Serial No. KN-67-9

Copy No. 6

E. I. DU PONT DE NEMOURS & COMPANY
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

NEW CHROMOPHORES

Period Covered January, 1966 - February, 1967

KN-67-9

FILE: 223

DATE: 5/5/67

KN-67-9

Copy No.

1. Research Numerical File
2. Research Office File No. 223
3. Library File No. 223
4. M. Hunt/E. Gonick, Wilmington
5. W. S. Struve/A. A. Brizzolara
6. R. H. Wetzel, Newport
7. F. F. Ehrich
8. H. R. Linton
9. B. H. Perkins
10. P. J. Monahan (X File)
11. G. R. Aldridge
12. Extra
13. Extra
14. Extra
15. Extra
16. Extra

NEWARK PLANT

PIGMENTS COLORS RESEARCH REPORT

SUBJECT: New Chromophores

PERIOD COVERED: January, 1966 - February, 1967

SUBMITTED BY: G. R. Aldridge DATE SUBMITTED: 3/31/67

APPROVED BY: F. F. EHRICH DATE RELEASED: 5/5/67

TABLE OF CONTENTS

I. INTRODUCTION

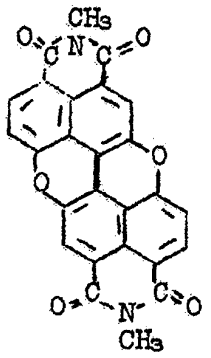
This report is a summary of the research on new chromophores, i.e., xanthenoxanthones, bis-phenanthridone-quinone, the fluorenone-analog of indanthrone, and chlorinated imides.

II. PERIOD COVERED BY REPORT

January, 1966 to February, 1967

III. SUMMARY AND CONCLUSIONS

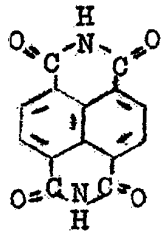
The di(N-methyl)imide (VI) of xanthenoxanthone tetracarboxylic acid dianhydride is an orange pigment,



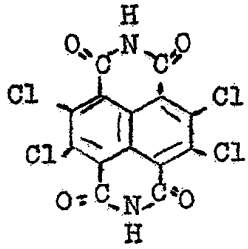
VI

which shows excellent lightfastness (Fadeometer). The reaction of 3-hydroxy-N-methylnaphthalimide with antimony pentachloride yields VII, the trichloro-analog of VI. VII is a red pigment which shows excellent lightfastness (Fadeometer) and is brighter and stronger than VI. Florida exposure of VI and its chlorinated analogs is planned. Tinctorially, VII is yellower, duller, and approximately as strong as "Monastral" Red (RT-790-D), and it is yellower, brighter, and stronger than "Monastral" Maroon (RT-792-D).

The replacement of the four hydrogen atoms in the naphthalene nucleus of the diimide of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (XXXI) with chlorine produced a bathochromic shift in color. Whereas



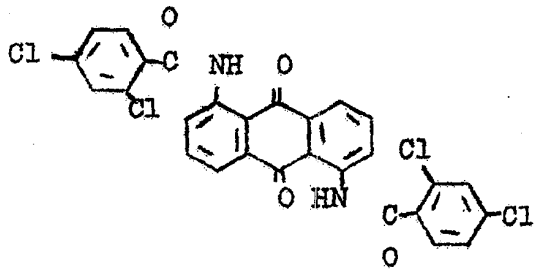
XXXI



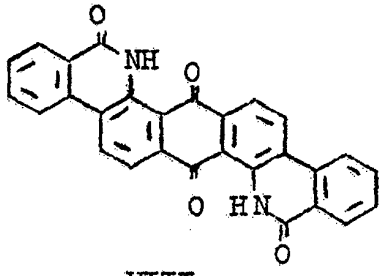
XXXII

XXXI is colorless, the 2,3,6,7-tetrachloro-analog (XXXII) of XXXI is a yellow pigment which shows good Fadeometer lightfastness. XXXII is on exposure in Florida.

The solubility of 1,5-bis(2,4-dichlorobenzamido)anthraquinone (Yellow 50) in boiling 1-chloronaphthalene and in plastics



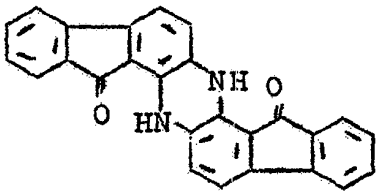
Yellow 50



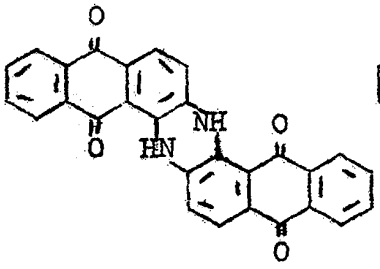
VIII

systems is attributed to the 2,4-dichlorobenzamido-groups being free to rotate with respect to the anthraquinone nucleus. The chlorine-free, phenanthridone analog of Yellow 50, bis-phenanthridone-quinone (VIII) was synthesized because it was expected to be an insoluble, lightfast yellow pigment. VIII was prepared, after considerable difficulty, and found to be an insoluble gold pigment which was brighter and redder than Newport Gold (RT-748-D). VIII showed good lightfastness (Fadeometer) but the synthesis of additional material for Florida exposure was not practical.

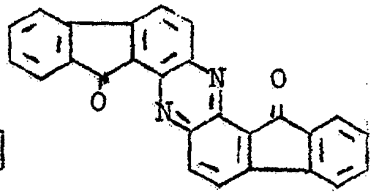
The fluorenone-analog (XX) of indanthrone is a blue pigment which is inherently weaker than indanthrone. (XX) was not evaluated in lithographic varnish because it readily underwent oxidation to the corresponding azine (XXI).



XX



Indanthrone



XXI

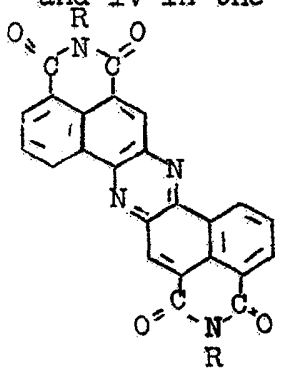
IV. PATENT STATUS

No patent applications have been made pending evaluation of the products.

V. DISCUSSION

1. Xanthenoxanthone Chromophores

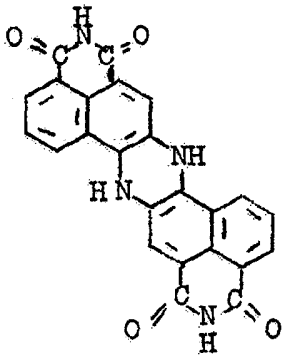
The diimide (I) of 4,5,10,11-dibenzo(a,h)phenazine tetracarboxylic acid dianhydride, an attractive yellow pigment, undergoes photoreduction to the N,N'-dihydrophenazine (II) in the absence of air. The relative rate of photoreduction of I, III, and IV in the absence of air is I < III < IV which order correlates



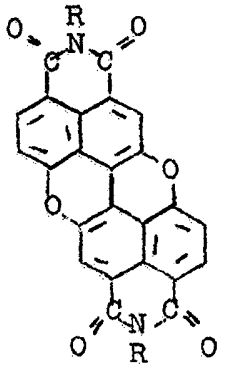
I (R=H)

III (R = phenyl)

IV (R = 2-chlorophenyl)



II

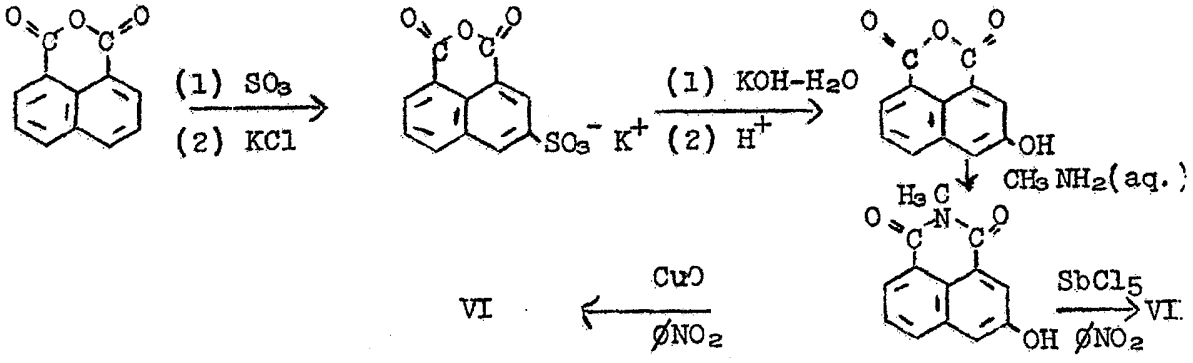


V (R=H)

VI (R = methyl)

well with their relative lightfastness order on outdoor exposure, I > III > IV. Because photoreduction to II or some related species may partly or largely account for the deficient Florida lightfastness of I, the synthesis of V which cannot undergo reduction to a N,N'-dihydrophenazine was undertaken.

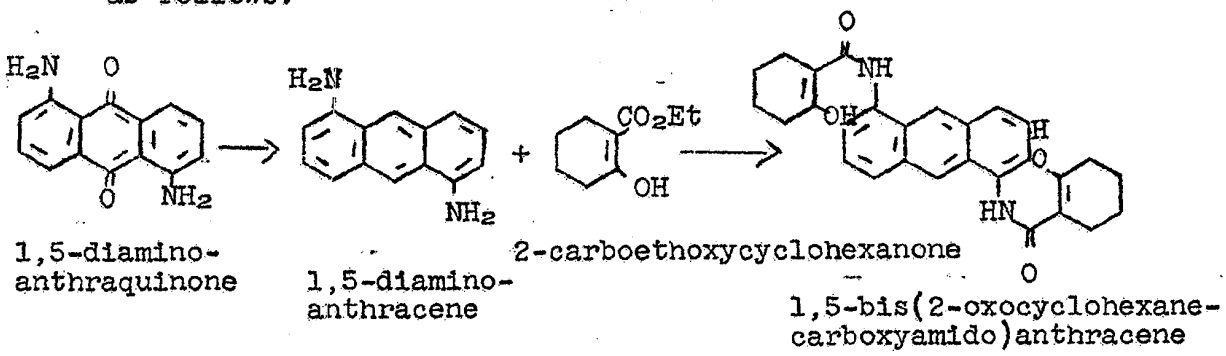
The N-methyl analog (VI) of xanthenoxanthone tetracarboxylic acid diimide (V) was prepared as follows:



The substitution of antimony pentachloride for cupric oxide in the last reaction yields VII, the trichloro-analog of VI. The structure assigned to VI is based upon the fact that the literature reports the formation of xanthenoxanthone tetracarboxylic acid dianhydride from 3-hydroxynaphthalic anhydride and cupric oxide in nitrobenzene. The structure assigned to VII is based upon its analysis, its ability to vat, and the near identity of its visible spectrum with that of VI (See Visible Spectra, Section 6). The reaction of 3-hydroxynaphthalimide with cupric oxide is expected to yield V.

2. Intramolecular Hydrogen-Bonded Chromophores

The bis-henanthridone-quinone (VIII) was synthesized as follows:



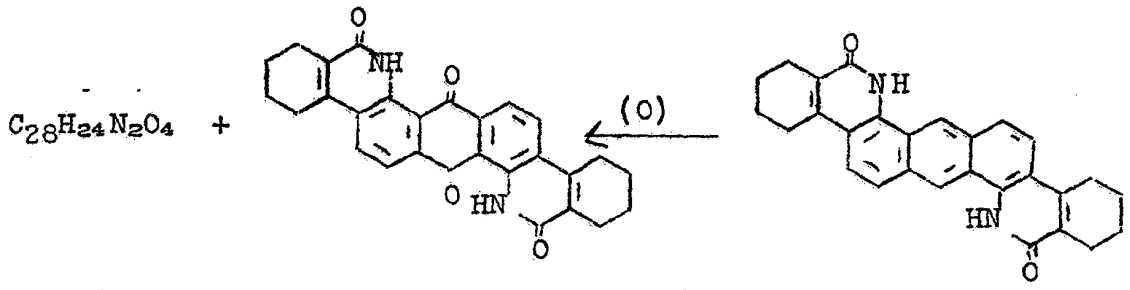
1,5-diamino-anthraquinone

1,5-diamino-anthracene

2-carboethoxycyclohexanone

1,5-bis(2-oxocyclohexane-carboxyamido)anthracene

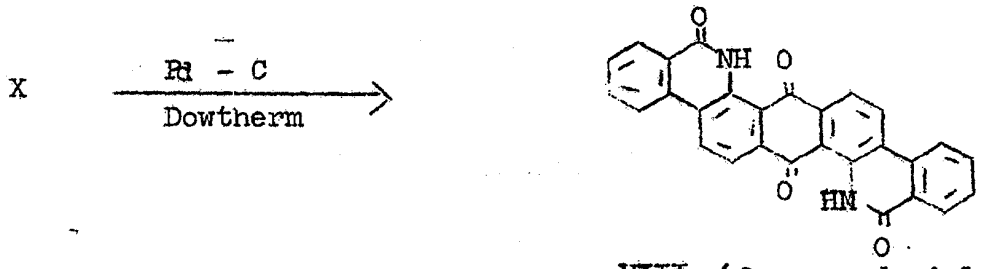
PPA



XIa (major product) (does not vat)

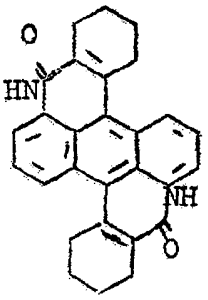
X (minor product) (forms violet vat)

IX

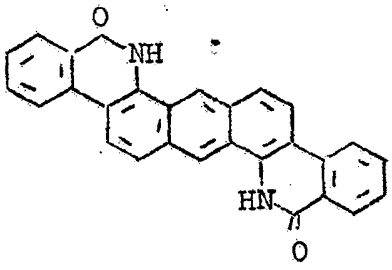


VIII (forms red-violet vat)

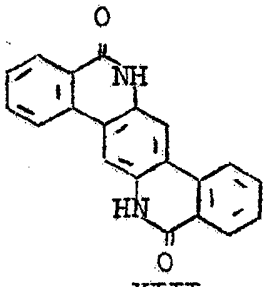
The alternative closure of 1,5-bis(2-oxocyclohexanecarboxyamido)anthracene into the 9- and 10- positions of the anthracene ring would lead to the seven-membered lactam (XI) which is isomeric with the six-membered lactam (IX). IX is the actual product based on its dehydrogenation to XII whose infrared and visible spectra are similar to those of XIII (prepared by an unequivocal synthesis), and the likely assumption that the infrared and visible spectra of the product from the dehydrogenation of XI would be noticeably different from those of XIII.



XI



XII



XIII

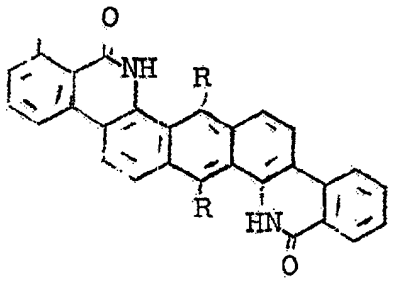
The structure assigned to X is supported by its analysis, vatting ability, infrared spectrum, and mode of formation. The structure of XIa is uncertain but its failure to vat suggests that it is not a quinone. The structure assigned to VIII is supported by its relative insolubility in boiling 1-chloronaphthalene, its vatting ability, infrared spectrum, and mode of formation.

The colors, relative solubilities and lightfastness of VIII, IX, X, and XII are tabulated below.

	Color	Solubility (g/l)	Fadeometer Lightfastness
VIII	Gold	$<$ 0.05 g in boiling 1-$C_{10}H_7Cl$	517 hrs. - good
IX	Yellow	Soluble	24" considerable fading
X	Orange	Soluble	72" slight fading
XII	Yellow	Relatively insoluble	72" slight fading

The order of lightfastness is: VIII $>$ X, XII $>$ IX. The poor lightfastness of IX and X (both octahydro-compounds) is not surprising in view of previous findings that octahydroquinacridone (from cyclohexanone and diethyl diamino terephthalate) is considerably less lightfast than quinacridone. The greater solubility of IX and X relative to that of VIII is attributed to the non-planarity of the terminal cyclohexene rings. The inferior lightfastness of XII relative to that of VIII is believed to be due to the readiness of the meso-positions in XII to undergo photo-oxidation.

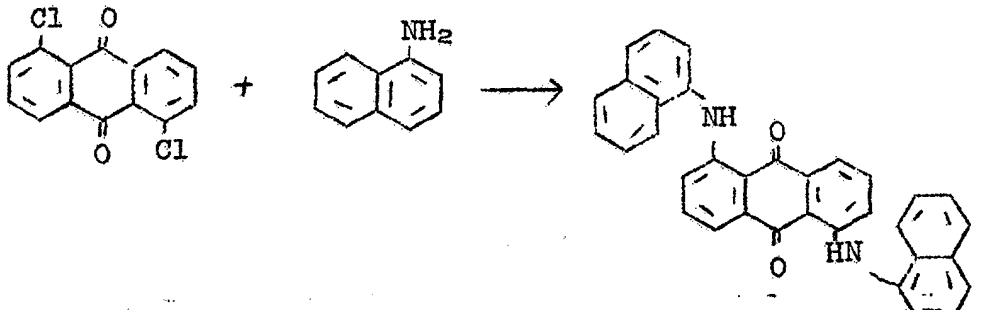
XIV might be more lightfast than XII but a practical synthesis of XIV is not likely. Attempts to prepare XV and XVI for a study of the effect of substituents at the meso-positions on lightfastness were unsuccessful.



XIV R= F
XV R= Cl
XVI R= OAc

3. Alternate Syntheses of VIII

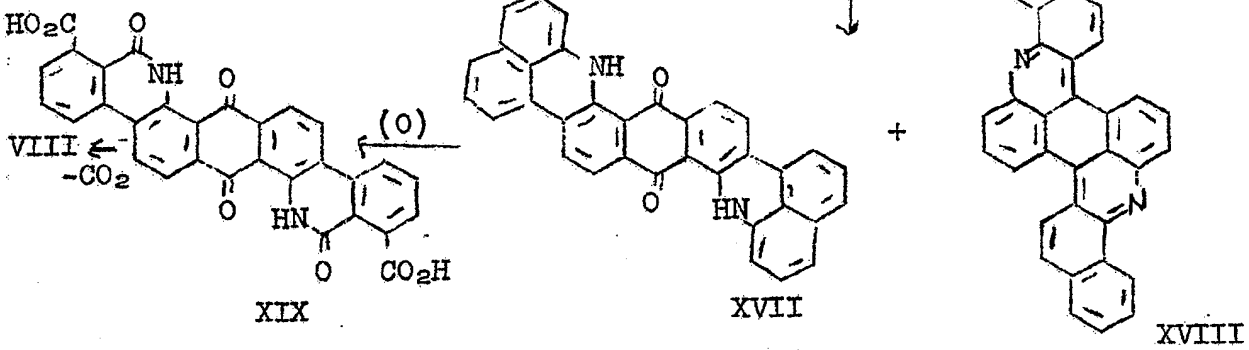
The following synthesis of VIII was attempted.



1,5-dichloro-anthraquinone

1-naphthyl-amine

1,5-bis(N-1-naphthyl-amino)anthraquinone

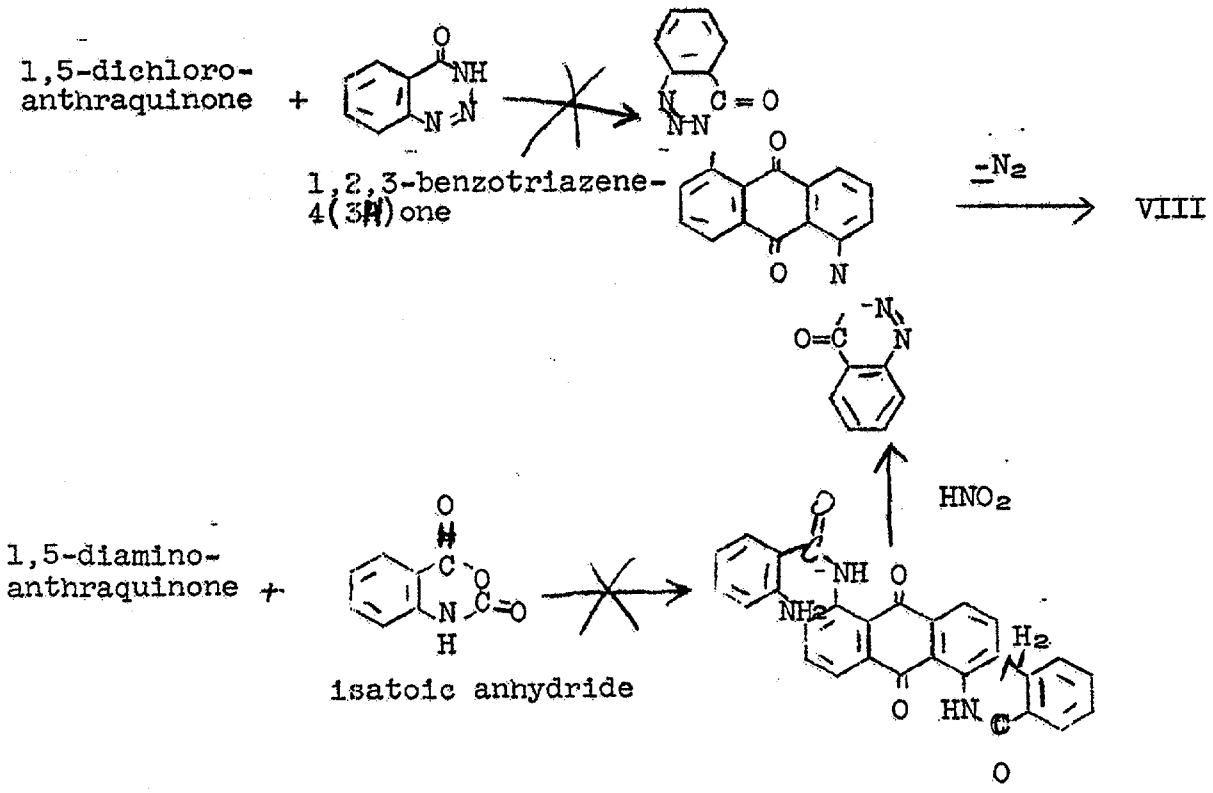


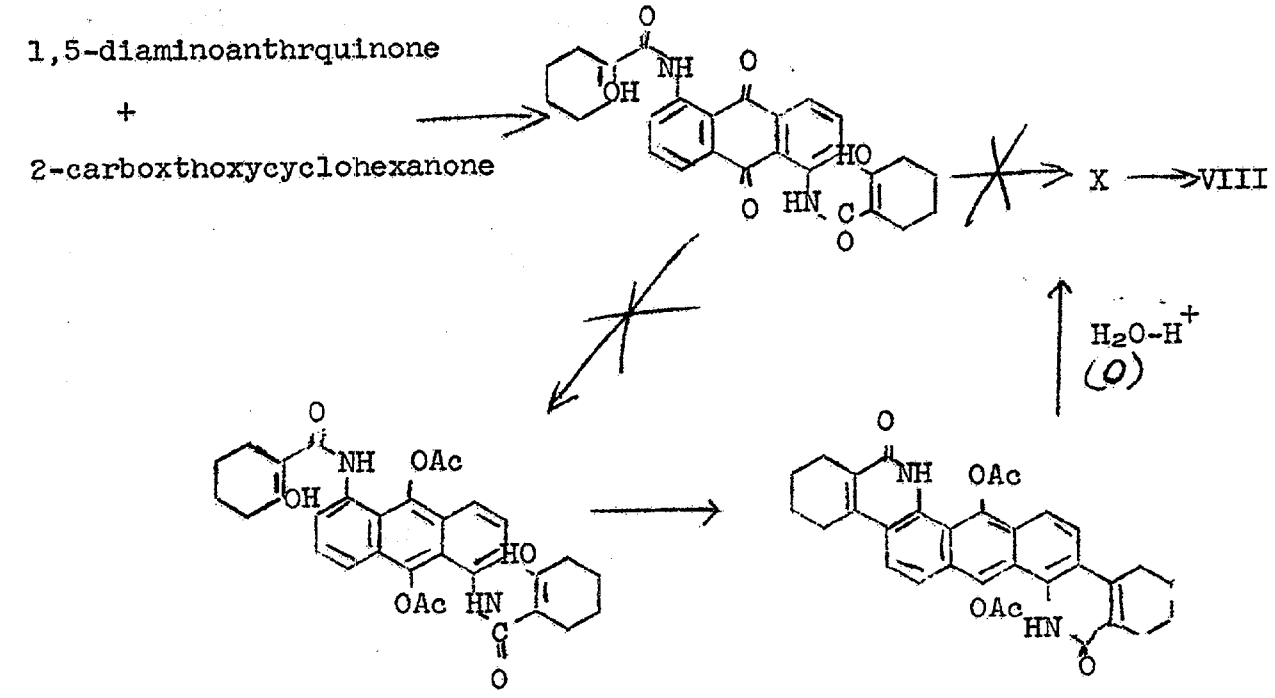
XIX

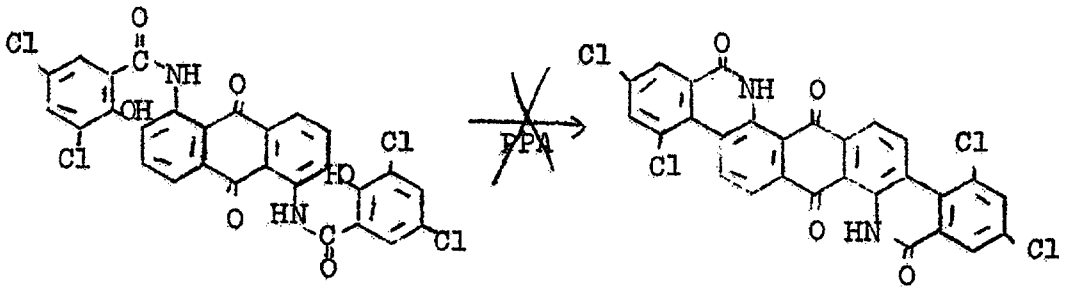
XVII

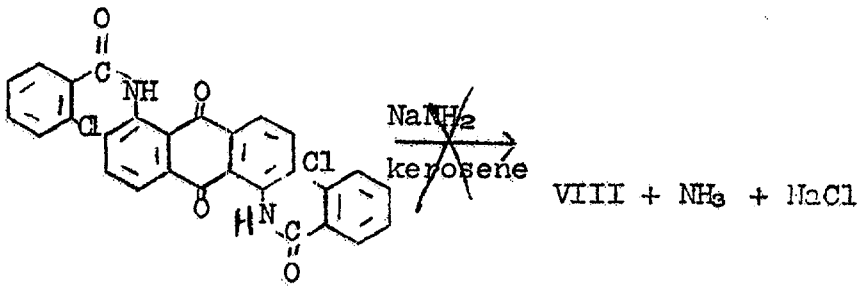
XVIII

XVII and XVIII are violet and red pigments, respectively, and both show poor lightfastness (Fadeometer). For the visible spectra of 1,5-bis(N-1-naphthylamino)anthraquinone, XVII, and XVIII see Visible Spectra (Section 6). Attempts to oxidize XVII to XIX were unsuccessful. Other attempted but unsuccessful synthesis of VIII follow (⟶✗ indicates the step in the reaction sequence that failed):

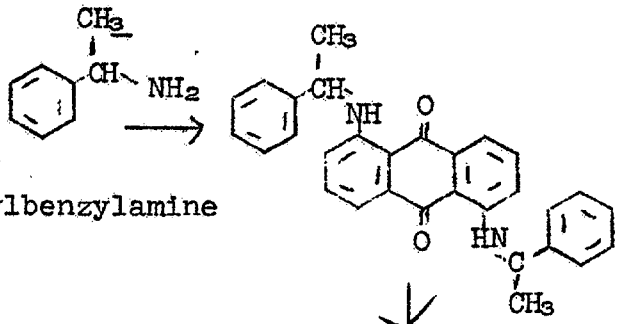


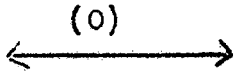


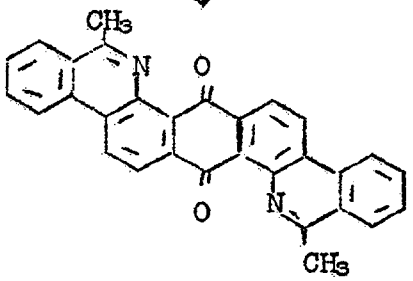




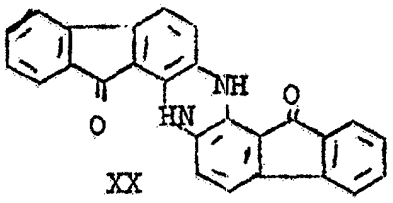
1,5-dichloro-anthraquinone +



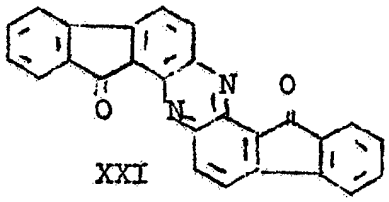
VIII 



1,6-Dibenzoylphenazine was ring-closed in an aluminum chloride eutectic melt to give the fluorenone-analog (XX) of indanthrone. The oxidation of XX with acid dichromate yields the bis-fluorenone-azine (XXI).



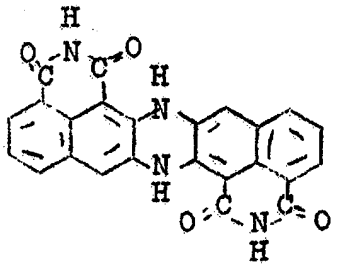
XX



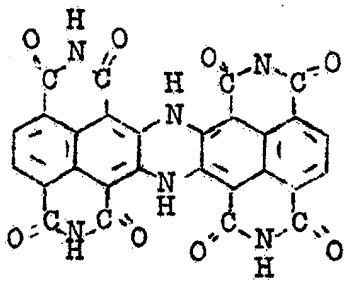
XXI

For the visible spectra of XX, XXI and 7-chloroindanthrone, see Visible Spectra (Section 6).

By analogy to the formation of "Yellow 100" (I) from 3-amino-naphthalimide and antimony pentachloride the reaction of 2-aminonaphthalimide and antimony pentachloride should yield the indanthrone analog (XXII). The actual reaction, however, failed to yield XXII. The synthesis of another indanthrone analog, XXIII, from the diimide of 2-amino-1,4,5,8-naphthalene



XXII

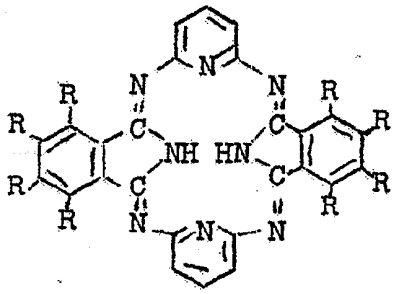


XXIII

tetracarboxylic acid dianhydride was abandoned after an attempt to nitrate the diimide of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride failed.

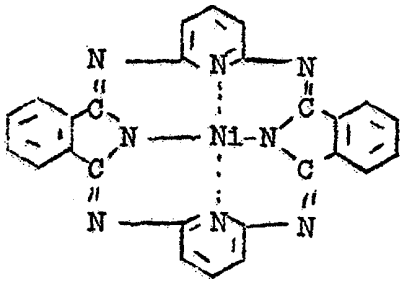
4. Macrocycle Chromophores

The macrocyclic imide (XXIV) from phthalonitrile and 2,6-diaminopyridine was colorless and, therefore, was evaluated as an ultraviolet absorber. Its lightfastness, however, was not as good as that of Tinuvin P. The nickel chelate (XXV) prepared from XXIV and nickel acetatewas a tinctorially unattractive yellow pigment. The reaction of 1,3-diimino-4,5,6,7-tetrachloro-soindoline with 2,6-diaminopyridine yielded two products, XXVI (presumably) and metal-free polychlorophthalocyanine green. The yellow pigment, XXVI, showed poor lightfastness (Fadeometer). An attempt to prepare the nickel chelate of XXVI was unsuccessful.



XXIV R = H

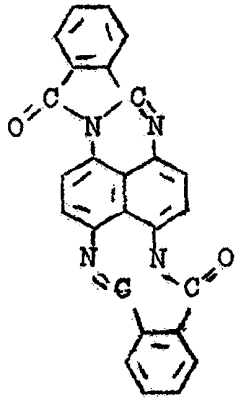
XXVI R = Cl



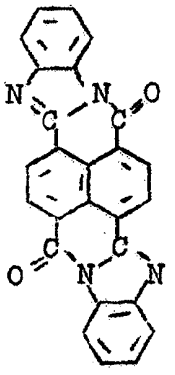
XXV

5. Imidazole Chromophores

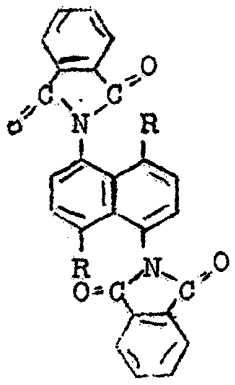
The synthesis of XXVII was undertaken because it is an isomer of Orange GR (XXVIII), the brightest of the commercial lightfast organic orange pigments. The dinitration of 1,5-diphthalimidonaphthalene gave a dinitro-1,5-diphthalimido-naphthalene, presumably XXIX. The reduction of XXIX was carried out under conditions, iron and acetic acid, that would favor ring closure of the initially formed diamino-compound (XXX) to XXVII. The actual product was a red-brown pigment and its failure to vat suggests that XXVII was not obtained.



XXVII



XXVIII



XXIX R = NO_2

XXX R = NH_2

VI. VISIBLE SPECTRA

The absorption maxima (λ_{max}) and molecular extinction coefficients (ε_{max}) of many of the compounds in this report are as follows:

Solvent: 1-chloronaphthalene

	λ_{max} (mμ)	ε_{max}	Band Description
I. (Yellow 100)	450	24,600	Sharp
	420	19,400	"
N-methyl analog of I	450	23,600	"
	420	17,900	"
N-phenyl analog of I(III)	450	25,600	"
	425	19,500	"
Xantheonoxanthone	449	10,700	"
	420	7,900	"
XI	549	16,700	"
	505	11,800	"
	472	6,100	Broad
	438	4,900	"
VII	546	22,900	Sharp
	504	16,200	"
	472	5,600	Broad
	437	2,300	"
VIII	480	Incomp. Sol.	"
X	490	17,000	Broad
XII	No definite peaks.	At 450 mμ $\varepsilon >$ 10,800	
XIII	No definite peaks.	At 450 mμ $\varepsilon >$ 6,250	
1,5-dianilinoanthraquinone	543	12,600	Broad
1,5-bis(N-1-naphthylamino) anthraquinone	544	11,500	Broad
XVII	555	>16,300	Broad
		>17,300	"
XVIII	543	32,000	"
	503	24,000	"
XX	620-660	8,600	"
7,chloroindanthrone	710	106,000	"
XXI	544	6,500	"
	506	7,100	"
	415	11,500	"
XXIV	350-400	At 390mμ	"
		ε= 25,500	"
XXV	461	22,000	"
	406	27,000	"
XXVIII (Orange GR)	498	19,900	"
	470	22,300	"
XXIX Reduction Product	550-560	8,700 (if MW = 412)	"