Serial No. KN-66-11

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NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

PIGMENT PHOTOCHEMISTRY

Period Covered MAY, 1966 to NOVEMBER, 1966

FILE: 141

DATE: 12/19/66

KN-66-11

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

SUBJECT: PIGMENT PHOTOCHEMISTRY

PERIOD COVERED: MAY, 1966 to NOVEMBER, 1966

SUBMITTED BY: J. R. GIACIN Date Submitted: 12/12/66

APPROVED BY: F. F. EHRICH Date Released: 1967

NB 1834

ABSTRACT:

An extensive series of quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solutions was prepared, and the samples were evaluated for outdoor durability. Quantitative studies were carried out on quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solutions under anaerobic conditions, and the rates of photodegradation of quinacridonequinone were determined.

INTRODUCTION

Previous workers have shown that the photostability of quinacridonequinone (QAQ) is increased when N,N'-diphenyl-p-phenylenediamine (DPD) is incorporated into solid solution with quinacridonequinone. A simple admixture appears to have no effect. A quantitative study was carried out on both quinacridonequinone and quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solution with the long range objective of elucidating the mechanism of quinacridonequinone photodegradation and the mechanism by which the N,N'-diphenyl-p-phenylenediamine inhibits the degradation of quinacridonequinone.

These studies were carried out by incorporating the quinacridonequinone or quinacridonequinone/N,N'-diphenyl-p-phenylenediamine samples into "Butacite" laminates and irradiating the slides. This technique affords an anaerobic system which can be studied by visible spectroscopy.

RESULTS AND DISCUSSION

An extensive series of quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solutions was prepared and the samples were evaluated for outdoor durability. In this study, the solid solutions were prepared with both recrystallized and crude quinacridonequinone (the crude QAQ was found to contain 2.4% CrO_3). The samples were evaluated in "Lucite" acrylic lacquer, and in 32J acrylic enamel. The samples were evaluated in both paint systems as metallics at aluminum concentrations of 10% and 75%. The samples were also evaluated in both paint systems as tints at a toner concentration of 95%. In all cases, the paint systems were evaluated both with and without nickel carbonate. The results of this study after three months exposure are tabulated in the following Exposure Series #66477.

1. W.S.Struve/A.A.Brizzolara/Res.File.
2. B.H.Perkins/B.J.Godfrey, Newark
3. F.F.Enrich/W.J.Marshall, "
4. J.R.Giacin
5. Extra
6. Extra
7. Extra

Newark, New Jersey
June 24, 1966

SERIES NO. 66477

EVALUATION OF THE OUTDOOR DURABILITY OF A SERIES OF SOLID SOLUTIONS PREPARED FROM QAQ/DPD 32J TYPE ACRYLIC ENAMEL

OBJECT: (a) Evaluation of a series of QAQ/DPD solid solutions for durability evaluation, with purified QAQ being used in the 1834/15 series and plant material being used in the 1834/25 series. (b) To examine the effect of $NiCO_3$ on pigment durability.

PIGMENTS EVALUATED: The following with and without $NiCO_3$.

1834-15A - Pure QAQ (recrystallized from H_2SO_4)
15B - QAQ/DPD solid soln. initial ratio 99%/1%
15C - " " " " " " 95%/5%
15D - " " " " " " 90%/10%
15E - " " " " " " 85%/15%
15F - " " " " " " 80%/20%
15G - Pure DPD
15H - Admixture QAQ/DPD ratio 90%/10%
15I - " " " " 80%/20%
25A - Crude QAQ
25B - QAQ/DPD solid soln. initial ratio 99%/1%
25C - " " " " " " 95%/5%
25D - " " " " " " 90%/10%
25E - " " " " " " 85%/15%
25F - " " " " " " 80%/20%
25G - Admixture - QAQ/DPD ratio 90%/10%
25H - " " " " 80%/20%
16A - Pure YT-752-D
16B - YT-752/DPD solid soln. - initial conc. 99%/1%
16C - YT-752/DPD " " " " 95%/5%
16D - " " " " " 90%/10%
16E - Admixture YT-752/DPD ratio 95%/5%
16F " " " " 90%/10%

REFERENCES: R/W 66-343A, 344A, S-66480 "Lucite" Lacquer

EXPERIMENTAL DETAILS:
Vehicle: Aroset 777/Cymel 243-3, 70/30 on vehicle solids
Means of Grinding: 1/2 pt. jar - steel balls
Drying Schedule: Baked 1/2 hr. at 250°F.
Pigment Binder (P/B): 14/100
Other Data: Alcoa #726 aluminum was used to prepare the metallics. "TiPure" R-902 was used to prep. the tints of the enamels.

EXPOSURE:
Means of Application: Spray
Panels and Finishes Prepared by: J.J.Fox
Start of Exposure: Fla. July, 1966

LOCATION	SETS	TYPE PANEL AND SIZE	PRIMER COATING	PANEL MARKS
Fla.5°S	2	Aluminum 4x12	Preparakote 65-3012	F-A, B

B. J. GODFREY/J. R. GIACIN
RESEARCH DIVISION

Panel	Pigment	Al/Toner	Initial Gloss 20°	
1	1834-15A	10/90	87	6d
2	15A + $NiCO_3$	"	91	10-
3	15B	"	89	6d
4	15B + $NiCO_3$	"	91	10-
5	15C	"	92	8d
6	15C + $NiCO_3$	"	94	8f
7	15D	"	81	9f
8	15D + $NiCO_3$	"	87	6f
9	15E	"	88	7f
10	15E + $NiCO_3$	"	90	-7f
11	15F	"	84	-7f
12	15F + $NiCO_3$	"	88	-7f
13	15G	"	89	2f
14	15G + $NiCO_3$	"	88	0
15	15H	"	90	7d
16	15H + $NiCO_3$	"	88	7f
17	15I	"	91	6d
18	15I + $NiCO_3$	"	88	7f
19	25A	"	82	-6d
20	25A + $NiCO_3$	"	86	-10
21	25B	"	88	6d
22	25B + $NiCO_3$	"	90	9.5
23	25C	"	88	6d
24	25C + $NiCO_3$	"	88	6f
25	25D	"	85	5f
26	25D + $NiCO_3$	"	88	6f
27	25E	"	86	5f
28	25E + $NiCO_3$	"	88	6f
29	25F	"	87	-6f
30	25F + $NiCO_3$	"	92	-5f
31	25G	"	87	6d
32	25G + $NiCO_3$	"	86	9.5f
33	25H	"	87	4d
34	25H + $NiCO_3$	"	87	9f
35	16A	"	88	8f
36	16A + $NiCO_3$	"	89	9.5f
37	16B	"	90	9.5f
38	16B + $NiCO_3$	"	89	10
39	16C	"	88	9f
40	16C + $NiCO_3$	"	88	9.5f
41	16D	"	89	8f
42	16D + $NiCO_3$	"	88	9f
43	16E	"	87	8f
44	16E + $NiCO_3$	"	87	9f
45	16F	"	88	9f
46	16F + $NiCO_3$	"	89	8f
47	RT-795-D	"	82	9.5f
48	1834-15A	75/25	71	4f
49	15A + $NiCO_3$	"	75	8f
50	15B	"	74	5f
51	15B + $NiCO_3$	"	79	9f
52	15C	"	80	6f
53	15C + $NiCO_3$	"	69	9f
54	15D	"	78	8f
55	15D + $NiCO_3$	"	75	10-
56	15E	"	74	7f
57	15E + $NiCO_3$	"	72	9f

S-66477

58	1834-15F	75/25	76	8f
59	15F + $NiCO_3$	"	78	8f
60	15G	"	82	4f
61	15G + $NiCO_3$	"	79	4f
62	15H	"	77	4f
63	15H + $NiCO_3$	"	78	8f
64	15I	"	79	4f
65	15I + $NiCO_3$	"	82	8f
66	25A	"	79	0
67	25A + $NiCO_3$	"	75	10-
68	25B	"	82	3f
69	25B + $NiCO_3$	"	83	8f
70	25C	"	87	5f
71	25C + $NiCO_3$	"	79	10-
72	25D	"	81	9f
73	25D + $NiCO_3$	"	81	10-
74	25E	"	77	0.5f
75	25E + $NiCO_3$	"	78	9f
76	25F	"	82	7.5f
77	25F + $NiCO_3$	"	83	9f
78	25G	"	78	0
79	25G + $NiCO_3$	"	82	10-
80	25H	"	82	0
81	25H + $NiCO_3$	"	82	8f
82	16A	"	76	7f
83	16A + $NiCO_3$	"	76	9f
84	16B	"	81	9.5f
85	16B + $NiCO_3$	"	80	10-
86	16C	75/25	77	9f
87	16C + $NiCO_3$	"	75	10-
88	16D	"	79	9f
89	16D + $NiCO_3$	"	83	10
90	16E	"	81	7f
91	16E + $NiCO_3$	"	84	9.5f
92	16F	"	83	7f
93	16F + $NiCO_3$	"	77	9.5f
94	RT-795-D, 97189	"	72	10
Tints	5/95 Toner/White			
95	1834-15A		72	3f
96	15A + $NiCO_3$		77	8f
97	15B		78	4f
98	15B + $NiCO_3$		83	10-
99	15C		74	6f
100	15C + $NiCO_3$		77	9f
101	15D		74	5f
102	15D + $NiCO_3$		76	7f
103	15E		83	5f
104	15E + $NiCO_3$		80	5f
105	15F		79	5f
106	15F + $NiCO_3$		78	5f
107	15G		82	0
108	15G + $NiCO_3$		80	2f
109	15H		66	3f
110	15H + $NiCO_3$		72	8f
111	15I		63	3f
112	15I + $NiCO_3$		74	8f

113	1834-25A	72	1f
114	25A + $NiCO_3$	78	9.5f
115	25B	82	2f
116	25B + $NiCO_3$	81	10-
117	25C	73	3f
118	25C + $NiCO_3$	75	7f
119	25D	78	5f
120	25D + $NiCO_3$	85	7f
121	25E	62	5f
122	25E + $NiCO_3$	61	5f
123	25F	60	5f
124	25F + $NiCO_3$	69	5f
125	25G	73	2f
126	25G + $NiCO_3$	78	8f
127	25H	77	1f
128	25H + $NiCO_3$	72	8f
129	16A	72	6f
130	16A + $NiCO_3$	79	8f
131	16B	75	6f
132	16B + $NiCO_3$	66	7f
133	16C	75	5f
134	16C + $NiCO_3$	76	6f
135	16D	75	4f
136	16D + $NiCO_3$	78	4f
137	16E	68	6f
138	16E + $NiCO_3$	76	8f
139	16F	78	6f
140	16F + $NiCO_3$	81	7f
141	RT-795-D	73	10
142	YT-748-D 10/90	86	8.5f
143	" 75/25	74	8.5f
144	" 5/95	73	6f

Both sets at 5°S

S-64480

"LUCITE" ACRYLIC LACQUER

Panel	Pigment	Initial Gloss 20°	
Metallics	75/25 Al/Toner		
1	1834-15A + $NiCO_3$	52	5f
2	15B "	40	6d
3	15C "	34	6d
4	15D "	29	9.5
5	15E "	27	7f
6	15F "	51	7f
7	15H "	43	5f
8	15I "	37	4f
9	16A "	31	9f
10	16B "	52	9.5
11	16C "	44	9.5
12	16D "	40	8f
13	16E "	36	6f
14	16F "	32	6f
15	RT-795-D	63	10
Tints	5/95 Toner/White		
16	1834-15A + $NiCO_3$	72	3f
17	15B "	72	5d
18	15C "	63	7d
19	15D "	70	7f
20	15E "	72	5f
21	15F "	63	5f
22	15H "	74	3f
23	15I "	73	3f
24	16A "	67	7f
25	16B "	70	10-
26	16C "	60	7f
27	16D "	49	5f
28	16E "	73	5f
29	16F "	66	5f
30	RT-795-D	63	9.5
31			7f
32			8f

In an attempt to determine the role played by the N,N'-diphenyl-p-phenylenediamine as a stabilizing agent for quinacridonequinone, a series of solid solutions was examined by infrared spectroscopy in the N-H and C=O stretching regions. The data obtained are tabulated in Table II.

TABLE II

Sample QAQ/DPD	Average N-H[a]	Average N-H	Average C=O
100%/0%	3.243±0.001μ	3.298±0.001μ	6.15 ±0.001μ
99%/1%	3.25 ±0.001μ	3.296±0.001μ	6.153±0.001μ
95%/5%	3.246±0.001μ	3.297±0.001μ	6.152±0.001μ
90%/10%	3.252±0.001μ	3.297±0.001μ	6.153±0.001μ
85%/15%	3.251±0.001μ	3.300μ	6.153±0.001μ
80%/20%	3.251±0.001μ	3.300μ	6.153±0.001μ

a - Infrared frequencies reported are the average of three individual measurements.

It can be concluded that the incorporation of N,N'-diphenyl-p-phenylenediamine into solid solution with quinacridonequinone has little or no effect on the N-H and C=O stretching frequencies of quinacridonequinone.

In a continuation of the study of quinacridonequinone photochemistry, a series of quinacridonequinone/N,N'-diphenyl-p-phenylenediamine "Butacite" laminates was prepared and the slides were exposed. The degradation of quinacridonequinone was followed by measuring the visible spectrum and obtaining the change in optical density at 420mμ. A plot of the data obtained from this experiment showed the disappearance of the quinacridonequinone followed a first order rate expression.

$$\frac{d\,(QAQ)}{dt} = K\,(QAQ)$$

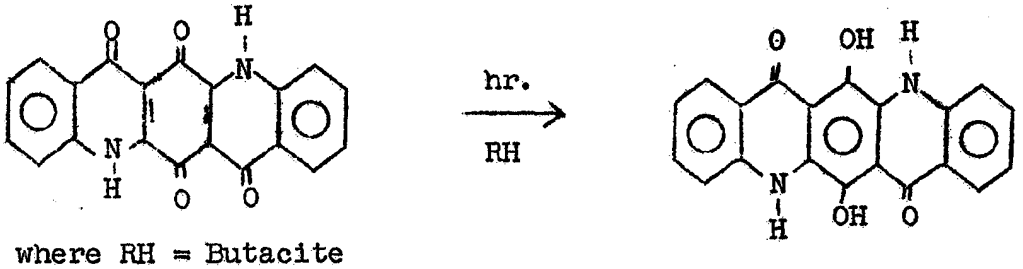
A tabulation of the rate constants obtained is listed in Table III.

TABLE III

Sample QAQ/DPD	K x 10^2 $hrs.^{-1}$
100%/0	3.9
100%/0	3.2
95%/5%	3.7
95%/5%	-
85%/15%	3.2
85%/15%	3.4

From these results it was concluded that N,N'-diphenyl-p-phenylenediamine does not enhance the photostability of quinacridonequinone in the absence of oxygen. This is in contrast with its effect in the presence of oxygen. This finding was confirmed in another experiment.

It was shown that in the absence of oxygen, quinacridonequinone, which is incorporated into a "Butacite" laminate, will undergo a rapid photoreduction to give 6,13-dihydroxyquinacridone



where RH = Butacite

The 6,13-dihydroxyquinacridone was found to be unstable toward oxidation back to the quinone. Although the quinacridonequinone was shown to undergo photoreduction in the absence of oxygen, the reduction reaction may not be a quantitative process and the loss of quinacridonequinone under these conditions may be accounted for by a photoreduction process plus secondary processes. Still to be answered is the question as to whether photoreduction is a chemical process whereby the quinacridonequinone undergoes degradation upon outdoor exposure.

To determine the wavelength and/or wavelengths of light responsible for initiating photoreduction of quinacridonequinone, a series of quinacridonequinone "Butacite" laminates was exposed employing various filters. The disappearance of the 420mμ absorption band was followed and the rate constants determined. The data are tabulated in Table IV.

TABLE IV

Experimental Conditions	$K \times 10^{2}$ hrs.$^{-1}$
1. No filter	6.0
2. No filter - quartz slides	7.4
3. 350mμ cut-off filter	8.16
4. 325-385mμ transmitting filter	16.6
5. 400mμ cut-off filter	17.0

It is concluded from these experiments that photoreduction of quinacridonequinone can be initiated by a visible and/or ultraviolet light source. The 400mμ cut-off filter and the 325-385mμ transmitting filter were examined after irradiation and no deterioration was detected.

A series of "Butacite" laminates of quinacridonequinone, quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solution and quinacridonequinone/quinacridone solid solution ("Newport" Gold) was exposed and the rate constants for the disappearance of quinacridonequinone determined. The data are tabulated in Table V.

TABLE V

Sample QAQ	Average K^a
QAQ - Pure QAQ - Pure	$8.2 \times 10^2 hrs.^{-1}$
QAQ/QA 75%/25% QAQ/QA 75%/25%	$9.2 \times 10^2 hrs.^{-1}$
QAQ/DPD 80%/20% QAQ/DPD 80%/20%	$8.2 \times 10^2 hrs.^{-1}$

a - Average value for two runs.

It was concluded that neither the N,N'-diphenyl-p-phenylenediamine nor the quinacridone will enhance the photostability of quinacridonequinone in the absence of oxygen. These findings are in contrast with the results obtained in the presence of oxygen.

SUGGESTED WORK ON QUINACRIDONEQUINONE PHOTOCHEMISTRY

1. Prepare solid solutions of quinacridonequinone and substituted p-phenylenediamines. The two phenylenediamine derivatives suggested are:

(a) N,N'-bis(p-nitrophenyl)-p-phenylenediamine
(b) N,N'-bis(p-methoxyphenyl)-p-phenylenediamine

Their effect on quinacridonequinone photostability should be evaluated both in a laminate and under outdoor conditions.

2. Effect crystal growth of quinacridonequinone and determine the effect of particle size on the rate of photoreduction.

3. Exposure of quinacridonequinone and quinacridonequinone/N,N'-diphenyl-p-phenylenediamine solid solutions under various atmospheres and determine their effects on photoreduction. This procedure should afford a means of determining whether the reduction of quinacridonequinone to the dihydroxy-derivative and its reoxidation to starting material are quantitative processes. It is suggested that the photolysis be carried out under

(a) N_2
(b) H_2
(c) O_2
(d) NO

4. Determine the intrinsic viscosity of the "Butacite" resin and determine the effect of its exposure in the presence of quinacridonequinone on the intrinsic viscosity. Such a study could determine whether quinacridonequinone was undergoing reduction to either its semi-quinone or the dihydroxy derivative in the presence of oxygen, since the radical reactions undergone by the "Butacite" resin should be non-reversible.

5. Devise experiments to determine whether the quinacridonequinone reacts in the singlet or triplet excited state. This may be done by employing triplet quenching agents and determine their effect on the rate of quinacridonequinone photoreduction. The quinacridonequinone may also be employed as a possible sensitizing agent. For example, it might be employed as a sensitizing agent for the photo oxidation of tetramethylethylene. This oxidation requires singlet oxygen which is obtained through a triplet-triplet annihilation reaction involving a triply excited species and ground state oxygen.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer as mujol mulls. The visible and ultraviolet spectra were recorded on a Beckman DU spectrophotometer. All laminates were prepared with glass slides unless otherwise stated. All exposures were carried out with a carbon arc light source unless otherwise stated.

PREPARATION OF SOLID SOLUTIONS

Pure samples of quinacridonequinone were obtained by recrystallization from conc. sulfuric acid. The N,N'-diphenyl-p-phenylenediamine used was recrystallized several times from ethanol and then methylenechloride. Crude quinacridonequinone was used in the preparation of several samples for outdoor evaluation. The samples used in the rate studies employed recrystallized quinacridonequinone. The solid solutions were prepared by salt milling. The solid solutions were assayed for quinacridonequinone and N,N'-diphenyl-p-phenylendiamine. The quinacridonequinone was analyzed by visible spectroscopy. The N,N'-diphenyl-p-phenylenediamine was first extracted from the solid solution by continued saxlet extraction with methanol and the conc. determined spectroscopically. The x-ray diffraction patterns taken showed the absence of a peak characteristic of N,N'-diphenyl-p-phenylenediamine although control experiments showed that the N,N'-diphenyl-p-phenylenediamine was present in concentrations great enough to afford characteristic peaks if it was present as a simple admixture. From this evidence it was concluded that solid solution had been attained.

DETERMINATION OF RATE CONSTANTS

The laminate slides were exposed and the absorption spectra were recorded at pre-determined time intervals. The rate studies were based on the disappearance of the 420m_μ absorption band characteristic of quinacridonequinone. A first order rate relationship was obtained by plotting the log of absorance (420m_μ band) vs. time. A least squares calculation was used to obtain the slope and to fit the data points. The rate constant was obtained from the slope by the relationship:

$$K = \frac{-2.3}{\text{Slope}}$$

6,13-DIHYDROXYQUINACRIDONE

An authentic sample of 6,13-dihydroxyquinacridone was prepared by chemical reduction of quinacridonequinone by sodium hydrosulfite. Twenty (20) grams of quinacridonequinone was dissolved in 250 ml. of 50.0% sodium hydroxide solution and charged into a 5 liter flask. Five hundred (500) ml. of water and 1,000 ml. of dimethylformamide were also charged into the flask. The reaction mixture was stirred and maintained under a nitrogen atmosphere. To the reaction mixture was added 500 ml. of sodium hydrosulfite saturated solution, at a dropwise rate. The temperature was maintained at 50°. After complete addition, the reaction mixture was filtered under a nitrogen stream and the filter cake was washed until the filtrate was base free. A sample of the 6,13-dyhydroxyquinacridone was dried under a nitrogen atmosphere under reduced pressure and sublimed onto a quartz slide. The visible and ultraviolet spectra were immediately measured. The visible spectrum showed a broad band between 550-650m_μ. Upon inadiation of quinacridonequinone laminate the development of a broad band between 550-650m_μ was assumed to be characteristic of the reduction product. Exposure of the 6,13-dihydroxyquinacridone to oxygen afforded a rapid oxidation to the parent quinone. This reaction can be carried out as a dark reaction, or can be photo initiated.