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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

HEAT RESISTANT QUINACRIDONE PIGMENT (PART I)

Period Covered March, 1966 to August, 1967 (Part Time)

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: HEAT RESISTANT QUINACRIDONE PIGMENT (PART I)

PERIOD COVERED: MARCH, 1966 to AUGUST, 1967 (Part time)

SUBMITTED BY: G. R. ALDRIDGE Date Submitted: 7/30/68

APPROVED BY: F. F. EHRICH Date Released: 9/3/68

ABSTRACT

Of fifteen substituted quinacridones tested in polystyrene plastic, 2,9-dicarboxyquinacridone exhibited the best heat (color) stability. 2,9-Dicarboxyquinacridone also exhibited excellent heat stability in "Zytel" nylon, a very rigorous system for testing heat stability.

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I. OBJECT OF INVESTIGATION

To find a heat stable red pigment for use in high temperature plastics applications (Part I) and to develop an economically feasible process for its manufacture (Part II).

II. PERIOD COVERED BY REPORT

March, 1966 to August, 1967 (Part Time)

III. INTRODUCTION

Quinacridone is a relatively insoluble red pigment which is suitable for use in some plastics but not all. Quinacridone in a polyamide system such as "Zytel" nylon is sufficiently soluble at higher temperatures so that the color in low concentrations is a fluorescent yellow characteristic of quinacridone in solution. This color is also shown by quinacridone solutions in dimethylformamide and 1-chloronaphthalene.

From a consideration of the relative solubilities of quinacridone (.08 g/l) and 2,9-dimethylquinacridone (.027 g/l) in a model solvent such as boiling 1-chloronaphthalene, and the fact that the latter quinacridone shows better heat or color stability than the former in polystyrene plastic, it follows that the heat-stability of such chemically inert pigments is determined by their solubility in the plastic. Specifically, pigments soluble in the plastic will show poor heat (color) stability and pigments insoluble in the plastic will show good heat stability.

The solubility of 2,9-dicarboxyquinacridone (I) in boiling 1-chloronaphthalene was found to be very low (< 0.01 g/l). The evaluation of I and other substituted quinacridones in polystyrene and "Zytel" nylon plastic showed I to have relatively outstanding heat stability.

IV. SUMMARY AND CONCLUSIONS

The following table lists the results of heat stability tests on fifteen substituted quinacridones in polystyrene plastic.

Substituent	Color Difference (400°F. vs. 600°F.)	UV Fluorescence
2,9-dicarboxy	little	no
2,9-dicarboxyamido	"	yes
2,9-dicarboethoxy	"	"
2,9-dicyano	"	"
2,9-dichloro	"	"
2,9-dibromo	"	"
2,9-difluoro	"	"

Substituent	Color Difference (400°F. vs. 600°F.)	UV Fluorescence
2,9-dimethyl	little	yes
2,9-dimethoxy	"	"
2,3,9,10-tetrachloro	"	"
2,4,9,11-tetrachloro	considerable	"
4,11-dibromo	"	"
4,11-dimethoxy	"	"
4,11-dichloro	"	"
4,11-difluoro	"	"

All of the 4,11- disubstituted quinacridones were poor in heat stability. All the 2,9- substituted quinacridones were good in heat stability except for the one which was also substituted in the 4,11- positions, i.e., the 2,4,9,11-tetrachloro isomer. The remarkable difference in heat stability between the 2,9- and 4,11- substituted quinacridones is not surprising in view of the appreciably lower solubility of the former versus the latter in 1-chloronaphthalene.

Examination of the 600°F. chips under ultraviolet light reveals that I is essentially insoluble whereas all the other substituted quinacridones are soluble to some extent.

That the heat stability of I is unique can be seen from the following table which lists the results of heat stability tests run by the Plastics Department in Parkersburg, West Virginia, on five substituted quinacridones in "Zytel" nylon. The latter is regarded as a very rigorous system for testing heat stability.

QA Substituent	Color	UV Fluorescence
2,9-dicarboxy	Violet	Violet-weak
2,9-dicarboxyamido	"	Green
2,9-difluoro	Yellow	Yellow
2,9-dichloro	"	"
2,9-dimethyl	"	"

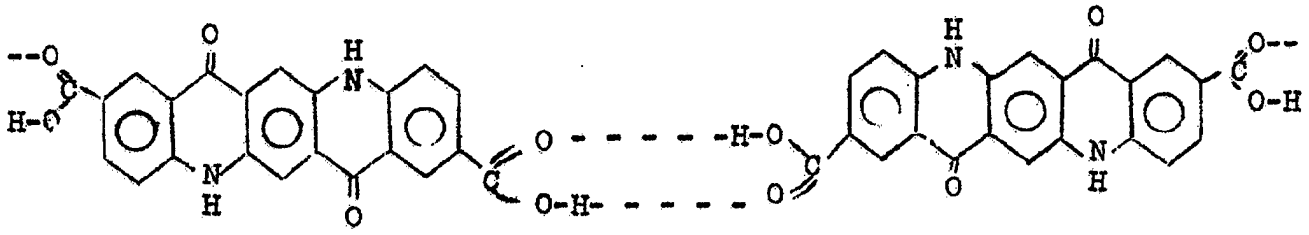
Of the quinacridones tested in this polyamide system at 540°F., only the diacid and diamide retained their red color, and the stronger fluorescence of the diamide versus the diacid suggests that it is the more soluble of the two.

V. PATENT STATUS

CP-75, Polar Quinacridones, was submitted to the Patent Liaison Group at Newport for the preparation of a composition of matter case on 2,9-dicarboxyquinacridone. A use case on this product may also be advisable.

VI. DISCUSSION

The extreme insolubility of 2,9-dicarboxyquinacridone (I) in organic solvents and in plastics systems is believed to be due to intermolecular hydrogen bonding between the carboxy groups in the 2- and 9- positions as follows:



This presumption is supported by the well-known existence of carboxylic acid dimers and the fact that the unique insolubility of I is associated with the carboxyl groups in the 2- and 9- positions. 4,11-Dicarboxyquinacridone would certainly be more soluble than I and, probably, more soluble than the unsubstituted quinacridone because the intramolecular hydrogen bonding between the carboxyl carbonyl and amino groups would reduce the intermolecular hydrogen bonding between the acridone carbonyl and amino groups. One can only speculate about the properties of 1,8- and 3,10-dicarboxyquinacridones. A x,x_1-dicarboxyquinacridone from the reaction of quinacridone, oxalyl chloride, and aluminum chloride in nitrobenzene showed considerable fluorescence in polystyrene indicating the presence of dicarboxyquinacridone isomers other than the 2,9-.

The lightfastness (12 months - Florida exposure, 5° South) of I versus "Monastral" Red (RT-790-D) and "Monastral" Violet (RT-795-D) is summarized in the following table.

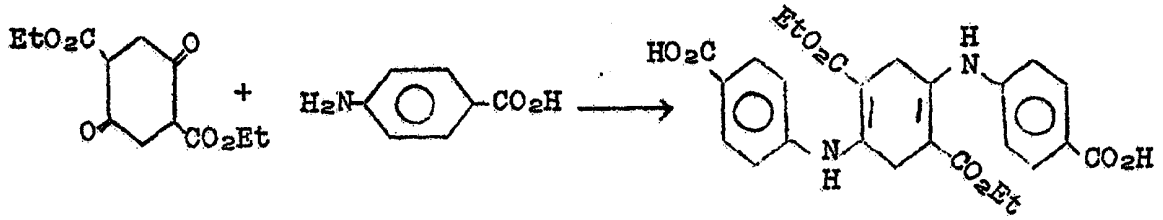
	Series 66479 "Lucite" Acrylic Lacquer			Series 66481 32J Thermosetting Enamel		
	Al/Toner		Tint	Al/Toner		Tint
	10/90	75/25	5/95	10/90	50/50	5/95
I (crude)	4f	0	1f	-	-	-
I (milled)	3f	0	1f	4f	3f	2f
RT-790-D	4d	4f	4f	7f	6f	6f
RT-795-D	4d	5	4f	8d	6f	6f

The reason for the inferior lightfastness of I to that of unsubstituted quinacridone is a matter of speculation. The failure of I in metallics (aluminum-containing systems) and tint may be due to the interaction of the acidic carboxyl group with aluminum and titanium dioxide, respectively. Another possible explanation is that the average particle size of I

may be considerably smaller than that of the quinacridone samples evaluated. A third factor affecting the lightfastness of 2,9-disubstituted quinacridones is likely the nature of the substituent, i.e., whether it is electron-donating or electron-withdrawing.

VII. EXPERIMENTAL

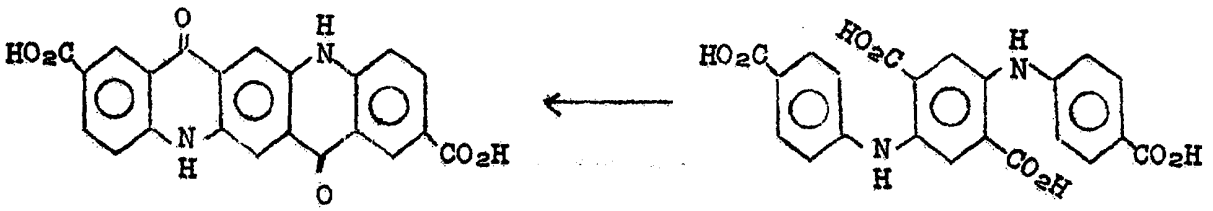
Preparation of the sample of I submitted to Chestnut Run (polystyrene evaluation) and to Parkersburg, W. Virginia ("Zytel" nylon).



$C_{12}H_6O_6$
SSE (diethyl)

p-aminobenzoic acid

$C_{26}H_{26}N_2O_8$
2,5-Di(4-carboxyanilino)-3,6-dihydroterephthalate ester



$C_{22}H_{12}N_2O_6$

2,9-Dicarboxyquinacridone

$C_{22}H_{16}N_2O_8$

2,5-Di(4-carboxyailino)-3,6-terephthalic acid

The characterization of the intermediates, $C_{26}H_{26}N_2O_8$ and $C_{22}H_{16}N_2O_8$, and the final product, $C_{22}H_{12}N_2O_6$, is reported in Patent Memorandum, CP-75, Polar Quinacridones.

Preparation of $C_{26}N_{26}N_2O_8$

See 1835/12A.

Preparation of $C_{22}H_{16}N_2O_8$

See 1835/12K.

Preparation of $C_{22}H_{12}N_2O_6$

See 1835/12L.

Acid Recrystallization of $C_{22}H_{12}H_2O_6$

See 1835/12M,N.

Dimethylformamide Treatment

See 1835/31A.

Dispersion Milling and Preparation of Calcium Rosinate Lakes

See 1835/31B,C.

Preparation of x,x'-Dicarboxyquinacridone

See 1835/23E.

Acid Recrystallization of X,X'-$(COOH)_2$QA

See 1835/23F,G.

Found:	C, 65.58	C	H	N	O	req	C, 66.0
	H, 3.70						H, 3.0
	N, 6.79						N, 7.0

Preparation of 2,9-Dicyano- and 2,9-Dicarboxyamido

SSE (diethyl) + p-aminobenzonitrile → 2,5-Di(4-cyanoanilino)-3,6-dihydroterephthalate ester $C_{26}H_{24}N_4O_4$

↓

2,9-Dicyanodihydroquinacridone $C_{22}H_{12}N_4O_2$ ← 2,9-Dicyanoquinacridone $C_{22}H_{10}N_4O_2$

Preparation of $C_{26}H_{24}N_4O_4$

See 1507-13. Found: N, 12.3 12.5 $C_{26}H_{24}N_4O_4$ req. N, 12.3

Preparation of $C_{22}H_{12}N_4O_2$

See 1507-14. Found: N, 14.7 14.7 $C_{22}H_{12}N_4O_2$ req. N, 15.42

Preparation of $C_{22}H_{10}N_4O_2$

See 1507-15. Found: N, 15.0 $C_{22}H_{10}N_4O_2$ req. N, 15.47

Band at 5.99μ suggests the presence of some amide.

Summary of Attempts to Prepare Pure 2,9-Dicyanoquinacridone

N.B.	Oxidation Medium	Heating Cycle	Result
1507-15	Sitol-H_2O-NaOH-glycol	2 hr.at 110-20°	Oxidation - yes. Some amide present.
1835/5B	" " " "	2 hr. at 80-90°	Incomplete oxida'n. Amide - no.
1835/5C	" " " "	2 hr. at 90-100°	Oxidation-yes, based on dimethyl-formamide soln.: max = 510,477 448mμ Amide - little. Low carbon and nitro-gen analysis.
1835/5E	" " " "	2 hr.at 85-95°	Incomplete oxida'n. Amide - no
1835/16D	Chloranil - TCB	5 hr.at reflux	No oxidation.

2,9-Dicarboxyamidoquinacridone

SSE(Me,Et) + p-aminobenzamide → 2,5-di(4-$CONH_2$-aniline) 3,6-dihydroterephthalate ester $C_{25}H_{26}N_4O_0$

↓ Dowtherm Δ

2,9-dicarboxyamidodihydroquinacridone $C_{22}H_{16}N_4O_4$

← Sitol

2,9-dicarboxyamidoquinacridone $C_{22}H_{14}N_4O_4$

Preparation of $C_{25}H_{26}N_4O_6$

See 1835/65A. Found: C, 62.41 H, 5.05 N, 10.75 $C_{25}H_{26}N_4O_6$ req. C, 62.8 H, 5.44 N, 12.1

The band at 5.85μ seems low for the type of carbonyl groups in $C_{25}H_{26}N_4O_6$.

Preparation of $C_{22}H_{16}N_4O_4$

See 1835/65B. Found: C, 67.61 H, 4.02 N, 11.64 $C_{22}H_{16}N_4O_4$ req. C, 66.0 H, 4.0 N, 14.0

IR Spectrum: 2.90 and 3.00μ ($-NH_2$), 3.18μ ($>NH$), 5.95 and 6.10μ ($>C=O$). Low nitrogen analysis suggests that this may not be good quality 2,9-$(CONH_2)_2$DQA.

Preparation of $C_{22}H_{14}N_4O_4$

See 1835/78A. Found: N, 9.64 $C_{22}H_{14}N_4O_4$ req. N, 14.1

The low nitrogen analysis of the product suggests that the desired product was not obtained.

Alternate Synthesis

2,5-Di(4-$CONH_2$-anilino)-3,6-dihydroterephthalate ester
$C_{25}H_{26}N_4O_6$

2,5-Di(4-CONH-anilino)-terephthalate ester
$C_{25}H_{24}N_4O_6$

PPA

2,9-Dicarboxyamido QA
$C_{22}H_{14}N_4O_4$

Preparation of $C_{25}H_{24}N_4O_6$

See 1876/5B. Found: N, 11.36 $C_{25}H_{24}N_4O_6$ req. N, 11.8

IR Spectrum: 2.80 and 2.99μ ($-NH_2$), 3.16μ ($>NH$), 5.90-5.95μ (ester $>C=O$ and amide $>C=O$), 6.48μ (terephthalate ester).

Preparation of $C_{22}H_{14}N_4O_4$

See 1876/15D. Found: N, 11.28 $C_{22}H_{14}N_4O_4$ req. N, 14.1

IR Spectrum: 3.00 and 3.10μ ($-NH_2$), 3.18μ ($>NH$), 6.03μ (amide $>C=O$), 6.15μ (acridone $>C=O$).

The red color of this product suggests that ring closure occurred and the low nitrogen analysis suggests that some hydrolysis of the amide group also took place.

Preparation of 2,9-Dicarboethoxyquinacridone

SSE (diethyl) + ethyl p-aminobenzoate → 2,5-Di(4-COOEt-aniline)-3,6-dihydroterephthalate ester
$C_{30}H_{34}N_2O_8$

↓

2,9-Dicarboethoxyquinacridone ← 2,9-Dicarboethoxydihydroquinacridone
$C_{26}H_{20}N_2O_6$ $C_{26}H_{22}N_2O_6$

Preparation of $C_{30}H_{34}N_2O_8$

See 1835/62G. Found: C, 66.27; H, 6.25; N, 5.29 $C_{30}H_{34}N_2O_8$ req. C, 65.5; H, 6.18; N, 5.09

IR Spectrum: 3.19μ (>NH), 5.85μ (aromatic ester> C=O), 6.06μ (> C=O of β-anilinoester).

Preparation of $C_{26}H_{20}N_2O_6$

See 1835/68B. Found: C, 70.75; H, 6.02; N, 6.09 $C_{26}H_{22}N_2O_6$ req. C, 68.2; H, 4.80; N, 6.12

Preparation of $C_{26}H_{20}N_2O_6$

See 1507/18. Found: C, 60.51; H, 4.43; N, 5.45 $C_{26}H_{20}N_2O_6$ req. C, 68.4; H, 4.39; N, 6.14

VIII. SUGGESTIONS FOR ADDITIONAL WORK

1. Determine rheological behavior of 2,9-dicarboxy-, 2,9-dicyano-, 2,9-dicarboxyamido- and 2,9-dicarboethoxyquinacridones, both as self-colors and as additives for other quinacridones.

2. Determine outdoor durability of 2,9-dicyano-, 2,9-carboxyamido- and 2,9-dicarboethoxyquinacridones.

IX. NOTEBOOK REFERENCES

1507
1835
1876
1894

dc

KM-68-6 DEVELOPMENT OF "KROLOR" ORANGE YELLOW, KO-789-D By: J. Jackson 9/66 - 7/68

1/79 (1)

(6) ~~R. W. Nelson~~ 8/1/80
Corp, Newark

(6) K. N. Dietz 7/24/81

(13) ~~J. L. Higgins~~ 10/13/81