2,5-dihydroxy-p-benzoquinone, $2NH_2$, 1 Cl, anthraquinone, 1,5-disulfonate (Na) anthraquinone, none of which are as effective as β monosodium sulfonate of anthraquinone.

At this stage of the study, we felt that the dehydrogenation of the DQA is caused by two factors:

1. Direct oxidation with the oxidized quinone form.
2. Secondary oxidation caused by $H_2O_2$ resulting from regeneration of the hydroquinone.




We have found that $H_2O_2$ will oxidize DQA to QA in the alkaline system we are using, but at an inefficient rate unless AQS is present.

Study of the Use of $O_2^=$ Catalyst System

The speculation that a secondary source of oxidation caused by $O_2^=$ resulting from regeneration of the hydroquinone by air (Ref. 1803-41) led to the concept of introducing into the system an $O_2^=$ generator.

This was done by studying the effect of the addition of $Fe^{++}$ to the system utilizing the reaction.

$$2\ Fe^{++} + O_2 \longrightarrow 2\ Fe^{+++} + O_2^=$$

We have demonstrated that the addition of $FeSO_4$ to the reaction mass along with the anthraquinone sulfonic acid salt results in a process which is more rapidly oxidized and permits the use of less of the quinone. We have not been able to see a quantity of $Fe^{+2}/Fe^{+3}$ $(OH)_3$ in the suspension (by microscopic examination) to

make us believe that the iron is in hydrated oxide form. The existence of $FeO_4^=$ may explain this observation. This compound is, of course, a powerful oxidizing agent and can be formed by reactions between $Fe(OH)_3$ and $Na_2O_2$ (Ref. 1803-40,45).

In addition, we have determined that DQA plus our standard ingredients ($H_2O/OH^-$/AQS) will react with $Fe(OH)_3$ to give significant quantities of QA, indicating that production of $Fe^{+++}$ may also be involved (Ref. 1803-47). By this approach, we can reduce the quantity of AQS from .034 moles/mole DQA to .009 mole/mole DQA at a significant cost savings.

This work led to the development of the process called Type II.

Type II - Preparation of βQA in Presence of $Fe^{+++}$ Catalyst

90 g αDQA (U.S. 2,821.529)
into 200 cc $H_2O$[1]
2 cc Dowanol EP
1.5 cc Surfynol #485
1.0 cc Emcol P10-59
stir 5 min.
add under reflux
50% NaOH 214 cc[2]
Wash in 15 cc $H_2O$
Heat to 105-110°C.
Hold at 105-110°C. 30 min.
add 1.33 g β sodium anthraquinone monosulfonate (AQS)[3]
18.5 g $FeSO_4.7H_2O$/30 cc $H_2O$[4]
Turn on air
Hold at 105-110°C. for 2-1/2 hrs.[5]
Wash down at 1,2 hrs. - 60 cc $H_2O$
Discharge into 6 l $H_2O$
106 cc 98% $H_2SO_4$ pH 11.5
Adjusted to pH 1.6 with conc. HCl
Heated to 95°C.
Held 45 min.
Filtered, washed $SO_4^=$-free.
Dried
Yield 93.5 g
Infrared - Nujol Rub - No DQA 6.6, 14.37 microns (6)
X-ray - Pure βQAβ

Comments
[1]Up to 450 cc seems OK - lower limit governed by viscosity (1803-62).
[2]25% reduction gave poorer degree of oxidation (1803-48A).
[3]Note lowered amount required decreasing cost vs. Type I.
[4]Reduction to .83 g. OK (1803-48B), reduction to .5 g. NG (1803-45B), reduction to 13.9 g OK (1803-49)?
[5]Note shortness of cycle vs. Type I, decreasing cost.

The development of seeding techniques (see attached Type III). βQA process gave rise to additional ingredient savings in that the amount of AQS could be substantially reduced at a good oxidation rate.

## Type III-Preparation of βQA in Presence of $Fe^{++}$ Catalyst and βQA Seed

Ref. 1900-18

90 g α-DQA (U.S. 2,821,529)
4.5 g RT-795-D (Disp.Milled small particle size βQA) Ex. V U.S. 3,030,370
into 200 cc $H_2O$[1]
2 cc Dowanol EB
1.5 cc Surfynol #485
1.0 cc Emcol P10-59
stir 5 min.
add under reflux - good agitation
50% NaOH 214 cc
wash in with 15 cc $H_2O$
heat to 105-110°C
hold 30 min. at 110° under reflux
add .5 g β sodium anthraquinone[2] monosulfonate (AQS)
13.9 g $FeSO_4.7H_2O$ 30 cc $H_2O$
Turn on air
Hold at 105-110°C. for total 5 hrs.
Sampled at 3 hrs.,15 min. and 5 hrs.
Wash down at hourly intervals.
50 cc $H_2O$
Isolation route - 1. filtered washed neg. to BY paper
2. $H_2SO_4$ acid extracted.
Yield 96 g.
Infrared-Nujol rub completely oxidized at 3 hr.15 min.[3]
No absorption 6.6, 14.37 microns
X-ray - β phase

Comments
[1]300 cc OK.
[2]Note lower requirement for AQS.
[3]Note good oxidation cycle.

## Process for Manufacture of γQA Crude

It was decided at this stage of the study that the economics of this operation could be made more attractive by:

1. Utilizing the βQA-type crude in HF milling operations.
2. Development of methods to manufacture γQA crude since the economics of γQA pigment manufacture via dispersion milling are quite attractive and little incentive exists to develop an HT-tube drowning method. Dispersion milling requires γQA crude feed.

The successful routes are attached hereto.

Type IV shows the manufacture of γQA via oxidation of βDQA in an $Fe^{++}/Fe^{+++}$ quinone catalyzed system.

**TYPE IV Preparation of γQA ex βDQA**

**Reference 1900-2B**

**Make** βDQA ex αDQA[1] (U.S. 2,821,529)

90 g αDQA
**into** 105 cc $H_2O$
400 cc methanol
**add** 56.2 g 50% NaOH
**Stir** 20 minutes.
**Add** 2 cc Dowanol EB
1.5 cc Surfynol #485
1.0 cc Emcol P10-59

**Heat** to reflux.
**Hold** 10 min. at reflux.
**Distill** off methanol until 98°C. reached.
**Add** water 110 cc
**50%** NaOH 159 cc.
**Add** 1.5 g β sodium anthraquinone monosulfonate
13.9 g $FeSO_4.7H_2O$ in 30 cc $H_2O$
**Aerate** at 105-110° under reflux.
**Add** 50 cc $H_2O$ at 5 hrs.
**Stop** aeration at 8 hrs.
**Isolate** via acid extraction.
**Infrared** - Nujol rub - No DQA at 6.6, 14.37 microns
**X-ray** γQA

Comments

1 Alternatively βDQA ex cyclization of a dialkyl 2,5-dianilino-3,6-dihydroterephthalate in a high boiling inert medium may be utilized i.e., Britisl 1,093,692 or βDQA made by solvent contact with αDQA U.S. 3,007,930.

Table V shows the development of a successful method of oxidation to γQA by means of γ seeding.

**TYPE V - Preparation of γQA ex αDQA via γQA Seeding**

**Ref. 1900-10B**

10 gr. γQA crude[1] ex U.S. 2,821,529
90 gr DQA
**into** 200 cc $H_2O$
2 cc Dowanol EB
1.5 cc Surfynol 485
1.0 cc Emcol P10-59
**Stir** 5 min.
**Add** under reflux - good agitation
50% NaOH 214 cc
**Wash in** 15 cc $H_2O$
**Heat to** 105-110°C.
**Hold at** 105-110°C. 30 min.

Add .5 g β-anthraquinone monosulfonate (2)
13.9 g $FeSO_4.7H_2O$/30 cc $H_2O$
Aerate 5 hrs.
Wash down hourly 50 cc $H_2O$
Acid extract
Filter
Wash
Dry
Yield 101.6 g.
Infrared - Nujol Rub-No detectable αDQA 6.6, 14.37 microns
X-ray - pure gamma phase.

Comments
1 - a - 4.5→10 g satisfactory
b - A suspension of air oxidized slurry can be utilized as seed.
c - γ pigment RT-796-D (US 2,030,370) also works 1.5→2.5 g.

This work is detailed in NB-1900.

Elucidation of Mechanism

Hydrolysis of $Na_2DQA$ - β Oxidations

These processes involve as the first step the formation of a saturated solution of $Na_2DQA$ and is conducted at 110° with a 30 minute hold period. Isolation of the grayish white compound showed the probable existence of $Na_2DQA$ and some βDQA after this period (Ref. 1803-38).

Role of β Monosulfonate Anthraquinone

In addition to its role as an oxygen carrier, the presence of this compound seems to be essential in controlling phase direction, perhaps by inhibiting the hydrolysis of $Na_2DQA$. Oxidation in the presence in sufficient quantity to insure completeness of oxidation always gives β phase. Decreased quantities result in incompletely oxidized γQA and βDQA (the latter perhaps inside the particles of γQA). This could result from the hydrolysis of the $Na_2DQA$. A study of the DQA/AQS ratio in the presence of γQA seed showed that larger amounts of AQS could be used with resultant more complete and rapid oxidations (1803-45, 1900-19).

Role of Surfactants

In addition to controlling viscosity and foaming, the surfactants (Dowanol EB, Surfynol #485, Emcol P10-59) are assisting degree of oxidation achieved with $O_2$ or $H_2O_2$ (Ref. 1803-45).

Mechanism of γQA Seeding

An attempt was made to determine the mechanism of the γ seeding. The $Na_2DQA$ formation was accomplished in the presence of and in the absence of γQA. X-ray examination of these products, as filtered, without washing, showed the presence of similar peaks which are not identified as being any known DQA or QA types, or $Na_2QA$ or NaOH.

We must assume then that they are $Na_2DQA$ and that γ seeding does not work by alteration of the sodium salt of DQA or by a βDQA mechanism. The latter point is also supported by the lack of UV fluorescence of this salt. αDQA fluoresces yellow and βDQA fluoresces as a redder yellow or orange shade. Unknown 2θ values were 8.5, 9.8, 11.4, 12.6, 25.6. (Ref. 1900-13D,E)

The addition of γQA seed <u>after</u> the formation of $Na_2DQA$ resulted in a γQA type oxidation. This supports the premise that phase direction results from a seeding mechanism (Ref. 1900-16).

β phase seeding was also studied and led to more rapid oxidation at lower levels of AQS. Ref. 1900-18.

<u>Miscellaneous Experiments - βQA Oxidations</u>

| | |
|---|---|
| 1803-9,10 | Size reduction of DQA prior to air oxidation had little influence on result. |
| 1803-11 | Fusion of DQA/NaOH/sodium salt 2 anthraquinone sulfonic acid gave rise to low level of QA, DQA, and no QAQ. |
| 1803-9,12,13, 14,15 | Attempts to substitute KOH for NaOH in early work had little influence on course of oxidation. The object was to obtain greater solubility of K salt. |
| 1803-151 | Attempts to utilize $H_2O_2$ in place of air did not give rise to greater levels of oxidation although oxidation does take place. |
| 1803-23 | Decreasing total alkalinity (to maximize solubility of $Na_2DQA$ and AQS)was not beneficial. |
| 1803-24,26 | Topping of reaction mass with AQS or Sitol did not benefit degree of oxidation. |
| 1803-19A,B | Attempts to utilize the following in the system were unsuccessful.<br>1. 2,5-dihydroxy-p-benzoquinone.<br>2. 2-amino/chloro anthraquinone.<br>3. 2-chloroanthraquinone. |
| 1803-19C | Complete oxidation of $Na_2DQA$ with equimolar quantities of AQS can be accomplished in the absence of $O_2$. |
| 1803-39B | The use of DQA/NaOH/2-pyrrolidone/air as in British 1,080,850 was briefly studied. Incomplete oxidation resulted. |
| 1803-39C | The use of hydroquinone-air, and hydroquinone-$NaClO_3$ in the system otherwise similar to our standard operation did not give evidence of oxidized QA. |

1803-46 The use of anthraquinone and β anthraquinone carboxylic acid was not satisfactory.

1803-50,56 Presence of QAAF during air oxidation to βQA reduced particle size obtained, but the products were not pigmentary.

1803-59,62 Study of DQA/$H_2O$/NaOH ratio shows wide variations possible.

1900-11,12,20 Attempts to oxidize 2,9-dimethyldihydroquinacridone in a manner similar to that used for DQA failed. Attempts to increase solubility by means of KOH were not successful.

1900-16 $CoSO_4$ found to act similarly to $FeSO_4$ as an $O_2$ carrier.

1900-20,22 Attempts to oxidize 2,9-difluoroDQA and 4,11-dimethyl-DQA showed the presence of considerable levels of oxidation.

Analytical Procedures

Surfynol #475 and also sodium salt of 2-anthraquinone sulfonic acid solutions in sulfuric show similar absorption to DQA. Inadequate washing gives rise to apparently low QA results.

SEMI-WORKS STUDIES (For details see DNS-68-1)

βQA air oxidations were successfully scaled up in the Semi-Works and converted to pigments via dispersion millings. (Ref. DSN 68-1, SW-00333,4,5,8,00342).

The pertinent findings are:

1. Air oxidation scaledup easily.
2. Crudes presented no filtration problems.
3. Can be directly converted to β-phase pigments (without prior acid extraction).
4. Gave dispersion-milled products which were close in masstone, darker and bluer in tint versus standard β-phase crude controls.

γQA Air Oxidation

Semi-Works studies on the air oxidation of γQA were not totally successful. Lower levels of conversion to γQA resulted that achieved in the laboratory. The γ-QA crude was dispersion-milled to convert to pigmentary form and presence of DQA further confirmed. (Ref. SDN 68-1, SW-00365, 00388, 00390). This phase of the work was not completed for reasons previously stated.

**REFERENCES**

1. NB 1803
2. NB 1900
3. DSN 68-1
4. Miscellaneous Product Improvement Studies 2/12/68
5. Klein KN-64-11 Oxidation of Dihydroquinacridone in Tetramethylene Sulfone
6. Griswold NB 5077-83,91,98,124.
7. Kolski, Exp. Station Request WPES167-8, 9/14/67
8. W.A.West, NB 5108-16, 5108-34B
9. CP-92, Air Oxidation DQA, J.Jackson 11/14/68
10. VanSant WPP 69-9, Air Oxidation of DQA - Economic Evaluation
11. Exposure Series 68450

dc