KN-70-6 YELLOW CHROMOPHORES By: P. S. Dhaliwal 9/15/68 - 12/15/69

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(14) Dan Jackson - 1/29/80
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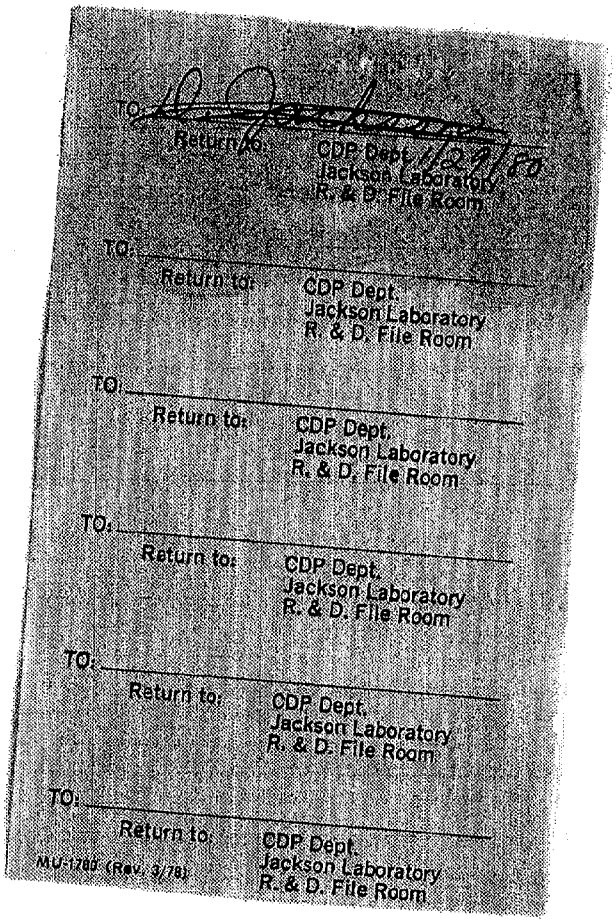

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256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

YELLOW CHROMOPHORES

Period Covered September 15, 1968 - December 15, 1969

FILE: 223

DATE: 3/2/70

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2. Research Office File, Newark 223
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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: YELLOW CHROMOPHORES

PERIOD COVERED: September 15, 1968 - December 15, 1969

SUBMITTED BY: P. S. Dhaliwal Date Submitted: 2/2/70

APPROVED BY: E. E. JAFFE Date Released: 3/2/70

TABLE OF CONTENTS

I. INTRODUCTION

The purpose of this investigation was to prepare yellow compounds which possess high tinctorial strength, extreme insolubility in organic solvents, and excellent durability to photodegradation in coating compositions.

II. SUMMARY AND CONCLUSIONS

The nickel chelate of the Schiff base derived from 2,4-dihydroxy-3-formylquinoline and 9,10-diaminophenanthrene is a bleed resistant, transparent but relatively dull red-shade yellow pigment which shows excellent lightfastness (lithographic varnish) after 500 hours Fadeometer exposure. It is considerably stronger than Irgazin 3RLT and after 3 months exposure in Florida at 5° south, in thermosetting acrylic enamel (TSA), shows better lightfastness than Irgazin 3RLT or Green Gold. This pigment also shows excellent lightfastness in thermoplastic acrylic lacquer (TPA) paint system after 3 months exposure in Florida at 5° south.

Bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine is a bright yellow, bleed-resistant pigment which shows excellent lightfastness (lithographic varnish) after 500 hours Fadeometer exposure. It is 40% stronger than Irgazin 3RLT and shows good durability after 3 months Florida exposure in thermoplastic acrylic lacquer. It is, however, slightly inferior to Irgazin 3RLT.

Bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-benzidine is a bleed-resistant orange yellow pigment which shows good lightfastness both after 500 hours Fadeometer exposure (lithographic varnish) and three months Florida exposure in thermoplastic acrylic lacquer.

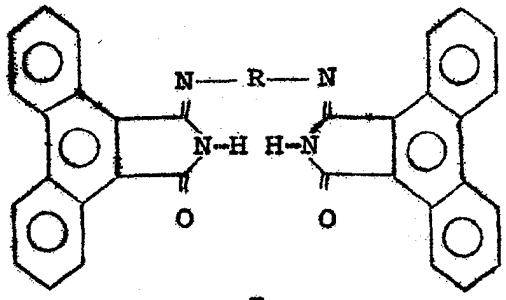
Bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)3,3'-dichlorobenzidine is a bleed-resistant, bright yellow pigment which shows excellent lightfastness (lithographic varnish) after 500 hours Fadeometer exposure. It is 40% stronger than Irgazin 3RLT and is currently on exposure in Florida in thermoplastic acrylic lacquer and thermosetting acrylic enamel paint systems both as a crude and particle size reduced forms.

III. DISCUSSION

A number of isoindolinone derivatives were prepared by reacting phenanthrene-9,10-dicarboximide with phosphorus pentachloride (PCl_5) followed by reaction with various aromatic diamines. Due to the structure of phenanthrene-9,10-dicarboximide, it was assumed that the derived isoindolinones might possess sterically hindered azomethine and carbonyl functions (see structure I). Based on this hypothesis which was also advanced in a previous report[1] steric hindrance of azomethine and carbonyl functions in isoindolinone type pigments may afford an avenue for the photochemical stabilization of these compounds.

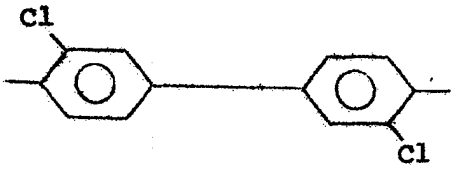
In an effort to establish whether steric effects are primarily responsible for the observed photostability of such compounds, the following derivatives of the basic system I were prepared.

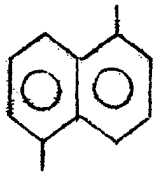
[1] P.S.Dhaliwal, KN-68-13

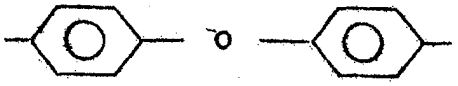


I

R =



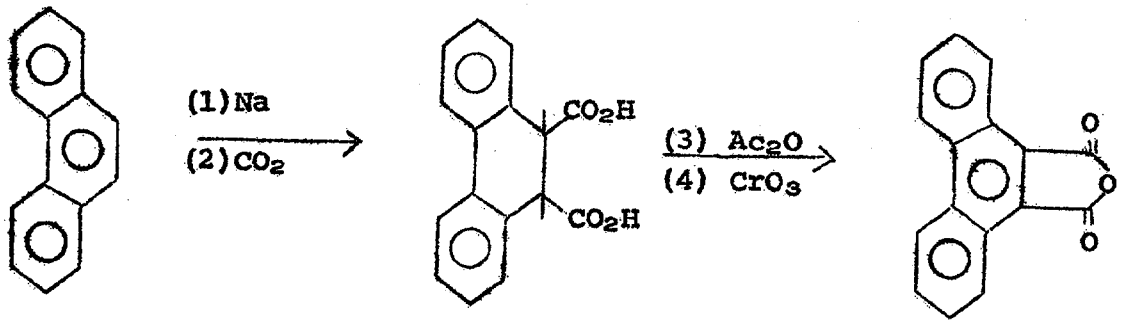


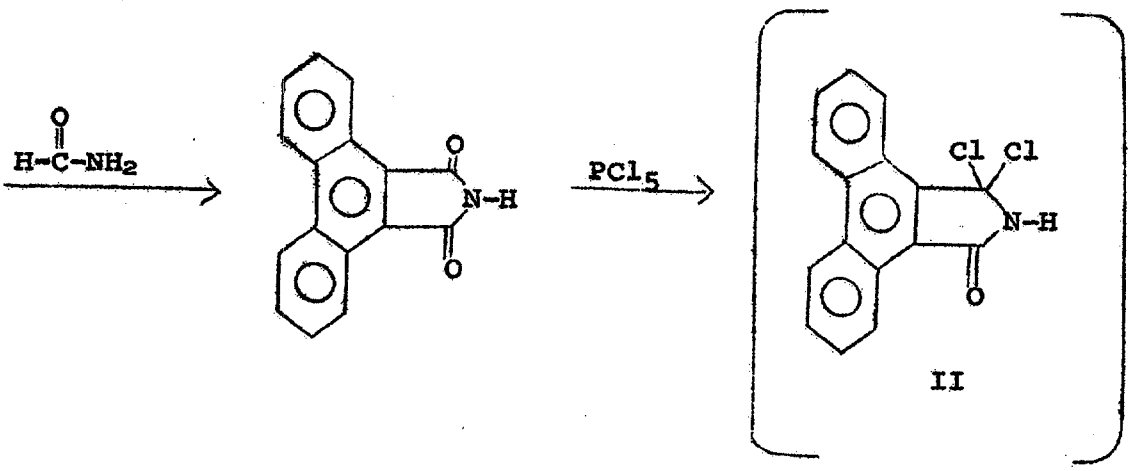


A. Isoindolinone Pigments

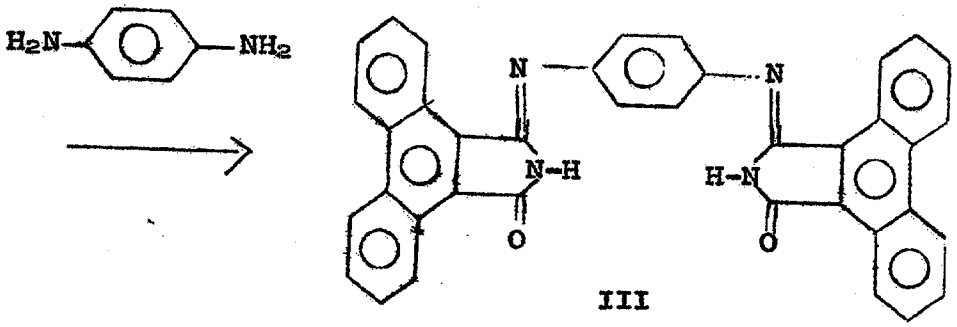
Phenanthrene-9,10-dicarboxylic anhydride[2] was obtained by the sodiation and carbonation of phenanthrene as shown below followed by oxidation. The anhydride was converted to the imide in hot formamide (method 1). The imide was reacted with phosphorus pentachloride and the formed dichloride (II), without isolation, was reacted with p-phenylenediamine, to give a bright yellow solid identified as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine (III).

2 R. Adams and A. Jeanes. U.S.P. 2,231,787; J.Am.Chem.Soc., 59, 2608 (1937).


(1) Na
(2) CO_2
CO_2H
CO_2H
(3) Ac_2O
(4) CrO_3
O
O
O


H-C-NH2
O
N-H
O
PCl_5
Cl Cl
N-H
O

II


H_2N
NH_2
N
N
N-H
O
H-N
O

III

This tetrabenzo analog of Irgazin showed excellent lightfastness (lithographic varnish) after 500 hours Fadeometer exposure. The compound is a red-shade yellow of very low solubility (200 mg/l in boiling α-chloronaphthalene at 264°C. and less than 2 mg/l in boiling dimethylformamide at 155°C.) and considerable strength, being 40% stronger than Irgazin 3RLT by rubout and in paint.

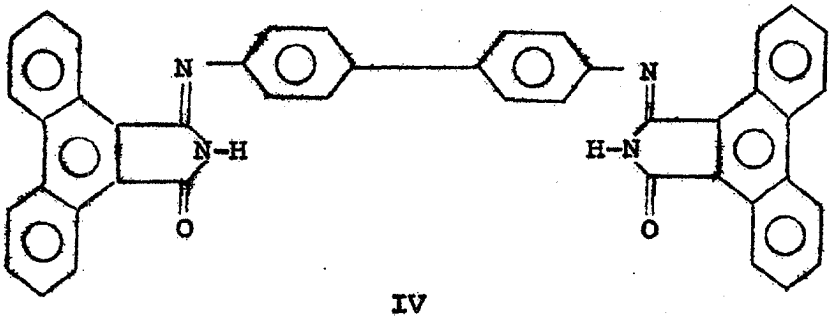
The milled counterpart of this product is superior in transparency to the crude product, presumably as a result of reduced particle size of the former which also showed considerably greater two-tone effect in automotive metallics compared to Irgazin. This product is also more intense and more transparent than Irgazin 3RLT. It is approximately the same shade and strength as Flavanthrone. After 500 hours in the Fadeometer, the milled product shows lightfastness comparable to Irgazin 3RLT both in tint and masstone.

The extinction coefficient of the various Irgazin type compounds in α-chloronaphthalene at λ max are shown in the following table, which also contains their solubility in α-chloronaphthalene.

Irgazin	λ max		Solubility in α-chloronaphthalene at 264°C.
Tetrachloro	395	10,640	6.82 g/l
Tetramethyl	372	11,600	5.15 g/l
Octachloro	410	10,000	1.32 g/l
Tetrabenzo	400	15,000	0.20 g/l

In order to extend the color range of the phenanthrene isoindolinone class of pigments, a number of diamines were used to synthesize a series of analogous compounds.

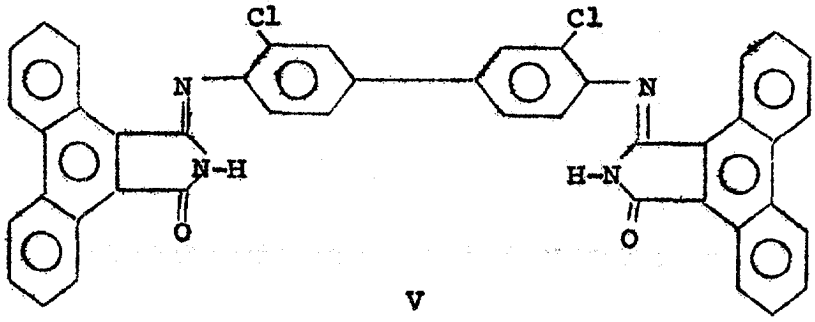
Phenanthrene-9,10-dicarboximide was reacted with phosphoros pentachloride and the formed dichloride (II), without isolation, was reacted with benzidine to give an orange-yellow solid identified as bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-benzidine (IV).



IV

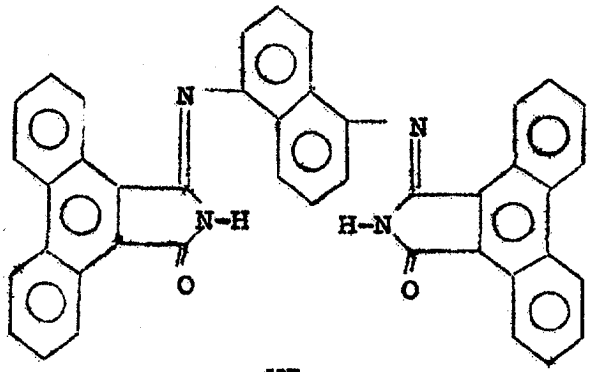
In order to increase the degree of steric hindrance and possibly decrease solubility, it was decided to introduce chlorine atoms into the aromatic diamine moiety.

In a manner similar to the synthesis of the above compounds, the intermediate dichloro compound (II) was reacted with 3,3'-dichlorobenzidine, to give a bright yellow solid identified as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3,3'-dichlorobenzidine (V).



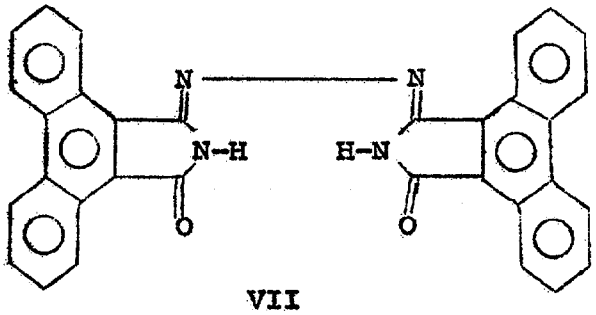
V

In order to shift the color into the red range, phenanthrene-9,10-dicarboximide was reacted with phosphorus pentachloride and the formed dichloride (II) was reacted, without isolation, with 1,5-diaminonaphthalene to give a red solid identified as bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-1,5-naphthalenediamine (VI).

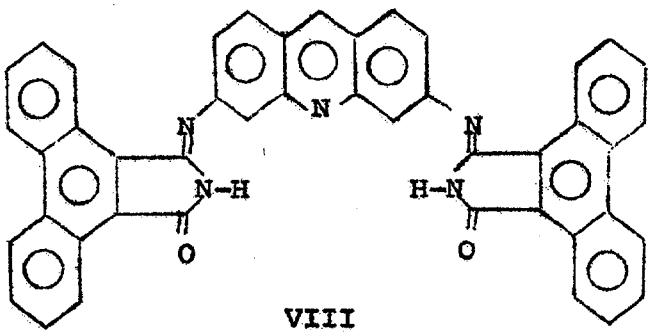


VI

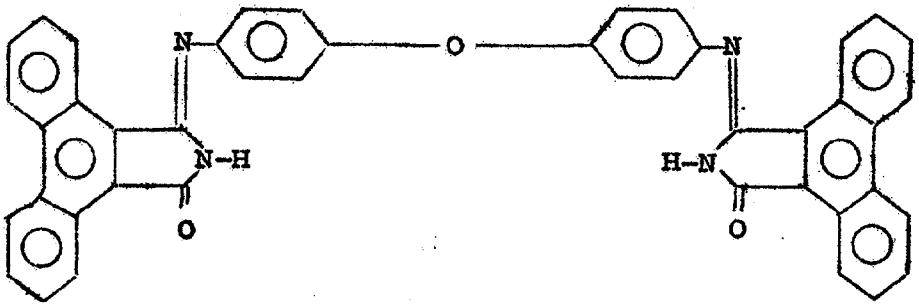
In an effort to further explore the range of colors achievable with these isoindolinone-type compounds, the intermediate dichloride (II) was reacted with hydrazine, 3,6-diaminoacridine, and 4,4'-diaminodiphenyl ether to give greenish-yellow solids, identified as bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-hydrazine (VII), bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3,6-diaminoacridine (VIII), and bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-4,4'-diaminodiphenyl ether (IX), respectively.



VII



VIII

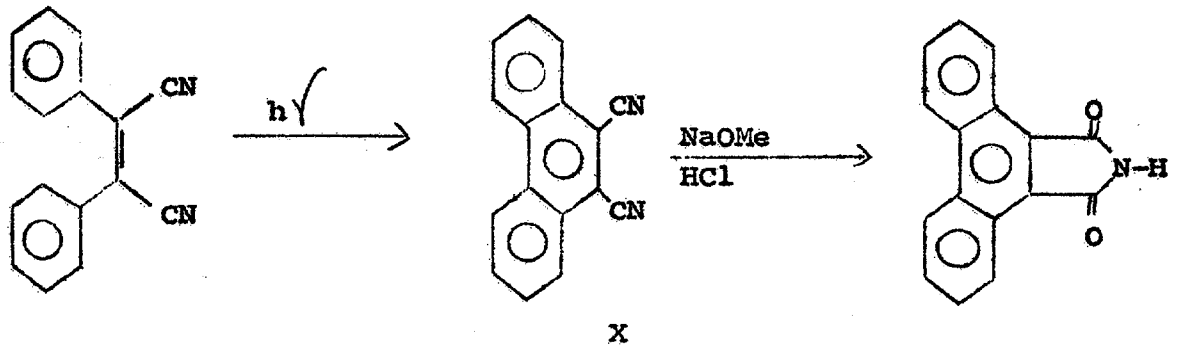


IX

Attempts to react compound II with m-phenylenediamine, 2,7-diaminonaphthalene, dianisidine, and 2,2'-diaminobiphenyl failed to yield insoluble pigments.

The above method for preparing phenanthrene-9,10-dicarboximide from phenanthrene was found to be impractical for scale-up experiments. In order to prepare larger samples of phenanthrene-9,10-dicarboximide, an alternate method was employed.

Diphenylmaleonitrile was photolyzed to yield 9,10-dicyanophenanthrene (X)[3]. The dicyanophenanthrene was reacted with sodium methoxide followed by acidification with hydrochloric acid to pH of 2 to give a greenish-yellow solid, identified as phenanthrene-9,10-dicarboximide (method 2). This compound possessed an infrared spectrum identical with the imide produced by the previous method.



X

Large samples of the isoindolinone pigments derived from the imide made by method 2 were prepared for Florida exposure.

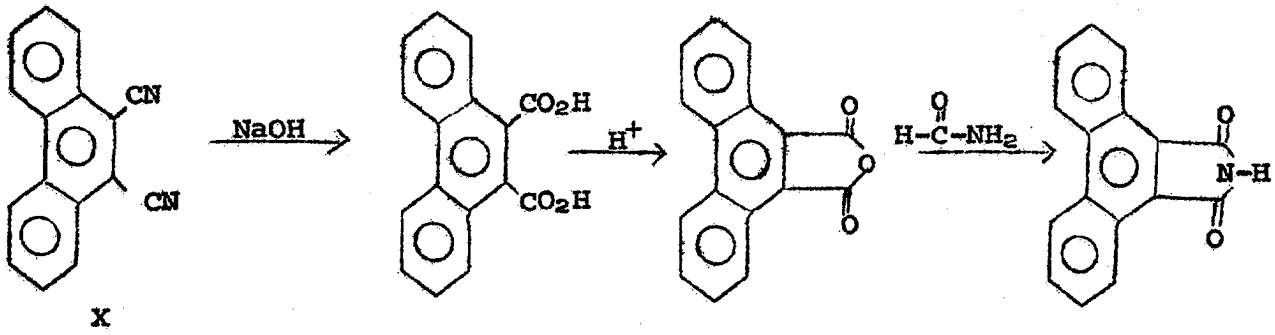
Although the final pigment samples prepared from the imide made by method 2 were of reasonable purity, they were not analytically pure.

In order to prepare analytically pure samples of the isoindolinone pigments, it was decided to prepare the imide in purer form. Although the IR spectrum of the imide made by method 2 was identical with the original imide, the nitrogen analysis was considerably higher than required, N = 6.8% vs calc. 5.68%. The analysis could not be improved even after repeated recrystallization from formamide.

In order to prepare a pure imide, the dicyanophenanthrene, X, was hydrolyzed to the diacid with NaOH in ethylene glycol, acidified with hydrochloric acid to give the anhydride which was converted to the imide in hot formamide (method 3).

Analysis: Found N = 5.87; calc. N = 5.68%.

[3]C.J.Timmons and M.V.Sargeant, J.Am.Chem.Soc.85, 2186-7 (1963).

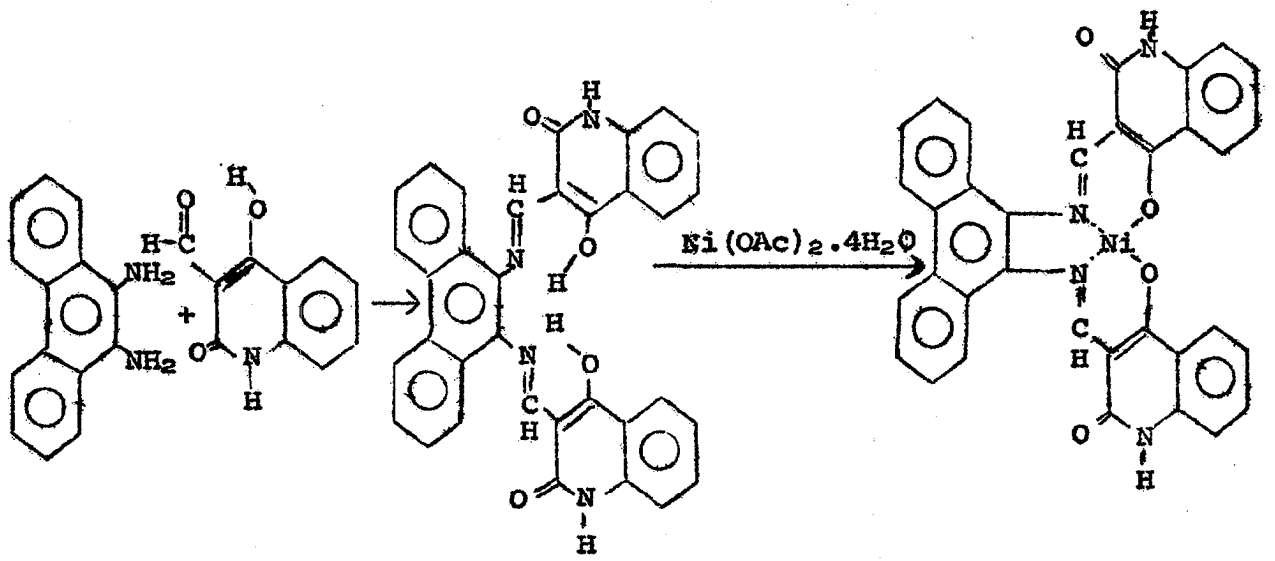


X

The isoindolinone pigments obtained from the imide made by method 3 were more intense than pigments obtained via imide made by methods 1 or 2, but were still not strictly analytically pure. The products are presently on outdoor exposure.

B. Chelates

In an effort to further explore the theory of steric inhibition of photochemical reactions of azomethine and carbonyl functions, it was decided to extend this hypothesis to Schiff base chelates. Consequently, the Schiff bases derived from 9,10-diamino-phenanthrene and o-hydroxy aromatic aldehydes, such as 2,4-dihydroxy-3-formylquinoline, were converted to several chelate compounds.

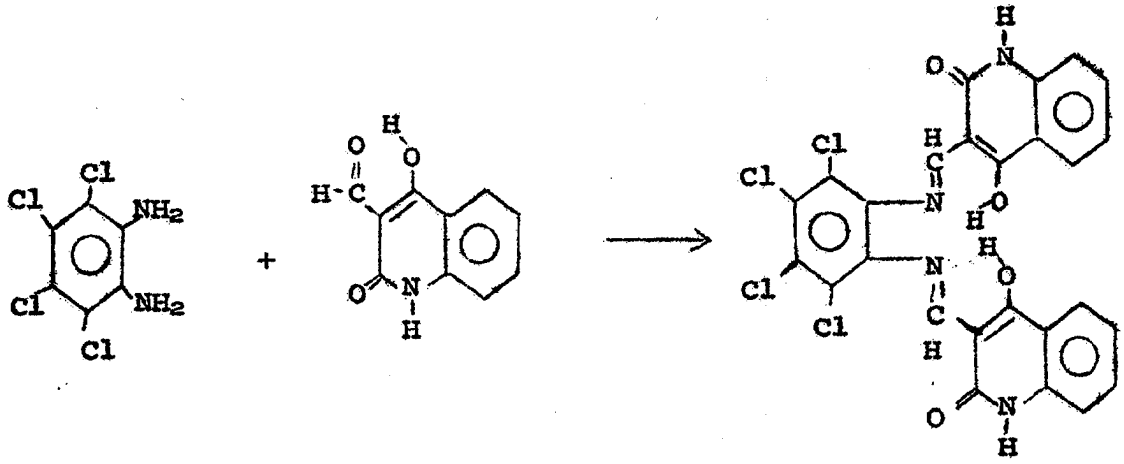


XI XII

It is obvious from structure XII, that the azomethine functions of this chelate have the same opportunity for steric inhibitions of photochemical reactions as the isoindolinone pigments discussed earlier.

9,10-Diaminophenanthrene was reacted with 2,4-dihydroxy-3-formylquinoline to yield a yellow solid identified as XI. This Schiff base was reacted with nickel acetate to yield a red-shade yellow solid identified as XII. This pigment after 3 months exposure in Florida at 5° south shows excellent lightfastness both in TSA and TPA.

In order to extend the idea of steric hindrance of Schiff base chelates, it was decided to prepare the chelate derived from Schiff base XIII. Tetrachloro-orthophenylene diamine was reacted with 2,4-dihydroxy-3-formylquinoline to give a yellow solid identified as XIII. Attempts to chelate this compound have so far been unsuccessful.



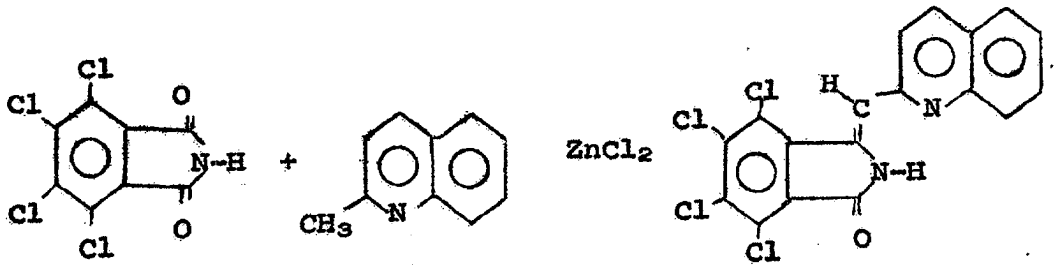
XIII

It is suspected that the basicity of the azomethine nitrogens may be too low for the formation of a stable chelate.

C. Miscellaneous Compounds

In an effort to extend the hypothesis of steric inhibition of photochemical reactions to other systems, a number of compounds were prepared for evaluation.

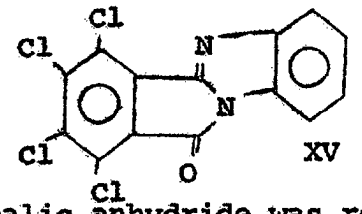
In order to evaluate this effect on carbon analogs of the Irgazin type, a model compound was prepared. Tetrachlorophthalimide was reacted with 2-methylquinoline using zinc chloride as a catalyst to give a bright yellow solid identified as XIV.



XIV

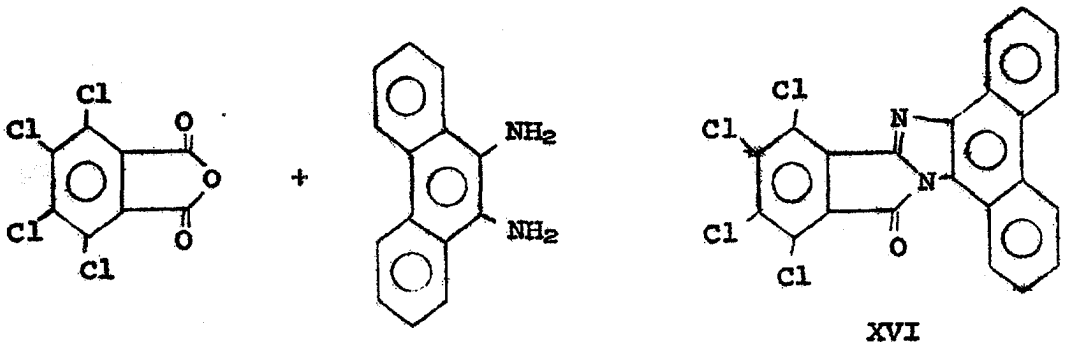
Unfortunately, all attempts to prepare the double-headed analog of XIV have been unsuccessful.

In view of the good daylight fluorescence of XV, a number of perinones were prepared as possible daylight fluorescent pigments.



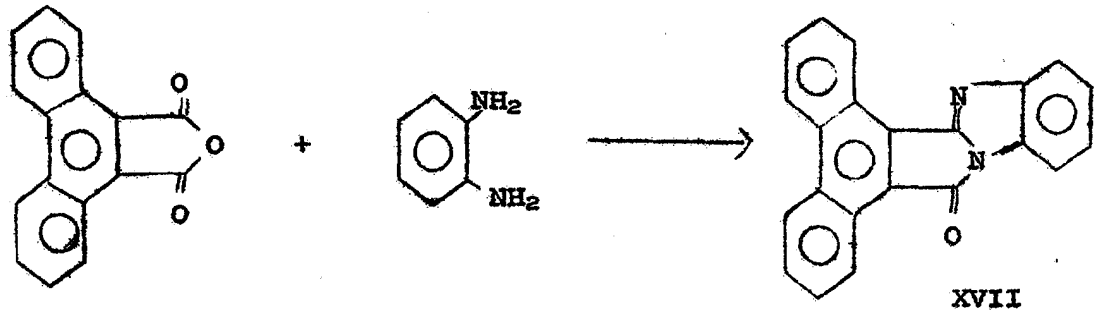
XV

Tetrachlorophthalic anhydride was reacted with 9,10-diamino-phenanthrene to give a bright red solid identified as XVI.



XVI

o-Phenylenediamine was reacted with phenanthrene-9,10-dicarboxylic anhydride to give a reddish yellow solid identified as XVII.

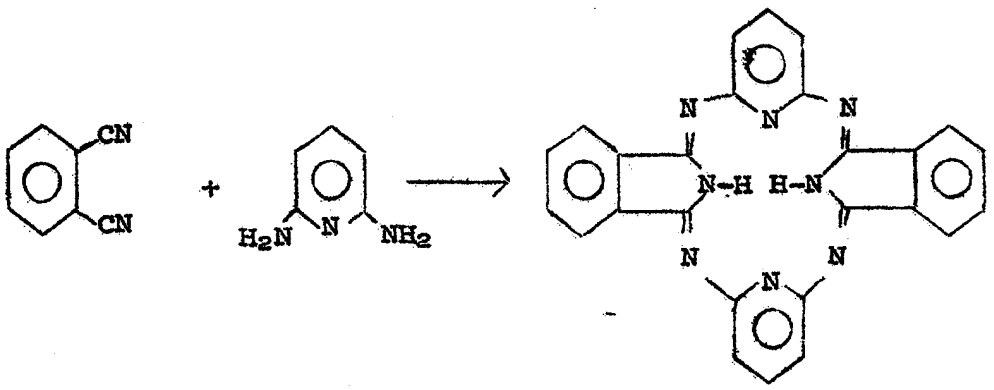


XVII

Unfortunately, both of the above compounds exhibited only feeble fluorescence.

D. Macrocycles

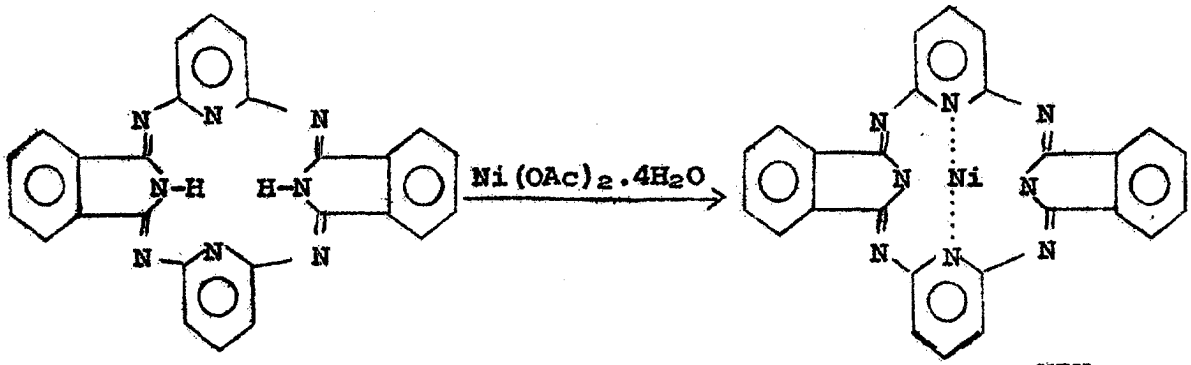
In an extension of this work, macrocycles possessing the phenanthrene moiety were prepared. It is known in the literature[4] that phthalonitrile and suitable aromatic diamines react to form large conjugated macrocycles similar to the annulenes and phthalocyanines. For example, 2,6-diaminopyridine and phthalonitrile react to form a brown compound shown to be XVIII[4].



XVIII

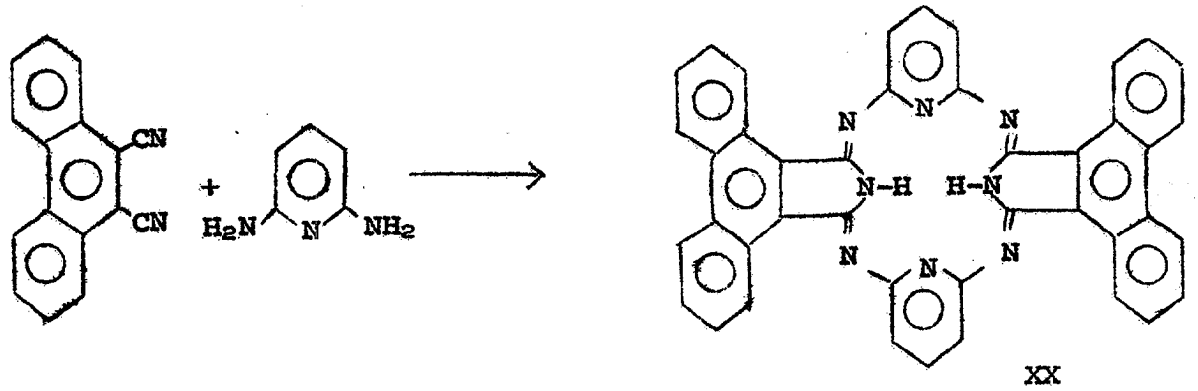
4 J.A.Elvidge and R.P.Linstead, J.Chem.Soc. 1952, 5008.

This macrocycle also formed a chelate with nickel to yield an olive green powder XIX[4].

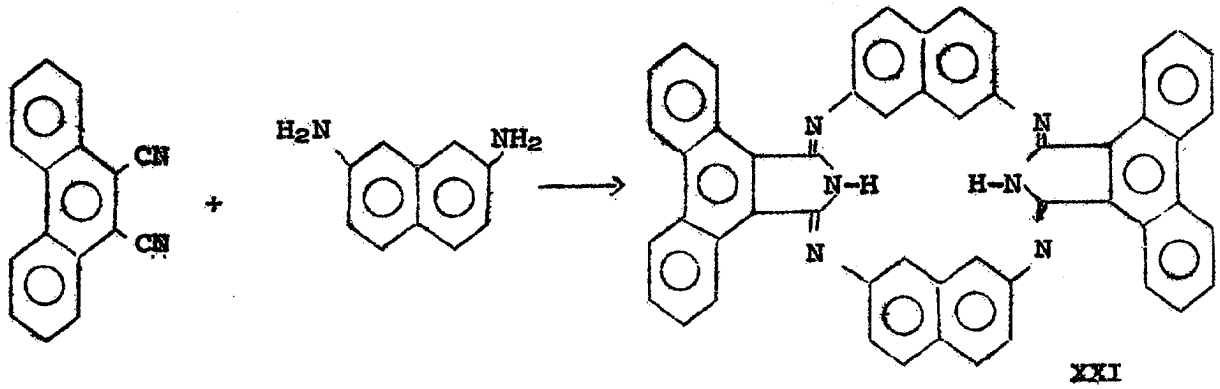


XIX

In view of the above, 9,10-dicyanophenanthrene was reacted with 2,6-diaminopyridine and 2,7-diaminonaphthalene to yield highly insoluble and high melting brown (XX) and greenish yellow (XXI) solids respectively.



XX



XXI

Unfortunately, the lightfastness of XX and XXI was not good and as a consequence, the hypothesis that steric hindrance of azomethine linkages inhibits photochemical degradation does not apply to the cyclic molecules. Attempts to chelate XVIII with Ni^{+2} were unsuccessful, possibly due to the insolubility of the Schiff base in DMF, the reaction solvent.

IV. EXPERIMENTAL

A. Isoindolinones

1. Preparation of bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine, with pyridine (III) NB 1924-18

In a 5 l flask, a mixture of 20 g of phenanthrene-9,10-dicarboximide and 25.0 g of phosphorus pentachloride and 2300 ml of dry orthodichlorobenzene was heated with stirring under reduced pressure (18-35 mm) at 120-130°C., and maintained at this temperature for one and one-quarter hours. During this period, the formed phosphorus oxychloride and some orthodichlorobenzene was distilled (distillate volume ~ 300 ml).

At the end of this time, 10 g of dry pyridine was added to the above solution and allowed to stir for 5 minutes at 120-130°C. To this mixture was then added 4.2 g p-phenylenediamine dissolved in 600 ml of dry orthodichlorobenzene at 130°C. Immediately upon addition of the p-phenylenediamine solution, a reddish-yellow solid began to precipitate from the reaction mixture. The mixture was then stirred at 120-130°C. for 2 hours. After completion of the reaction, the mixture was filtered at 120-130°C., and the precipitate was washed successively with alcohol, water, and alcohol and dried at 60°C. A yield of 15.0 g of a reddish-yellow solid was obtained.

A mixture of 15.0 g of the above solid was heated with 1100 ml of dimethylformamide at reflux temperature for 20 minutes. The product was isolated from the hot mixture by filtration, washing, and drying at 60°C. The recovery was 13.0 g.

Analysis:	Found:	Calc. for $C_{38}H_{22}N_4O_2$
	C, 77.96	C, 80.60
	H, 3.74	H, 3.89
	N, 9.68	N, 9.88

The analysis and the IR spectrum confirm the identity of the product as bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine.

Shot milling of bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine.

A 10 g sample of the above product (A), 300 g of 1/8 inch steel shot and 500 ml acetone was milled for 72 hours. The mill charge was extracted with 1% sulfuric acid at about 90°C., filtered and the

presscake was washed free of acid and sulfate and subsequently dried at 60°C. This product (B) was superior in transparency to product (A), presumably as a result of the reduced particle size of the former.

In order to enhance the dispersibility of the crude pigment, a 14.0 g sample of product A, 800 g of glass beads and 400 ml of acetone was milled for 72 hours. The mill charge was filtered, washed with alcohol, water and alcohol, and subsequently dried at 60°C. By rubout, this sample was 40% stronger than Irgazin 3RLT in tint by rubout and in paint.

2. Preparation of Bis-(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-p-phenylenediamine, without pyridine (III) NB 1924-18

In a 5 l flask, a mixture of 19.5 g phenanthrene-9,10-dicarboximide and 2300 ml of dry orthodichlorobenzene and 24.4 g phosphorus pentachloride was heated with stirring under reduced pressure (18-35 mm) at 120-130°C., and maintained at this temperature for 1-1/4 hours. During this period, the formed phosphorus oxychloride and some orthodichlorobenzene was distilled (distillate volume ~ 300 ml).

At the end of this time, a solution of 4.2 g of p-phenylene diamine dissolved in 600 ml of dry orthodichlorobenzene at 130°C. was added to the above solution. Immediately upon addition of the p-phenylenediamine solution, a reddish-yellow solid began to precipitate from the reaction mixture. The mixture was then stirred at 120-130°C. for 2 hours. After the completion of the reaction, the mixture was filtered at 120-130°C. and the precipitate was washed successively with alcohol, water and alcohol, and dried at 60°C. A yield of 13.4 g of a reddish-yellow solid was obtained.

Product A can also be prepared without the vacuum distillation (in the phosphorus pentachloride and phenanthrene 9,10-dicarboximide reaction), but the purity of product and yields are lower.

3. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)benzidine (IV) NB 1909-12

A mixture of 10 g of phenanthrene-9,10-dicarboximide and 12.5 parts phosphorus pentachloride and 2300 parts of dry orthodichlorobenzene was heated with stirring at 120°-130°C., under reduced pressure (18-30 mm) and maintained at this temperature for 1-1/4 hours. During this period, the formed phosphorus oxychloride and some orthodichlorobenzene was distilled (distillate volume ~ 200 ml).

At the completion of the reaction, 5.0 g of pyridine was added to the solution and allowed to stir for 5 minutes at the above temperature. To this solution was then added 3.2 g of benzidine dissolved in 700 ml dry orthodichlorobenzene. Immediately upon the addition of the benzidine solution, an orange solid began to precipitate from the reaction mixture. The mixture was stirred at 120-130°C. for 2 hours. At the end of this time, the mixture was

filtered at 130°C. and the presscake washed successively with alcohol, water, alcohol and dried at 60°C. The yield was 6.4 g.

A mixture of 19.2 g of the above pigment and 1,000 parts of dry nitrobenzene was heated at the reflux temperature for 20 minutes. The product was isolated from the hot mixture by filtration at 210°C. and successive washing with cold nitrobenzene, alcohol, water, and alcohol and dried at 60°C.

A mixture of the nitrobenzene extracted solid and 1000 parts of dimethylformamide were rapidly heated to the reflux temperature and maintained at this temperature for 20 minutes. At the end of this time, the product was filtered from the hot mixture and washed successively with alcohol, water and alcohol and dried at 60°C. A yield of 11.6 parts was obtained.

Analysis:	Found	Calc. for $C_{44}H_{26}N_4O_2$
	C = 80.57	C = 82.24
	H = 4.25	H = 4.16
	N = 8.77	N = 8.72

The analysis and the IR spectrum confirm the identity of the product as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)benzidine.

In order to enhance the dispersibility of the above crude product (D), it was subjected to a glass bead milling. An 11.6 g sample was milled for 72 hours with 600 g glass beads and 300 ml acetone. The mill charge was filtered, and washed successively with alcohol, water and alcohol, and dried at 60°C. This product (E) is redder, more intense and stronger than Irgazin 3RLT and after 500 hours Fadeometer exposure showed good lightfastness in both masstone and tint.

4. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3'3"-dichlorobenzidine (V) NB 1924-16

A mixture of 10 g of phenanthrene-9,10-dicarboximide, 12.5 g phosphorus pentachloride, and 1700 parts of dry orthodichlorobenzene was heated with stirring at 120-130°C. under reduced pressure (18-30 mm), for a period of one hour and fifteen minutes. During this period, the formed phosphorus oxychloride along with orthodichlorobenzene was distilled (distillate volume ~ 300 ml).

At the end of this time, 10 g of dry pyridine was added and the solution was allowed to stir at this temperature for 5 minutes. To this solution was then added 5.2 g of dichlorobenzidine dissolved in 750 ml dry orthodichlorobenzene at 125°C. Immediately upon the addition of the dichlorobenzidine solution, a bright reddish-yellow solid began to precipitate out. The temperature was then raised to 140°C. and maintained for two hours. The solid was filtered from the hot mixture and washed successively with alcohol, water and alcohol, and dried at 60°C. A yield of 9.3 g was obtained.

For analytical purposes, the above solid was successively extracted with boiling nitrobenzene, dimethylformamide, water and dimethylformamide, washed and dried.

Analysis:	Found	Calc. for $C_{44}H_{24}N_4Cl_2O$
	N = 7.84	N = 7.87
	Cl = 10.1	Cl = 10.1

The analysis and the IR spectrum confirm the identity of the compound as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3'3"-dichlorobenzidine. In order to enhance the dispersibility of the above crude product (F), a 10 g sample and 800 g glass beads and 400 ml acetone were milled for 72 hours. The mill charge was filtered, washed with alcohol, water and alcohol, and dried at 60°C. This product (G) is redder, more intense and 40% stronger than Irgazin 3RLT and after 500 hours Fadeometer exposure showed lightfastness comparable to Irgazin 3RLT both in tint and masstone.

Shot Milling of Product

A 10 g sample of product (F) with 3000 g 1/8" steel shot and 500 ml acetone was milled for 72 hours. The mill charge was extracted with 1% sulfuric acid at about 90°C, filtered, and the presscake was washed free of acid and sulfate and subsequently dried at 60°C. This product (H) was superior in transparency to product (F), presumably as a result of the reduced particle size of the former, and showed a considerably greater two-tone effect in automotive metallics relative to Irgazin 3RLT. Both by rubout and in paint, the product was more intense, more transparent, and stronger (40%) than Irgazin 3RLT. It is approximately the same shade and strength as Flavanthrone. After 500 hours in the Fadeometer, the milled product (H) shows lightfastness comparable to Irgazin 3RLT both in tint and masstone.

5. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-1',5"-naphthalenediamine (VI) NB 1924-12

A mixture of 5 g phenanthrene-9,10-dicarboximide, 6.25 g of phosphorus pentachloride and 1300 ml of dry orthodichlorobenzene was heated with stirring at 120-130°C. under reduced pressure (18-30 mm) for a period of one hour and fifteen minutes. During this period, the formed phosphorus oxychloride along with orthodichlorobenzene was distilled (distillate volume ~ 250 ml).

At the end of this time, 2.5 g of dry pyridine was added and the solution was stirred at 120-130°C. for 5 minutes. To this solution was then added 1.6 g 1,5-diaminonaphthalene dissolved in 650 ml orthodichlorobenzene at 130°C. Immediately upon the addition of the diaminonaphthalene solution, a bright red solid began to precipitate out. The mixture was then stirred at this temperature for 2 hours, filtered hot, washed with alcohol, water and alcohol, and subsequently dried at 60°C. A yield of 2.25 g was obtained.

A mixture of 2.25 g of above solid and 300 ml dimethylformamide was heated rapidly to reflux and maintained at this temperature for 20 minutes. The solid was filtered hot, washed with alcohol, water and alcohol, and dried at 60°C. The recovery was 2.0 g.

Analysis:	Found	Calc. for $C_{42}H_{24}N_4O_2$
	N = 9.02	N = 9.09

The analysis and IR spectrum show that the above product is bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-1',5'-diaminonaphthalene. By rubout, this compound is similar in shade to Irgazin Orange RLT and after 500 hours Fadeometer exposure shows good lightfastness.

6. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-hydrazine (VII) NB 1924-21

A mixture of 10 g of phenanthrene-9,10-dicarboximide and 12.5 g phosphorus pentachloride and 2300 ml dry orthodichlorobenzene was heated with stirring under reduced pressure (18-35 mm) at 120-130°C., and maintained at this temperature for 1-1/4 hours. During this period, the formed phosphorus oxychloride along with some orthodichlorobenzene was distilled under reduced pressure (distillate volume $\sim$ 500 ml).

At the end of this time, 1.0 g of hydrazine was added to the above solution. Immediately upon addition of the hydrazine, a bright yellow solid began to precipitate from the reaction mixture. The mixture was stirred at 120-130°C. for 2 hours. After completion of the reaction, the mixture was filtered at 120-130°C. and the precipitate was washed successively with alcohol and water and alcohol and dried at 60°C. A yield of 4.75 g of a yellow solid was obtained.

The product is believed to be bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)hydrazine.

7. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3,6-diaminoacridine (VIII) NB 1924-22

Using the exact same conditions as the above, Example-6, but using 4.5 g of diaminoacridine as the diamine, a greenish-yellow pigment identified as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-3,6-diaminoacridine was obtained.

8. Preparation of Bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-4,4'-diaminodiphenyl ether (IX) NB 1924-23

By using 4.5 g of 4,4'-diaminodiphenyl ether as the diamine and the same conditions as Example 6, a green-yellow solid identified as bis(4,5,6,7-dibenzoisoindolin-1-one-3-ylidene)-4,4'-diaminodiphenyl ether was obtained.

B. Chelates NB 1924-2

A mixture of 6.0 g 9,10-diaminophenanthrene with 12.9 g 2,4-dihydroxy-3-formylquinoline and 1400 ml n-butyl alcohol was heated to reflux and maintained at this temperature for 5 hours. The resulting solid was filtered hot, washed with alcohol and dried at 60°C. The yield was 12.0 g.

A mixture of 10.0 g of the above solid with 5.0 g nickel acetate and 2 l dimethylformamide was heated to reflux temperature and maintained at this temperature for 4 hours. After 10 minutes, a bright orange solid precipitated from the solution. Upon completion of the reaction, the solid was filtered, washed successively with ethanol, water, ethanol and dried at 60°C. The yield was 9.0 g. For analytical purposes, the solid was extracted with boiling DMF.

Analysis:	Found	Calc. for $C_{34}H_{20}N_4O_4Ni$
	H, 3.37	H, 3.37
	N, 9.03	N, 9.03
	Ni, 9.84	Ni, 9.70

The analysis and IR spectrum thus confirm that the above solid is XII.

C. Miscellaneous Compounds

1. Carbon Analog of Isoindolinones (XIV)

In a porcelain dish, 5.0 g of quinaldine was added to 5.0 g powdered fused zinc chloride. The components were thoroughly mixed and heated to 130°C. to obtain a homogeneous mass. To this mixture was then added 10 g tetrachlorophthalimide in small portions (while maintaining the temperature between 160-180°C.) over a period of ten minutes. The reaction mass was cooled to room temperature, pulverized to a fine powder and put into 250 ml 96% sulfuric acid and heated at 100°C. until complete solution occurred. The solution was cooled to room temperature and poured into 2 l ice water. The solid was filtered and washed acid free and dried. Yield = 8.0 g. The product was recrystallized from dimethylformamide:

Analysis:	Found:	Calc. for $C_{18}H_8Cl_4N_2O$
	C, 53.62	C, 55.0
	H, 2.70	H, 1.78
	N, 6.69	N, 7.13
	Cl, 34.4	Cl, 36.1

The analysis suggests that the compound is 4,5,6,7-tetrachloroisoindolin-1-one-3-ethyleneylquinoline.

2. a. Perinone (XVI)

In a 500 ml flask, a mixture of 2.0 g 9,10-diaminophenanthrene and 3.0 g tetrachlorophthalic anhydride and 100 ml trichlorobenzene were rapidly heated to the boil, refluxed for 3 hours and cooled to room temperature. On cooling, red crystals precipitated out, which were filtered and washed with alcohol and dried.

Analysis:	Found	Calc. for $C_{22}H_8Cl_4N_2O$
	N, 6.07	N, 6.3

The analysis thus confirms that the above compound is perinone XVI.

2. b. Perinone (XVII)

In a 250 ml flask, a mixture of 1.0 g phenanthrene-9, 10-dicarboxylic anhydride, 0.5 g o-phenylene diamine and 100 ml acetic acid was rapidly heated to reflux and maintained at this temperature for one and a half hours. After approximately 15 minutes at this temperature, a reddish-yellow solid began to precipitate from solution. The solid was isolated by filtration at 117°C. and washed successively with water and ethanol and dried at 60°C.

Analysis:	Found	Calc. for $C_{22}H_{12}N_2O$
	N, 8.79	N, 8,70

The analysis thus confirms that the above compound is perinone (XVII).

2. c. Macrocycle (XX)

In a 250 ml flask, a mixture of 1.0 g 2,6-diamino-pyridine, 2.0 g 9,10-dicyanophenanthrene and 100 ml ethyleneglycol were rapidly heated to reflux and maintained at this temperature for 1 hour and subsequently cooled to 130°C., filtered and washed with ethyl alcohol and dried. The yield was 2.3 g.

In order to purify the above product, it was subjected to two extractions with boiling pyridine (100 ml), followed by a dimethyl-formamide extraction (50 ml). The recovery was 0.1 g.

Analysis:	Found	Calc. for $C_{42}H_{24}N_8$
	N, 15.41	N, 17.5

2. d. Macrocycle (XXI)

In a 250 ml flask, a mixture of 3.0 g 2,7-diamino-naphthalene, 4.0 g 9,10-dicyanophenanthrene and 100 ml ethylene glycol were rapidly heated to reflux and maintained at this temperature for 1 hour. At the end of this time, the mixture was cooled to 130°C. and filtered and washed with alcohol and dried at 60°C. The yield was 3.3 g.

For analytical purposes, the product was subjected to a nitro-benzene and dimethylformamide extraction.

Analysis:	Found	Calc. for $C_{52}H_{30}N_6$
	C, 84.28	C, 84.82
	H, 4.03	H, 4.00
	N, 11.46	N, 11.38

The analysis confirms the identity of the compound.

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