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PIGMENTS DEPARTMENT

NEWPORT, DELAWARE

TITLE: OPAQUE ORANGE

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PREVIOUS RELATED REPORTS: NONE

PERIOD COVERED: 9/75 to 6/77

ABSTRACT

This report summarizes the laboratory work done to date to develop an organic orange pigment. A pigment of this type is needed, primarily in automotives, as a non-lead replacement for Molybdate Orange.

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I. INTRODUCTION

Lead pigments are being eliminated from automotive paints. This has resulted in a need for a very yellow RT-759-D type pigment; that is, a large particle size opaque pigment in the orange-scarlet color range. The composition chosen for obtaining this color was the solid solution between QA and 4,11-Cl_2QA. This report primarily covers the routes explored in trying to obtain such a product. A secondary objective was to develop a commercial process for making the byproduct free 4,11-Cl_2QA intermediate needed in the solid solution for intensity.

II. SUMMARY AND CONCLUSIONS

1. The best laboratory product made in this study was a 50-50 solid solution of QA in 4,11-Cl_2QA.
   a. The product was formed by premilling followed by a DMF reflux.
   b. This product was not commercialized because it had a milky masstone in both TPA and TSA paint systems.
2. Solid solution formation takes place by alpha QA dissolving in the 4,11-Cl_2QA crystal lattice.
3. Solvent milled (MeOH/NaOH) solid solutions were dull in masstone and lacked opacity because the particle size was too small.
4. Solid solutions formed from crudes appeared to maintain the particle size of the 4,11-Cl_2QA component and were too large for maximum opacity.
5. The DMF reflux time of premilled pigment could be adjusted for maximum opacity and gave a more uniform particle size than a methanol-NaOH reflux. The particle was more acicular than RT-759-D which probably accounts for the milky masstone in paint.
6. A polar solvent is needed for solid solution formation to take place.
7. The intensity of the solid solution is a function of the purity of the 4,11-Cl_2QA component. The required 4,11-Cl_2QA free of m-nitrosobenzenesulfonic acid-4,11-Cl_2DQA byproduct can be obtained by oxidizing either with Sitol in a high caustic media or with Silver salt (2-anthraquinone sulfonic acid sodium salt).
8. Co-premilled 4,11-Cl_2QA-QAQ did not form a solid solution when refluxed in DMF or methanol/NaOH.

III. PATENT STATUS

No patent action has been taken as a result of this study.

IV. DISCUSSION

1. QA/4,11-Cl_2QA

The initial experiment to make an opaque orange involved solvent milling in methanol, a 60/40 mixture of gamma QA and the sodium salt of 4,11-Cl_2QA. The milling supplied sufficient energy for the QA to go into the 4,11-Cl_2QA crystal lattice. Otherwise, solid solution formation only takes place with alpha QA. The solvent milling resulted in a very light opaque masstone vs. RT-787-D, the dispersion milled counterpart made from conventional 4,11-Cl_2QA (brown). The solvent milling route was not pursued because of a lack of solvent mills in the QA plant and expected problems with commercializing a process for making the sodium salt of 4,11-Cl_2QA. Subsequent rubout comparison with premilled/DMF products indicated that solvent milling resulted in a particle size that was too small for maximum opacity.

A more practical route to a product appeared to be the use of crude components. Solid solution formation could be done in two ways. In one, high purity 4,11-Cl_2QA (orange) was added at the end of the alpha QA oxidation and then extending the reflux. The other procedure involved refluxing the components in methanol-NaOH. In both cases, the particle size was too large for maximum opacity. Using the second procedure, attempts were made to reduce the particle size by reducing solvency. This was done by varying the NaOH concentration, replacing part of the methanol with water, and using QAAF as a growth inhibitor. None of these was effective. When the concentration of NaOH in MeOH was less than 0.22 moles (ca. 1%), solid solution formation was incomplete after refluxing for 8 hours. At 10% NaOH, solid solution formation was also incomplete because some of the 4,11-Cl_2QA formed the sodium salt and some of the alpha QA appears to have gone to the gamma phase. When over one-third (by volume) of the methanol was replaced with water, solid solution formation was incomplete after 8 hours at reflux. The presence of as little as 0.1% QAAF

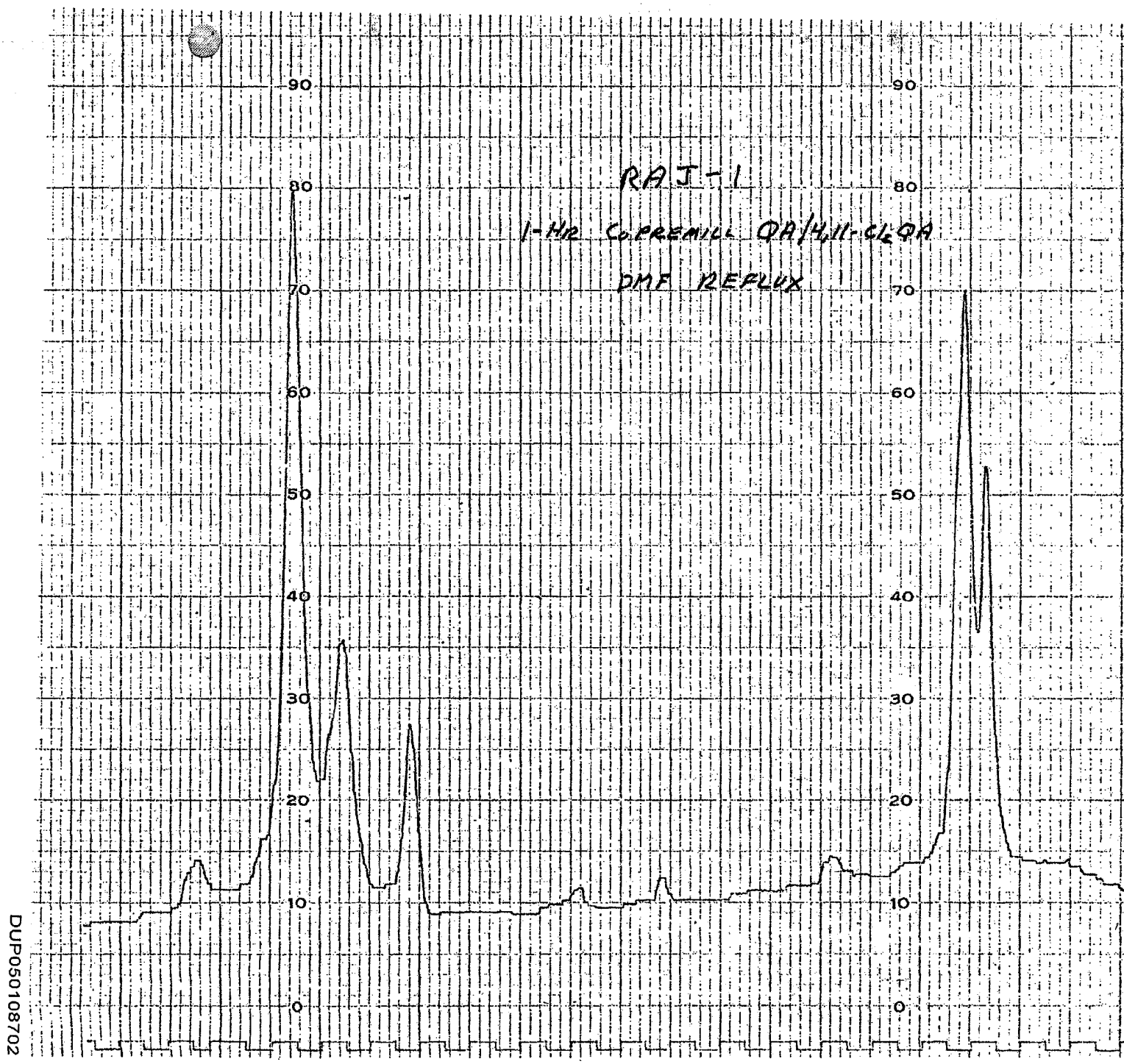
IV. DISCUSSION (Continued)

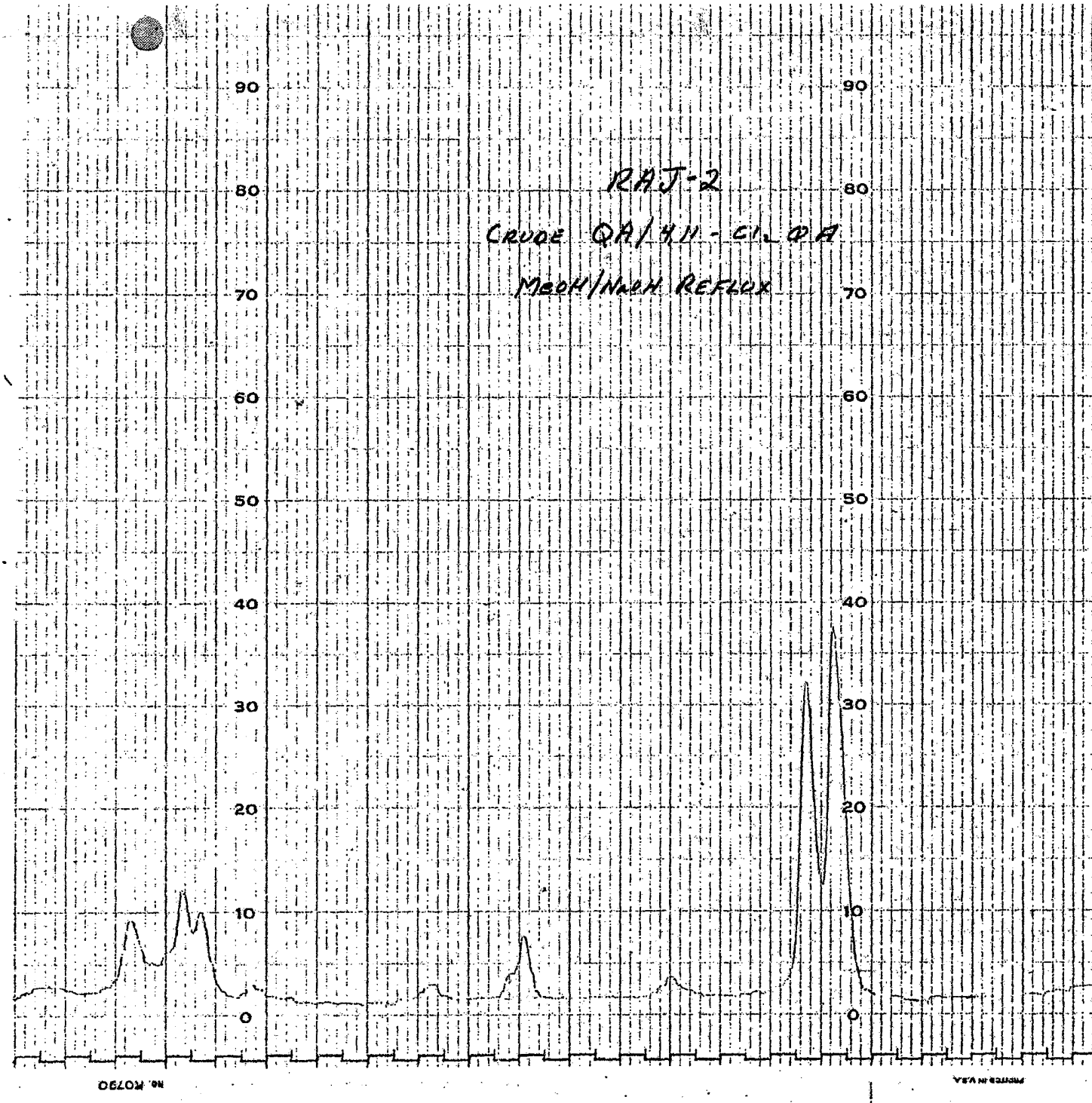
1. QA/4,11-Cl_2QA (Continued)

(pigment weight basis) was sufficient to inhibit solid solution formation. Professor Tiller has suggested that at considerably lower concentrations, QAAF may still be of interest as a means of obtaining a less acicular particle. A change in solvent system was also investigated. Refluxing the two components in DMF resulted in incomplete solid solution formation. Light microscope observations during reflux showed a mixture of orange square platelets and rods. The x-ray scan indicated that some of the alpha 4,11-Cl_2QA had converted to beta and possibly some gamma.

The work with the crude components indicated that the 4,11-Cl_2QA component controlled particle size. Light microscope observations suggested that solid solution formation took place by epitaxial growth. Hence, to maximize opacity, it was necessary to mechanically reduce the particle size of at least the 4,11-Cl_2QA component. As little as one hour of laboratory premilling was sufficient to reduce particle size below the maximum opacity level. Additional milling time (up to 22 hours) offered no advantages. Several solvent systems for growing the particles back were investigated. A mixture of water, Arquad 16/50, Renex 698 and 10% NaOH (Fitzgerald process) after 3 hours at reflux produced a solid solution from the co-premilled components that was too small in particle size for good opacity. Better opacity and intensity were obtained by refluxing in DMF. Methanol-NaOH, a more practical solvent, was also tried, but it resulted in a less uniform particle size than DMF. Opacity of the DMF solid solution was maximized by refluxing 2 hours. it is of interest to note that both premilling followed by solvent development (see RAJ-1) and solvent milling in methanol-NaOH (see RAJ-3) had a crystal habit that was different from the crystal habit of the solid solution formed from crudes (see RAJ-2).

The solid solution could also be obtained from the premilled components by heating them in a bomb containing a 36/64 (vol.) methanol-water mixture for 4 hours at 155°C. and by refluxing them in ethylene glycol. The methanol-water mixture was chosen because it had the same dielectric constant as DMF. Neither





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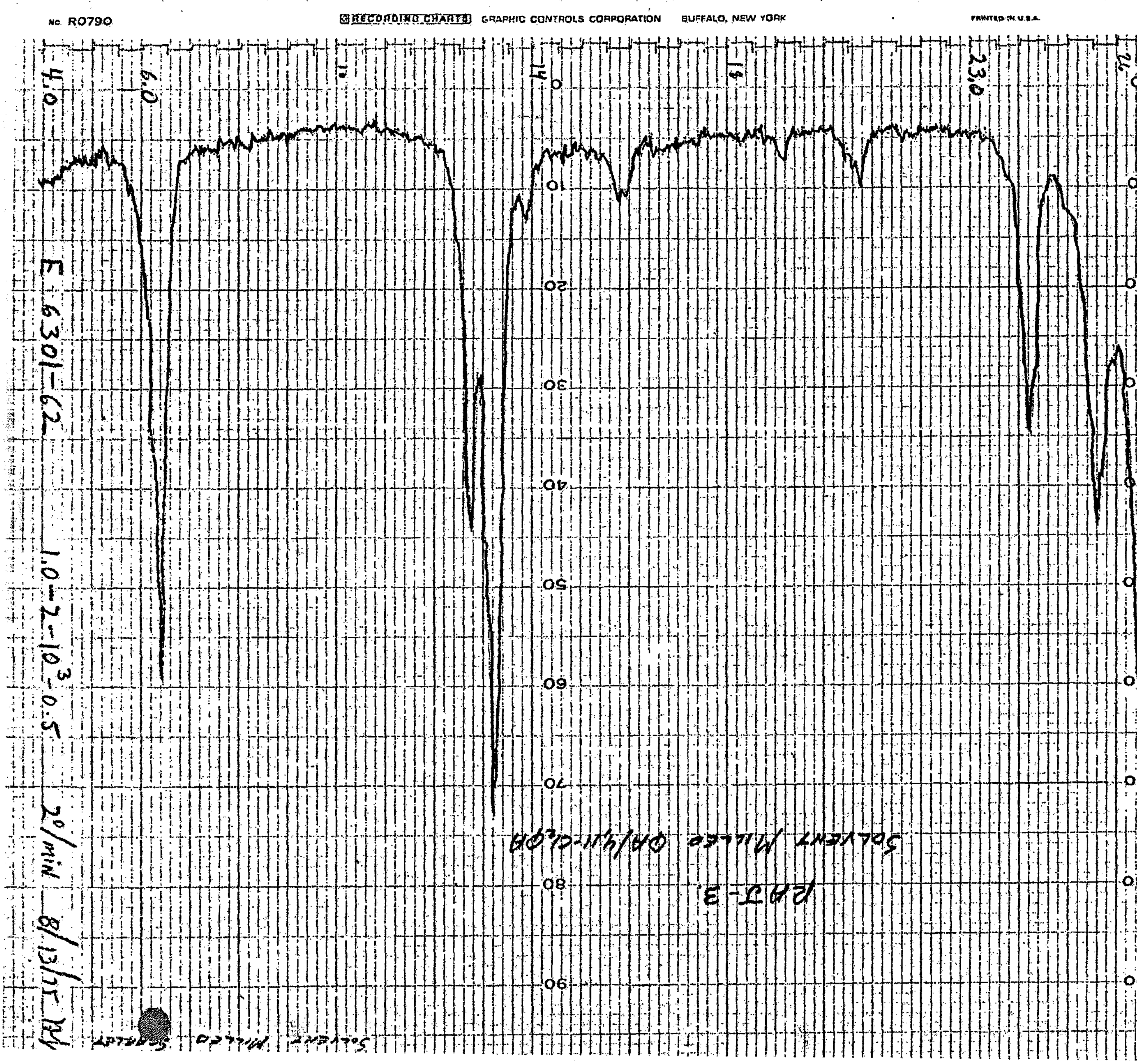

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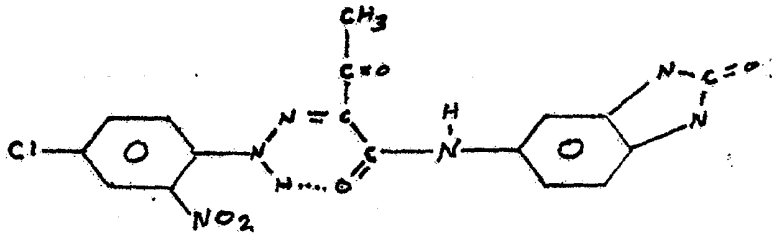
IV. DISCUSSION (Continued)

1. QA/4,11-Cl_2QA (Continued)

of these experimental products were as good as the DMF product because of their particle size and uniformity. Other solvent systems that were evaluated were H_2SO_4/H_2O, PTSA/H_2SO_4/H_2O and "Perclene". Solid solution formation did not take place in any of these.

Color, within limits, can be shifted by varying the composition of the solid solution. The initial studies were done using a 60/40 QA/4,11-Cl_2QA composition. This was later shifted slightly yellower by going to a 50/50 composition. Sales has indicated that they now want a product with the yellowness of HL-70.

A large sample of premilled QA/4,11-Cl_2QA (50/50) refluxed in DMF was prepared for evaluation in TSA versus Hoechst HL-70 at Chestnut Run by J. T. Hennessy (ANRD-9-77). Both as a masstone and in blends with RT-759-D, the experimental product was bluer, duller and lower in gloss (milky). The milkiness is believed to be due to the rectangular shape of the crystal plates. Sales indicated that the yellowness of HL-70, an established product, was most desirable. The competitive is an azo pigment having the following composition:



Its lightfastness is marginal.

2. Alternate Compositions

To obtain a yellower product, 20% of a third component (QAQ) was added. While both the QA and the 4,11-Cl_2QA were premilled, the QAQ component was evaluated both as premilled and as crude. Only the QA and 4,11-Cl_2QA appeared to have formed a solid solution by DMF reflux. By rubout, both were blue, dull and transparent in masstone versus HL-70.

IV. DISCUSSION (Continued)

2. Alternate Compositions (Continued)

Samples containing from 70% to 95% QAQ were prepared by refluxing for 5 hours in DMF, separately premilled gamma QA and premilled QAQ. A complete solid solution was only obtained when the QA content did not exceed 10%. In all cases, the pigment particle size was small resulting in a very dull transparent masstone versus HL-7-.

Premilled 4,11-Cl_2QA and QAQ were refluxed in DMF and in methanol-NaOH for 8 hours. In neither case was a solid solution formed. QAQ appears to have undergone very little growth (formed a salt in methanol-NaOH) while the 4,11-Cl_2QA grew very large in DMF. None of these alternate approaches appeared to be worth pursuing at this time.

3. 4,11-Cl_2QA Oxidation

4,11-Cl_2QA, made from Sitol by the standard plant oxidation, is brown in color. This can be converted to the pure orange color by acid recrystallization. The impurity responsible for the brown color is a reaction product between nitrosobenzenesulfonic acid and 4,11-Cl_2DQA (see P. A. Wriede's Monthly Summary 3/14/75). Other aromatic nitro oxidants, such as meta and para nitrobenzoic acids, which reduce to nitroso compounds, appear to form similar compounds with 4,11-Cl_2DQA that result in brown 4,11-Cl_2QA.

Byproduct formation can be suppressed by increasing the NaOH concentration so as to reduce the solubility of 4,11-Cl_2DQA. This resulted in blue crystals of the sodium salt of 4,11-Cl_2QA. Considerable problems were encountered in this synthesis with premature hysrolysis of the salt before isolation resulting in a dull orange 4,11-Cl_2QA. The addition of 0.5 to 1.0% QAAF, either before or after oxidation appeared to help stabilize the sodium salt. Hydrolysis of the sodium salt in a separate step in methanol gives the bright orange 4,11-Cl_2QA.

A somewhat duller orange is obtained when the sodium salt is hydrolyzed by H_2SO_4 before being isolated from the oxidation mixture. This procedure was used to make the 4,11-Cl_2QA used in this study (SW-12632). A

IV. DISCUSSION (Continued)

3. 4,11-Cl_2QA Oxidation

laboratory prepared sample, although equal in purity, was not as intense as the semi-works material. This procedure would be expected to give considerable variability in 4,11-Cl_2QA color quality.

The problem of byproduct formation can be eliminated by the use of oxidants other than aromatic nitro compounds. Silver salt (2-anthraquinone sulfonic acid sodium salt), albeit more expensive, gives an orange 4,11-Cl_2QA. No development work was done on this procedure.

V. FUTURE STUDIES

Future work on this problem has been turned over to G. H. Senkler, Jr. The following general recommendations were made:

1. Investigate methods of controlling particle shape (less acicular) to overcome masstone milkiness problem.

2. Consider the yellower 4,11-F_2QA in place of 4,11-Cl_2QA based on availability and cost of o-fluoroaniline.

VI. REFERENCES

1. N.B. E-6301

2. N.B. E-10544

3. N.B. E-12932

4. N.B. E-6143

5. Exposure Series No. 76466 (TPA)

6. Exposure Series No. 76439 (TSA)

7. Exposure Series No. 76510 (TPA)

8. Exposure Series No. 77400 (TSA)

VII. EXPERIMENTAL

A. Laboratory Premilling

1. Charge a one quart paint can:

1/2" steel balls	1500 g.
1" roofing nails	150 g.
Alpha QA	7.5 g.
4,11-Cl_2QA	7.5 g.

2. Rotate can at 86 rpm on a roller mill for one hr.

3. Separate pigment from balls and nails by screening.

B. Solid Solution Formation

1. Set up 500 ml, 4 neck flask with agitation, condenser, thermometer and heating mantle.

2. Charge:

Premill pigment	5.0 g.	5.0 g.
NaOH (100%)	3.2 g.	-
MeOH	150 ml	-
DMF	-	150 ml
3. Stir at reflux	8 hrs.	2 hrs.
4. Filter		
5. Wash	Hot water (BY-)	MeOH
6. Dry at 80°C.		

C. Sodium salt of 4,11-Cl_2QA-methanol hydrolysis

1. Set up a 1 liter, 4-neck flask with agitation, condenser, thermometer and heating mantle.

VII. EXPERIMENTAL (Continued)

C. (Continued)

2. Charge:

4,11-Cl_2DQA	40.0 g.
MeOH	400 ml.
50% NaOH	160 g.
Water	160 ml.

3. Stir 30 minutes at reflux (color green)

4. Cool to 70°C. and add 30 g. dry Sitol (color changes to dark reddish blue)

5. Stir 5 hrs. at reflux (purple)

6. Filter hot (65-70°C.) removing as much mother liquor as possible.

7. Wash BY- with cold water.

8. Dry at 80°C

9. Theoretical yield 44.39 g.

10. Hydrolyze by heating in methanol
4,11-Cl_2QA (purity) 93.0%

D. Sodium salt of 4,11-Cl_2QA - H_2SO_4 hydrolysis

1. Set up a 1 liter, 4-neck flask with agitation, condenser, thermometer and heating mantle.

2. Charge:

4,11-Cl_2DQA	40.0 g.
MeOH	250 ml.
Water	160 ml.

3. Add 160 g. 50% NaOH (50°C. max.)

4. Stir 2 hrs. at reflux (color pale green, very thick).

5. Cool below reflux and add 30 g. dry Sitol

VII. EXPERIMENTAL (Continued)

D. (Continued)

6. Stir 7 hrs. at reflux,

7. Cool externally to 50°C.

8. Slowly add 50 ml 78% H_2SO_4 (color changes from blue to orange)

9. Filter

10. Wash BY- and sulfate free with hot water

11. Dry at 80°C.

12. Theoretical Yield 39.79 g.

13. Analysis

4,11-Cl_2QA	97.1%
4,11-Cl_2DQA	0.5%

E. 4,11-Cl_2QA - Silver Salt Oxidation

1. Set up a 1 liter, 4-neck flask with agitation, condenser, thermometer and heating mantle.

2. Charge:

4,11-Cl_2DQA	40.0 g.
MeOH	404 ml.
Water	168 ml.

3. Stir 10 minutes

4. Add 36.5 g. 2-anthraquinone sulfonic acid sodium salt (97.5% min. purity).

5. Add 32.0 g. 50% NaOH (50°C. max.).

6. Stir 5 hrs. at reflux.

7. Adjust to 60°C. with water

VII. EXPERIMENTAL (Continued)

E. (Continued)

8. Filter

9. Wash BY- with hot water

10. Dry at 80°C.

11. Theoretical Yield 39.79 g

12. Analysis

4,11-Cl_2QA	89.7%
4,11-Cl_2DQA	6.5%

E. I. DU PONT DE NEMOURS & COMPANY

Pigments Department

cc: N. D. Cassel, Pigm. Wilm.
F. F. Ehrich, Pigm. Wilm.
C. W. Anderson, Pigm. Nwpt.
E. W. Stewart, Pigm. C.R.
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FIRST & FINAL - ANRD-9-77

Chestnut Run
August 9, 1977

TO: R. A. JOHNSON
PIGMENTS-NEWPORT

FROM: J. T. HENNESSY
PIGMENTS-CHESTNUT RUN

EXPTL. OPAQUE QUINACRIDONE ORANGE VS.
AMERICAN HOECHST'S PERMANENT ORANGE HL-70

- Based on color properties, experimental opaque quinacridone orange is not considered a satisfactory potential counteroffering for Hoechst's HL-70.(1)

Experimental orange is substantially less intense, bluer and slightly less opaque than HL-70 in masstone. It also had poor gloss vs. HL-70 at equal pigment loading, ~20 vs. ~60 at 20° at 0.25 P/B. Solid reds made with experimental orange and Monastral® Red Y, RT-759-D lacked color intensity and had a blue milkiness compared to similar reds made with HL-70 and RT-759-D. A similar lack of intensity was observed in blends of experimental orange and chrome titanate.

Efforts to enhance color intensity of reds and oranges made with experimental orange by adding Monastral® Magenta RT-243-D were not successful. Consequently, since color properties were not adequate, exposures were not issued as originally planned.

To stimulate automotive customers' interest to evaluate versus HL-70, the following improvements are needed in experimental orange:

- Color Intensity: Equal to HL-70. Includes not only color in masstone, but the need to stay "yellow red" on extension with white, rather than the blue red of current sample.
- Hiding: Equal to RT-759-D
- Gloss: Equal to RT-759-D

While obtaining hiding equal to RT-759-D would improve value-in-use of experimental orange if sold at the RT-759-D price, it will still be approximately 30% more costly than HL-70 in orange and light red finishes (current prices - RT-759-D @ $15.50; HL-70 @ $11.50). Several customers feel HL-70 has adequate lightfastness in straight shade oranges and in blends with quinacridone reds; consequently, better lightfastness anticipated for quinacridone compared to benzimidazolone azo (HL-70) may not overcome higher value-in-use of HL-70.(2)

An idea of relative hiding power is obtained from the contrast ratios of masstone finishes at 0.25 P/B at ~1.6 mils DFT.

	RT-759-D	HL-70	Exptl. Orange
Green Filter Contrast Ratio:	0.96	0.90	0.86

EXPERIMENTAL DETAILS:

Pigments Evaluated:

RT-759-D, PS-93526
Perm. Orange HL-70, C#76330
Exptl. Orange, NB#12932-2

Vehicle: 986/977 Lucite® acrylic lacquer

Dispersion: Jiffy steel ballmill - run at conditions which proceeded @ 0.5 P/B and 10% pigment; similar gloss and hiding for RT-759-D.

Other Detail: Notebook LCR-7704-1

REFERENCES:

(1) Exhibits and discussion at QA MRM meeting 3/24/77.
(2) Pigments R&D, F&F-Troy Technical Review, notes -- JTH, 5/4/77.

JTH:lb

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