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

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Yellow Chromaphores

Period Covered December 15, 1969 - January 15, 1971

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: Yellow Chromaphores

PERIOD COVERED: December 15, 1969 - January 15, 1971

SUBMITTED BY: P. S. Dhaliwal Date Submitted: 3/11/71

APPROVED BY: E. E. Jaffe Date Released: 9/13/71

ABSTRACT

The nickel chelate of the Schiff base derived from 2,4-dihydroxy-3-formylquinoline and phenanthrene-9,10-diamine is an extremely insoluble, but relatively dull red-shade yellow pigment of outstanding lightfastness. After one year exposure in Florida at 5° South in both thermosetting acrylic enamel (TAE-3) and thermoplastic acrylic lacquer (927) paint systems, it shows superior lightfastness to Irgazin 3 RLT, Green Gold, Flavanthrone, and Anthrapyrimidine Yellow in both tint and metallics.

Attempts to find an economic method for the synthesis of phenanthrene-9,10-diamine have not been very successfull.

TABLE OF CONTENTS

TABLE OF CONTENTS CONT'D

TABLE OF CONTENTS CONT'D

YELLOW CHROMOPHORES

I. Introduction

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

II. Patent Status

A patent proposal covering the Schiff base chelates derived from phenanthrene-9,10-diamine and its derivatives has been written and will be filed shortly.

III. Summary and Conclusions

The nickel chelate of the Schiff base derived from 2,4-dihydroxy-3-formylquinoline and phenanthrene-9,10-diamine is an extremely insoluble, but relatively dull red-shade yellow pigment of outstanding lightfastness. After one year exposure in Florida at 5° South in both thermosetting acrylic enamel (TAE-3) and thermoplastic acrylic lacquer (927) paint systems, it shows superior lightfastness to Irgazin 3 RLT, Green Gold, Flavanthrone, and Anthrapyrimidine Yellow in both tint and metallics.

The corresponding chelates derived from 3,6-dichlorophenanthrene-9,10-diamine and 3,6-dibromophenanthrene-9,10-diamine, which are extremely insoluble red-shade yellow pigments, also show excellent lightfastness after 3 months Florida exposure at 5° South in thermoplastic acrylic lacquer (927).

Attempts to find other orthodiamines to fulfill the function of phenanthrene-9,10-diamine in order to obtain a greener color and lower manufacturing costs have been unsuccessful.

Attempts to find an economic method for the synthesis of phenanthrene-9,10-diamine have not been very successfull. This problem deserves addtional attention.

IV. Discussion

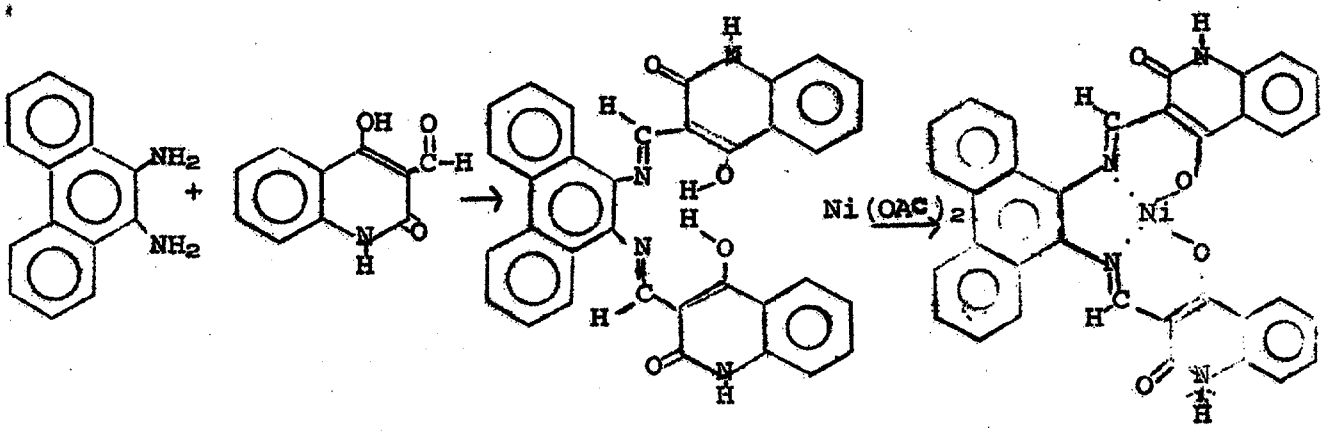
As a continuation of the program to study the factors which determine the degree of lightfastness of pigments, a number of chelates were prepared in which steric protection of azomethine linkages was incorporated. Previously (1) this hypothesis of steric protection of azomethine linkages was invoked in isoindolinone type pigments. The improvement in lightfastness due to such effects in isoindolinone pigments was quite pronounced.

In view of the good outdoor durability of the phenanthrene isoindolinone pigments (1), it was decided to incorporate the phenanthrene moiety into a chelate in which the protective steric effect would be utilized. To test this hypothesis, the chelate (II)

(1) P. S. Dhaliwal, KN Report #70-6

was prepared as indicated below:

Phenanthrenediamine was reacted with 2,4-dihydroxy-3-formylquinoline to yield the Schiff base (I) which was subsequently reacted with nickel acetate to yield the chelate (II)



I II

This chelate is an extremely insoluble, but a relatively dull red-shade yellow pigment of outstanding lightfastness. After one year exposure in Florida, in both thermosetting acrylic enamel (TAE-3) and thermoplastic acrylic lacquer (927) paint systems, it shows better lightfastness than Irgazin 3 RLT, Green Gold, Flavanthrone, and Anthrapyrimidine Yellow both in tint and metallics.

This chelate has all the desirable qualities of a "Monastral" Yellow", except that its color is redder and duller than desirable. In addition, the projected manufacturing costs are too high. In order to offset these disadvantages, a program was started along the lines outlined below, to obtain chelates which could be manufactured at a lower cost and which might be greener in color, but at the same time maintain all the desirable attributes of chelate (II). In order to achieve these desirable goals, the following methods were utilized:

(1) Introduce electronegative substituents on the phenanthrene-diamine moiety in order to effect an hypsochromic shift in the absorption spectrum of chelate (II).

(2) Utilize other ortho-hydroxy aromatic or aliphatic aldehydes to lower manufacturing costs and cause a hypsochromic shift in the absorption.

(3) Incorporate other sterically hindered ortho-diamines into chelates which will have lightfastness comparable to that of chelate II, but lower manufacturing costs and a greener color.

(4) Use other divalent metals.

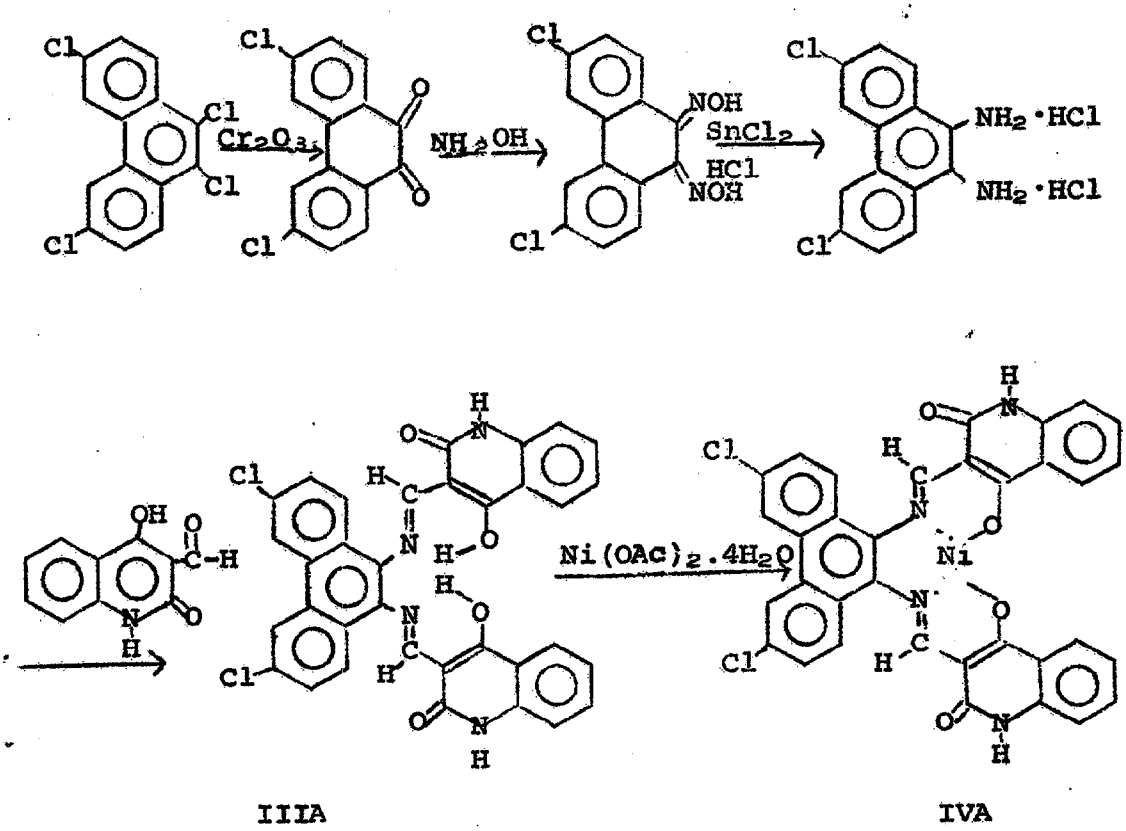
(5) Find an economic method for the manufacture of phenanthrene-9,10-diamine.

Method I Chelates Derived From Substituted Phenanthrene-9,10-diamines.

In an effort to effect an hypsochromic shift in the absorption spectrum of chelate II, and possibly to lower the manufacturing costs, the 3,6-dibromo and 3,6-dichloro derivatives of phenanthrene-9,10-diamine were prepared and incorporated into chelates. Both of these chelates (IVA and IVB) are greener than chelate II (X=H), and are red-shade yellows of extreme insolubility. After 3 months Florida exposure in thermoplastic acrylic lacquer (927) paint system, they show lightfastness comparable to the unsubstituted chelate II. The dihalophenanthrenediamines and their respective chelates were made as follows:

1. Chelate derived from 3,6 dichlorophenanthrene-9,10 diamine(IVA)

Tetrachlorophenanthrene (2) was oxidized to 3,6-dichlorophenanthrenequinone with chromium trioxide, followed by reaction with hydroxylamine to yield the dioxime, which was then reduced with stannous chloride to the corresponding diamine dihydrochloride. This diamine dihydrochloride was then reacted with 2,4-dihydroxy-3-formylquinoline to yield the schiff base (IIIA) which was converted to the chelate (IVA) using nickel acetate.

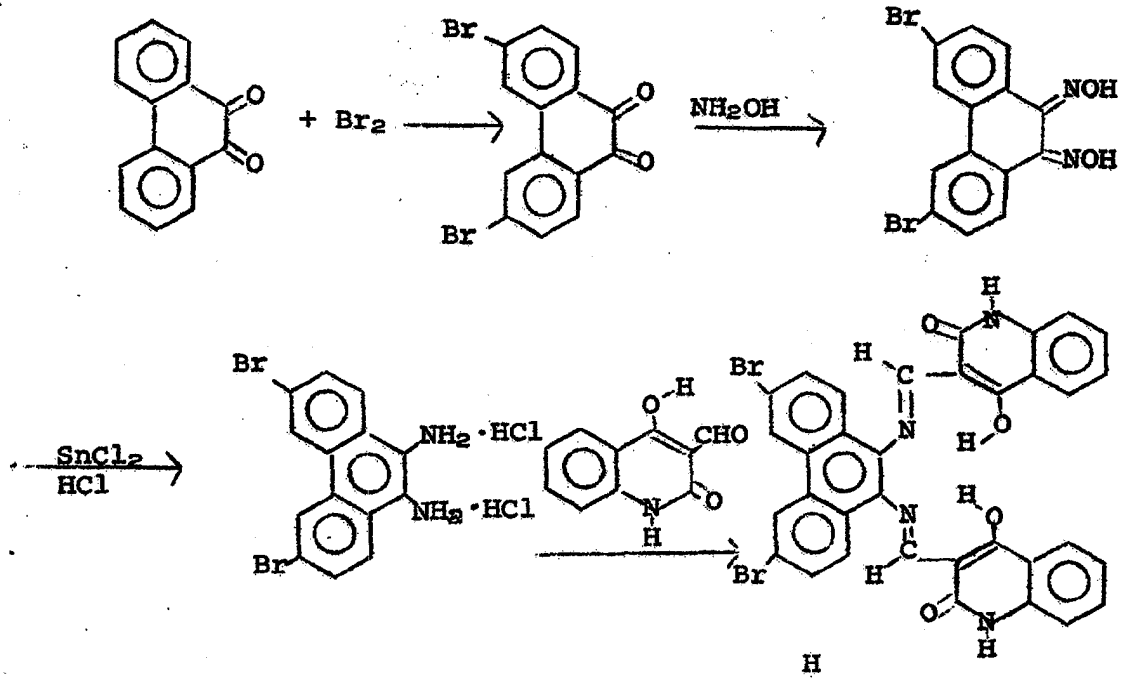


IIIA IVA

(2) C.D. Weiss, Helvetica Chimica Acta. 51, 1572 (1968)

2. Chelate Derived from 3,6-dibromophenanthrene-9,10-diamine(IVB)

Phenanthrenequinone (3) was brominated to yield 3,6 dibromophenanthrenequinone, followed by reaction with hydroxylamine to yield the dioxime, which was reduced with stannous chloride to the corresponding diamine dihydrochloride. This diamine dihydrochloride was reacted with 2,4-dihydroxy-3-formylquinoline to yield the schiff base III B, which was subsequently converted to the chelate (IV B) using nickel acetate.



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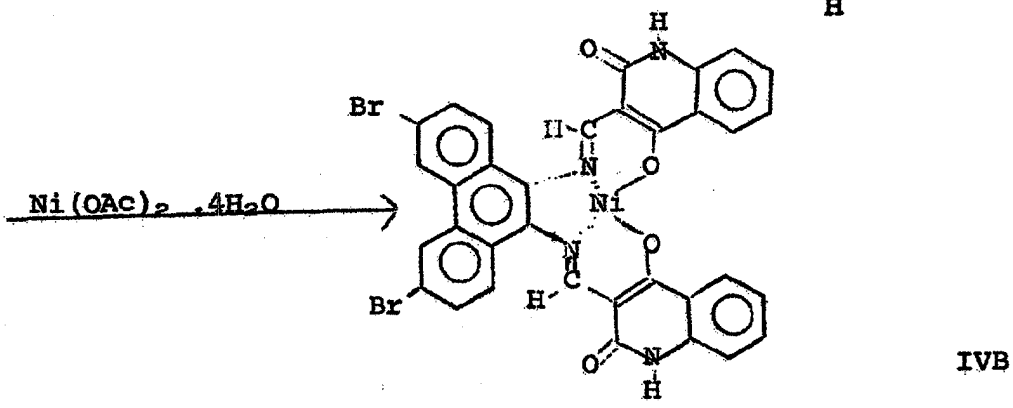


IVB

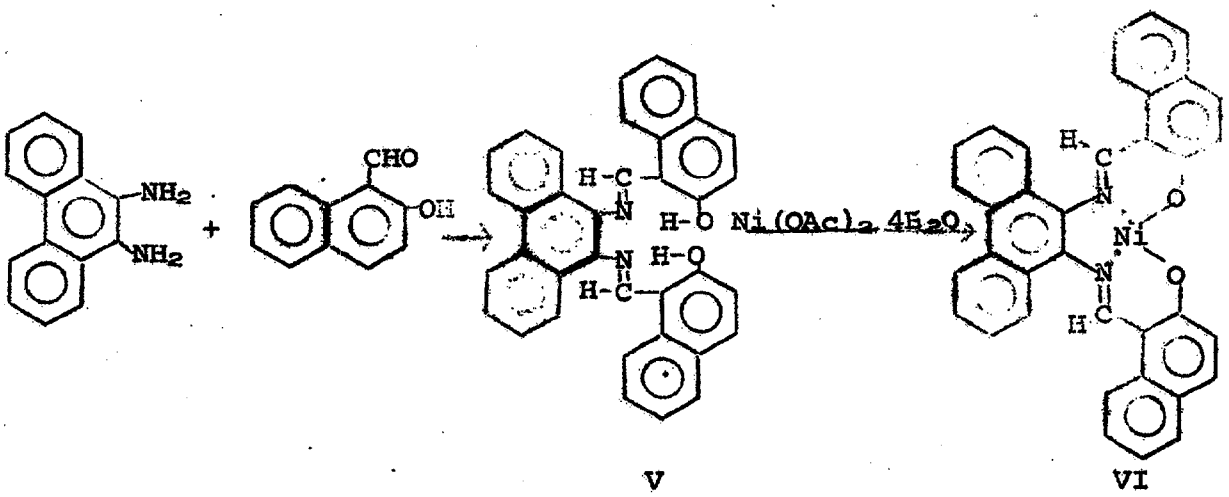
(3) Courtot and Knonstein, Chim. industrie 45,72(1941); Chemoc Abstr. 37,2729 (1943)

Method II Chelates Derived From Phenanthrene-9,10-Diamine and Other Ortho Hydroxy Aromatic Aldehydes.

The second method used to effect an hypsochromic shift in the absorption spectrum of the chelate II, was to use other o-hydroxy-aromatic and aliphatic aldehydes.

(1) Reaction with 2-hydroxy-1-naphthaldehyde

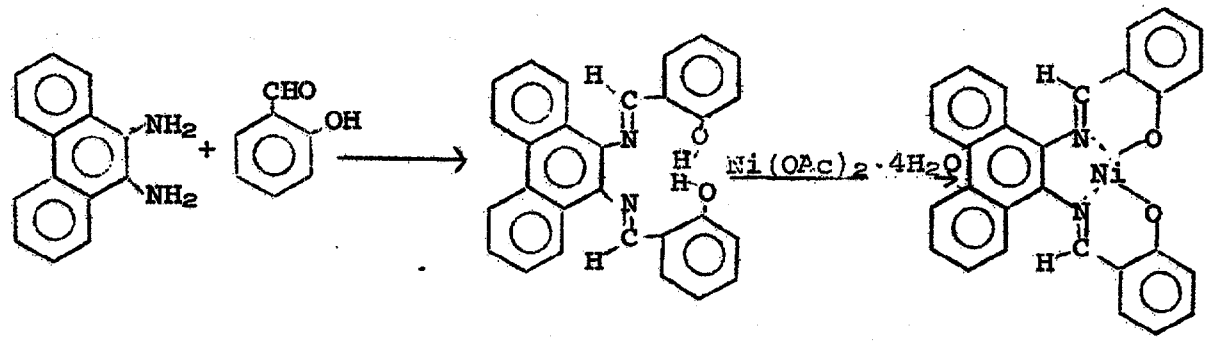
Phenanthrenediamine was reacted with 2-hydroxy-1-naphthaldehyde to yield the schiff base (V), which was converted to the chelate VI, with nickel acetate.



V VI

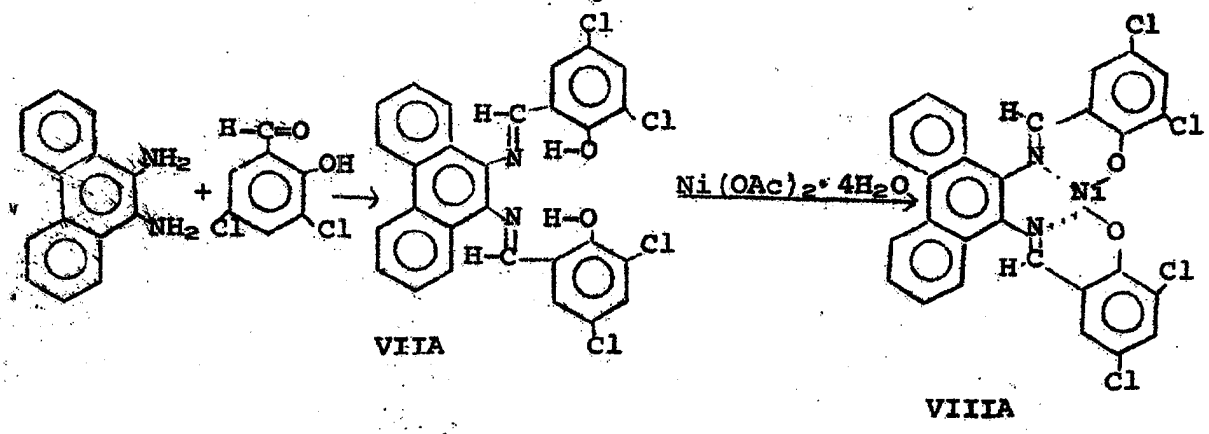
(2) Reaction with salicylaldehyde and derivatives

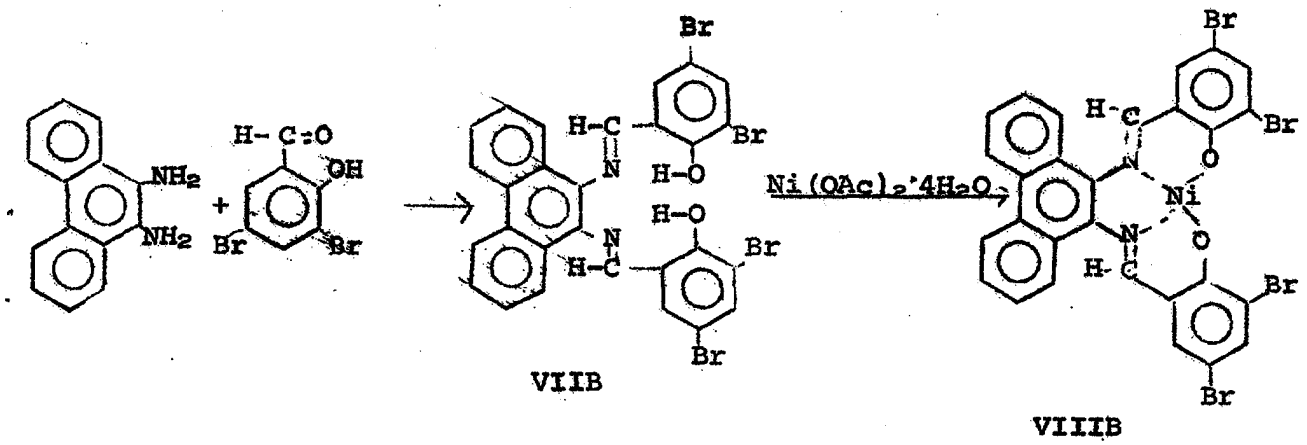
Salicylaldehyde was reacted with phenanthrene-9,10-diamine to yield the schiff base VII, which was subsequently treated with nickel acetate to yield the chelate VIII.



VII VIII

In order to obtain a more insoluble chelate, phenanthrene-9,10-diamine was reacted with both 3,5-dichlorosalicylaldehyde and 3,5-dibromosalicylaldehyde to yield the schiff bases VII A and VII B respectively, which were subsequently treated with nickel acetate to yield the corresponding chelates VIII A and VIII B.





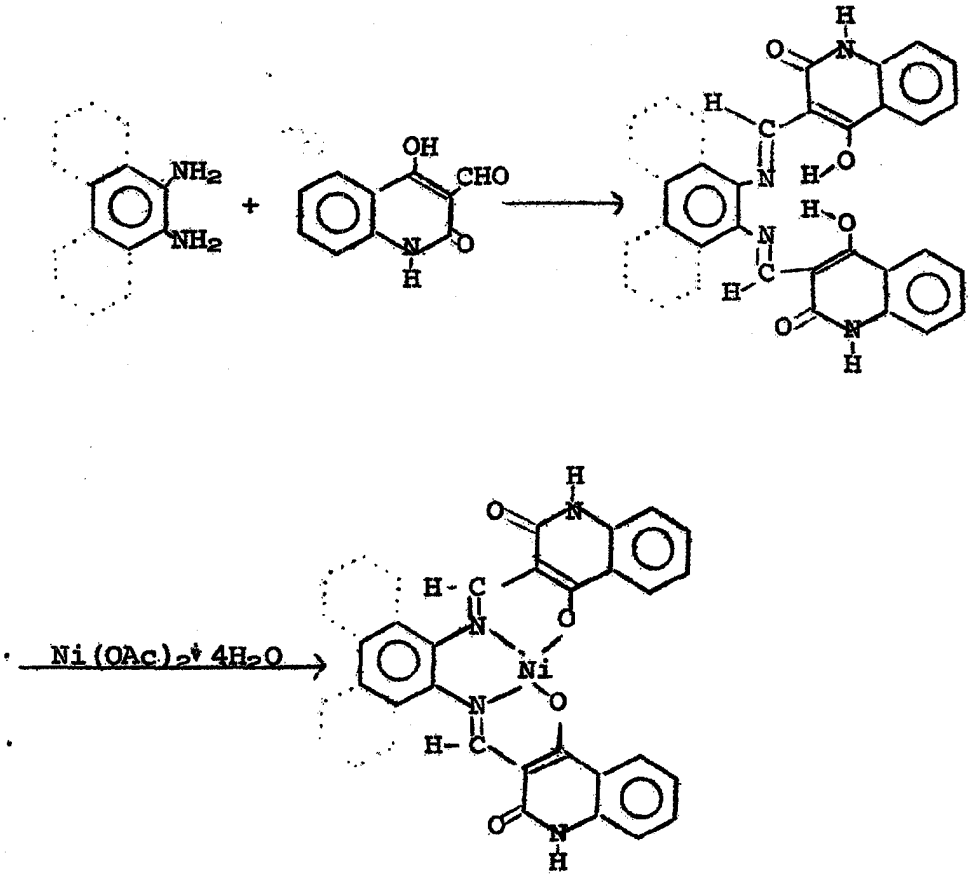
In the above chelates, when electronegative substituents are introduced on the phenanthrenediamine moiety, as in chelates IV A and IV B, there is a marked hypsochromic shift in the absorption relative to the unsubstituted chelate II. However, there is no noticeable difference in lightfastness. When 2,4-dihydroxy-3-formylquinoline in chelate II, is substituted by other ortho hydroxy aromatic aldehydes, such as 2-hydroxy-1-naphthaldehyde, salicylaldehyde, 3,5-dichlorosalicylaldehyde, and 3,5-dibromosalicylaldehyde, there is a significant bathochromic shift in the absorption and a decrease in lightfastness relative to chelate II. The reasons for this decrease in lightfastness are not clear, but are probably due to the fact that there is no isolated double bond in these aldehydes similar to the one that is present between the 3 and 4 positions of 2,4-dihydroxy-3-formylquinoline. The presence of this double bond in the dihydroxyquinoline moiety is believed to allow the formation of a 14 electron pseudo aromatic system in chelate II, which may be a significant factor in its photochemical stability.

In an effort to determine the effect of other aldehydes on the color and lightfastness of the analogous chelates, the following aldehydes will be used: tetrachlorosalicylaldehyde, 9-hydroxy-10 phenanthrenealdehyde, 3-hydroxy-4-formyl-1,8-naphthalimide, 1-formyl-2-hydroxy-3-carboxanilide-naphthalene and 3-hydroxy-1-butraldehyde.

Method III - Chelates Derived from other Ortho Aromatic Diamines and 2,4-dihydroxy-3-formylquinoline

The third method of achieving a greener color, and possibly a lower manufacture cost while maintaining the same degree of lightfastness as the phenanthrenediamine chelate (II), was to incorporate other aromatic ortho-diamines into chelates of general structure (IX).

In view of this method, a number of aromatic ortho-diamines (heterocyclic and carbocyclic) with various substituents were reacted with 2,4-dihydroxy-3-formylquinoline to yield yellow Schiff bases. These bases were subsequently chelated with nickel acetate to yield highly insoluble yellow chelates of good lightfastness. A representative reaction, to form chelates of the general structure[4] (IX), is shown below. In table I are listed the diamines and aldehydes along with the color of chelate and relative lightfastness.



IX

4 E.E.Jaffe, U.S.P. 3,132,140

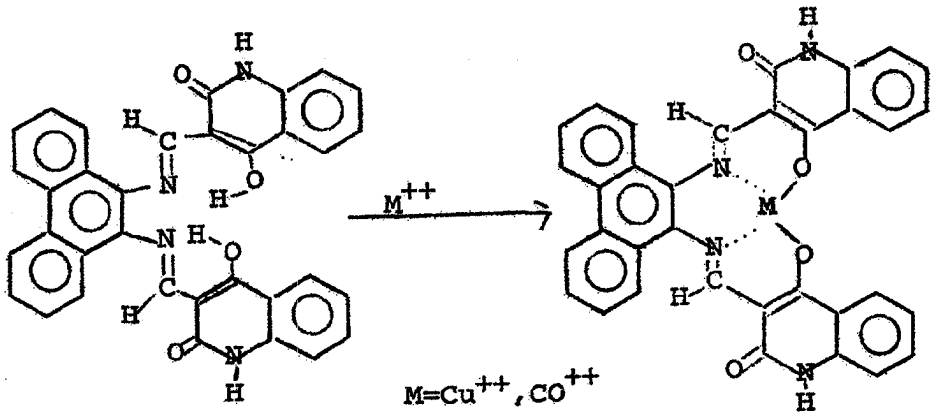
TABLE I

Chelates derived from 2,4-dihydroxy-3-formylquinoline and aromatic-orthodiamines

DIAMINES	CHELATE COLOR	LIGHTFASTNESS
1,2-Diaminonaphthalene	yellow	fair
2,3-Diaminonaphthalene	yellow	fair
1,8-Diaminonaphthalene		fair
4,5-Diamino-2,6-dihydroxypyrimidine	greenish yellow	poor
3,6-Dimethoxy-o-phenylendiamine	greenish yellow	fair
ortho-phenylenediamine	yellow	good
5,6-Diamino-1,3-dimethyluracil	greenish yellow	fair
2,3-Diaminoquinoxline	maroon	good
Diaminomaleonitrile	maroon	good
3,6-Dichloro-o-phenylenediamine	greenish yellow	fair
3,4,5,6-Tetramethyl-o-phenylenediamine	greenish yellow	fair

Phenanthrene-9,10-diamine chelates from other divalent metals.

The Schiff base derived from phenanthrenediamine and 2,4-dihydroxy-3-formylquinoline was reacted with cobaltous acetate as well as cupric acetate to yield chelates of the following structure. There was no significant hypsochromic shift in the absorption of the chelate.



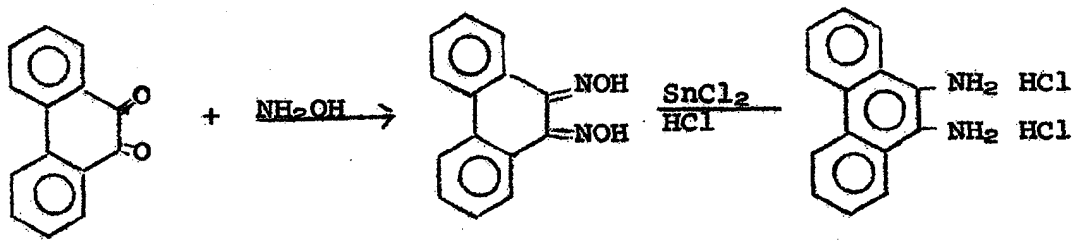
The lightfastness of the cobalt and copper chelates were slightly inferior to the nickel chelate II. Attempts to form a zinc chelate were unsuccessful.

Attempts to find an economic method for the manufacture of Phenanthrene-9,10-diamine.

In an effort to find an economic synthesis for the production of phenanthrene-9,10-diamine, a number of routes were investigated, a few of them are listed below.

Attempts were made to improve the quality and yield of the diamine obtained from phenanthrenequinone. This was primarily achieved by attacking the problem along the following lines.

(1) The literature method for the synthesis of phenanthrenediamine[5] involves the reaction of phenanthrenequinone with hydroxylamine to yield the dioxime, followed by reduction with stannous chloride in hydrochloric acid .

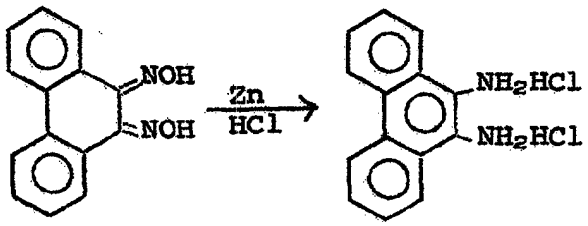


This is an excellent method in terms of yield, but the product always contains tin in varying amounts, depending on the reaction conditions. Attempts to change reaction conditions so as to minimize the tin content, but at the same time maintain high purity and yields resulted in failure, since high yields were always accompanied by high tin content and high purity diamine was obtained in low yield. The problem with the high yield diamine product, containing a considerable quantity of tin, was that in the reaction with 2,4-dihydroxy-3-formylquinoline, the yields of the Schiff base (I) was low and consequently the chelate yield was even lower. When the high purity but low yield diamine was used, the yield of the Schiff base and chelate were higher, but the overall yield from phenanthrenequinone to the chelate was still too low. Last but not least, the most serious drawback of this synthesis is that the cost of stannous chloride is $1.53/lb. and each pound of phenanthrenequinone uses 5 lbs. of (theoretical = 3 lbs.) stannous chloride.

In view of this economic factor, it does not appear economically feasible to produce phenanthrenediamine by this method.

(2) In an effort to avoid the expensive reducing agent stannous chloride, it was decided to investigate other reducing agents in order to produce phenanthrenediamine at lower cost. A few which were successful are listed below.

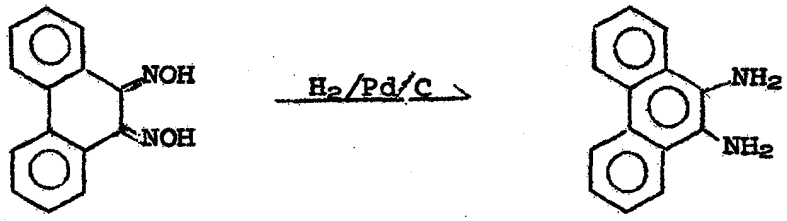
(a) The dioxime was found to be reduced by zinc (.20¢ lb.) and hydrochloric acid.



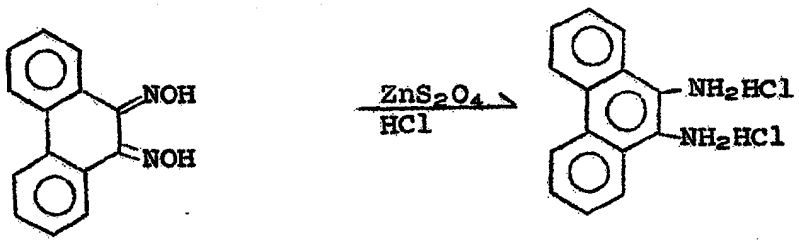
5 R. Pschor, Ber., 35, 2738, 1902.

This is an excellent method for reduction of the dioxime in terms of economics (Zn vs. $SnCl_2$) except that the yields and purity of product are not very good. The crude yields vary between 60 - 80% but the yields of the Schiff base and chelate from this diamine are low.

(b) The dioxime was also found to be reduced with hydrogen and palladium on charcoal; here the quality of diamine was high and the yields in the 50% range. The subsequent yields of the Schiff base and chelate were good. This method deserves additional investigation.

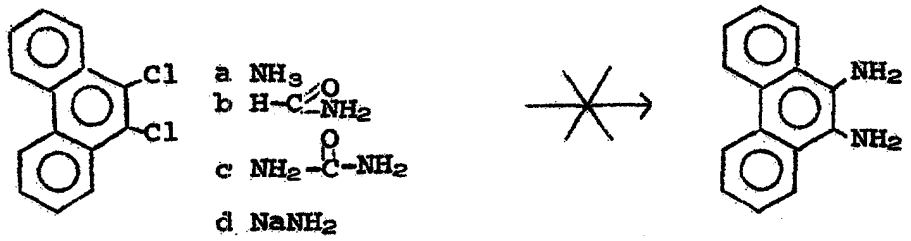


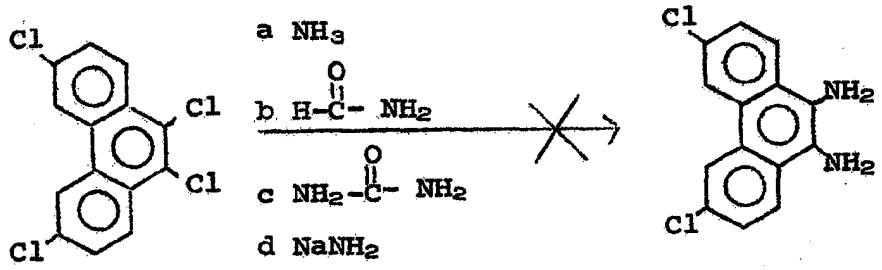
(c) Another reducing agent which was found to be effective in reducing the dioxime to the diamine was zinc hydrosulfite.



This reducing agent, which gives yields in the 60% range, appears to be the most promising in terms of economics and chemical purity of product. The yield of the Schiff base and chelate are good. Unfortunately the overall yields from the phenanthrenequinone to the chelate are not economically attractive. Improvement in yield is highly desirable.

In an effort to find an alternative method for the synthesis of phenanthrenediamine, one which will not involve the phenanthrene-quinone, it was decided to react 9,10-dihalophenanthrene with ammonia and its derivatives. All attempts to synthesize 9,10-dibromo-phenanthrene economically resulted in failure, and in view of this, efforts were made to react 9,10-dichlorophenanthrene and 3,6,9,10-tetrachlorophenanthrene with ammonia and its derivatives, in an effort to prepare phenanthrene-9,10-diamine and 3,6-dichloro-phenanthrene-9,10-diamine. Unfortunately all attempts to prepare the above diamines by these routes resulted in failure.





CONCLUSION

All attempts to obtain a chelate, which is greener in color, lower in manufacturing costs and which shows comparable lightfastness to chelate (II) have been unsuccessful. All attempts to establish the factors which determine the lightfastness of chelate (II) have not been very successful. Work in this area is still continuing.

Experimental

Phenanthrenediamine Chelates 1909-15D

Chelate II

a. Schiff base formation

Ten grams phenanthrene-9,10-diamine and 21.5g 2,4-dihydroxy-3-formylquinoline were suspended in 1800 ml butanol and heated to the boil and maintained under reflux for 5 hours. The slurry was filtered hot and the presscake washed with alcohol and dried. The yield of the Schiff base (I) was 22.5g.

b. Chelation

Fifteen grams of the above Schiff base (I), 10.0g of nickel acetate and 1800 ml of dimethylformamide were heated to reflux and maintained at reflux for four hours. The hot slurry was filtered, and the presscake washed successively with dimethylformamide, alcohol, water and alcohol and dried.The yield of the chelate(II) was 14.6g.

c. DMF Extraction

The above chelate (II) was extracted with 1,000 ml. of boiling dimethylformamide for 20 minutes, filtered hot, washed, and dried. The yield was 13.4g

Analysis:

Calculated for $C_{34}H_{20}N_4O_4Ni$	Found:
Ni = 9.71%	Ni = 9.84%
N = 9.22%	N = 9.03%
C = 67.21%	C = 66.24%
H = 3.29%	H = 3.37%

Method I: Chelates derived from substituted phenanthrenediamines.

A. Chelate derived from 3,6-dichlorophenanthrene-9,10-diamine(IVA)

a. Preparation of 3,6-dichlorophenanthrene-9,10-diamine

Forty five grams of 3,6-dichlorophenanthrenequinone, 62.5g of barium carbonate, 56.5g of hydroxylaminehydrochloride and 4 liters ethyl alcohol were heated at reflux for five hours. The solid was filtered hot and the presscake washed with alcohol. The filterate was concentrated to one half its original volume by distillation, cooled to 70°C and 260 g stannous chloride dissolved in 1200 ml concentrated hydrochloric acid, added over a period of 30 minutes while maintaining the temperature below 80°C. The slurry was stirred at 70-80°C for one-half hour, cooled to room temperature, filtered, and washed first with concentrated hydrochloric acid and then with water and dried. The yield was 38.5g

b. Formation of Schiff base

Thirty eight and a half grams of the above diamine dihydrochloride, 46.8g 2,4-dihydroxy-3-formylquinoline and 4000 ml of butanol were heated at reflux for five hours. The slurry was filtered, and the presscake washed with ethanol and dried. The yield was 60.0g.

c. Chelation

Thirty grams of the above Schiff base (IIIA), 20.0gnickel acetate and 3 liters dimethylformamide were heated at reflux for four hours. The slurry was filtered hot, and the presscake washed and dried. The yield of the chelate (IVA) was 24.5g.

d. DMF Extraction

The above chelate, (IVA) was pulverized and extracted for 25 minutes with 1500 ml boiling dimethylformamide. filtered hot, washed with dimethylformamide, alcohol, water, and alcohol. The yield was 23.0g.

Analysis:

Calculated for $C_{34}H_{18}Cl_2N_4O_4Ni$	Found
Ni = 8.60	Ni = 8.89
N = 8.29	N = 8.11,8.06
C = 61.48	C = 58.19,57.97
H = 2.67	H = 2.72,2.65
Cl = 10.51	Cl = 10.0

B. Chelate derived from 3,6-dibromophenanthrene-9,10-diamine (IVB) 1953-3D

a. Preparation of 3,6-dibromophenanthrene-9,10-diamine

Forty six grams 3,6-dibromophenanthrenequinone, 56.5g hydroxylamine hydrochloride, 62.5g barium carbonate and 2.6 liters ethanol were heated at reflux for five hours. The solid was filtered hot and the presscake washed with alcohol. The filterate was heated to 70°C and 250 g stannous chloride dissolved in 1 liter of concentrated hydrochloric acid, was added over a period of 20 minutes, while maintaining the temperature below 80°C. The slurry was cooled to room temperature and filtered, washed with hydrochloric acid and water and dried. The yield was 52.0g.

b. Formation of Schiff base

Twenty six grams of the above diamine dihydrochloride, 31.2g. 2,4-dihydroxy-3-formylquinoline and 3 l butanol were heated at reflux for five hours. The slurry was filtered hot, and the presscake washed with alcohol and dried. The yield was 40.0g.

c. Chelation

Forty grams of the above Schiff base IIIB, 20.8g nickel acetate and 3.5 l dimethylformamide were heated at reflux for 4 hours. The slurry was filtered hot, washed and dried. The yield of chelate IVB was 23g.

d. DMF Extraction

The above chelate IVB was pulverized and extracted with 1700 ml of boiling dimethylformamide. The slurry was filtered hot, and washed successively with dimethylformamide, alcohol, water and alcohol and dried at 60°C. The yield was 21.5g.

Analysis:

Calculated for $C_{34}H_{18}Br_2N_4O_4Ni$	Found
Ni = 7.59	Ni = 7.43,7.47
N = 7.33	N = 7.14,7.19
C = 53.40	C = 52.07,51.96
H = 2.35	H = 2.48,2.61
Br = 20.95	Br = 18.9

Method II Reaction of phenanthrene-9,10-diamine with other aromatic o-hydroxy aldehydes and chelates of the Schiff bases derived therefrom.

1. Reaction with 2-hydroxy-1-naphthaldehyde; 1924-50 Chelate VI

a. Schiff base formation

One gram phenanthrene-9,10-diamine, 2.2g,2-hydroxy-1-naphthaldehyde and a mixture of 200 ml ethanol and 200 ml butanol were heated at reflux for 5 hours. The slurry was filtered hot and washed with a small volume of ethanol. The yield was 1.27g.

Analysis: Calculated for $C_{36}H_{24}N_2O_2$	Found
C = 83.72	C = 82.64
H = 4.65	H = 4.59
N = 5.42	N = 5.84

b. Chelation

1.0g of the above schiff base V, 0.6g nickel acetate and 100 ml dimethylformamide were heated at reflux for four hours. The slurry was filtered hot, washed with alcohol, water and alcohol and subsequently dried at 60°C. The yield of chelate VI was 0.99g.

Analysis Calculated for $C_{36}H_{22}N_2O_2Ni$	Found
Ni = 10.14	Ni = 6.03
N = 4.9	N = 5.37
C = 75.2	C = 74.06
H = 3.84	H = 4.44

2. Reaction of Salicylaldehyde and Derivatives 1924-27 Chelate VIII

Five ml salicylaldehyde, 1g. nickel acetate, and 100 ml dimethylformamide were heated at reflux for one hour. After one hour, 1g. phenanthrene-9,10-diamine dihydrochloride was added and reflux continued for an additional 3 hours. At the end of this period the reaction mixture was cooled to room temperature, filtered, washed with alcohol and dried at 60°C. The yield of chelate VIII was 0.8g.

Analysis Calculated for $C_{28}H_{18}N_2O_2Ni$	Found
Ni = 12.29	Ni = 7.26
N = 5.93	N = 5.52

3. Reaction of 3,5-dichlorosalicylaldehyde 1945-52E Chelate VIIIA

Ten grams 3,5-dichlorosalicylaldehyde, 6.0g nickel acetate and 200 ml dimethylformamide were heated at reflux for 2 hours. At the end of this period 5.0g phenanthrene-9,10-diamine dihydrochloride was added and reflux continued for 2 more hours. The hot slurry was filtered, and washed with dimethylformamide, alcohol, water and alcohol and dried at 60°C. The yield was : 3.8g

Analysis Calculated For $C_{28}H_{14}N_2O_2Cl_4Ni$	Found
Ni = 9.50	Ni = 7.83
N = 4.59	N = 4.74,4.75
C = 55.08	C = 58.59,58.26
H = 2.29	H = 2.71
Cl = 23.27	Cl = 19.5

4. Reaction of 3,5-dibromosalicylaldehyde: 1945-52F Chelate VIIIB

Six grams nickel acetate, 10g, 3,5 dibromosalicylaldehyde and 200 ml dimethylformamide were refluxed for two hours. At the end of this time 5g phenanthrene-9,10-diamine dihydrochloride was added, and the reflux continued for an additional 2 hours. The hot slurry was filtered, washed with alcohol, water, and alcohol and dried at 60°C. The yield was: 5.4g.

Analysis: Calculated For $C_{28}H_{14}N_2O_2Br_4Ni$	Found
Ni = 7.35	Ni = 7.01
N = 3.55	N = 3.65
C = 42.75	C = 44.61
H = 1.77	H = 1.95
Br = 40.60	Br = 37.3

Method III Reaction of other aromatic ortho-diamines with 2,4-dihydroxy-3-formylquinoline and subsequent chelation of the Schiff bases derived therefrom

1. Reaction with 1,2-diaminonaphthalene: 1924-30

a. Schiff base formation

Four grams 1,2-diaminonaphthalene, 12 g, 2,4-dihydroxy-3-formylquinoline and 600 ml butanol were heated at reflux for five hours. The slurry was filtered hot, and the presscake washed with alcohol and dried at 60°C. The yield was 10.7g.

b. Chelation

One and two tenth grams nickel acetate, 2g of the above Schiff base and 150 ml dimethylformamide were heated at reflux for four hours. The hot slurry was filtered and the presscake washed successively with alcohol, water and alcohol and dried at 60°C. The yield was 1.6g.

c. DMF Extraction

The above chelate (1.6g) and dimethylformamide (100 ml) were heated to reflux and maintained at reflux for 20 minutes. The hot slurry was filtered, and washed with alcohol, water and alcohol and dried at 60°C. The yield was 1.1g.

Analysis Calculated for: $C_{30}H_{18}N_4O_4Ni$	Found
Ni = 10.43	Ni = 6.82
N = 10.06	N = 9.84,9.81
C = 64.38	C = 62.20,61.98
H = 3.23	H = 3.69,3.52

d. Copper Chelate:

One and one tenthgrams cupric acetate, 2g of the above Schiff base and dimethylformamide were heated at reflux for four hours. The hot slurry was filtered, and washed successively with alcohol, water and alcohol and dried at 60°C. The yield was 1.8g.

Analysis Calculated for: $C_{30}H_{18}N_4O_4Cu$	Found
N = 9.99	N = 9.81
C = 64.13	C = 61.98
H = 3.20	H = 3.53

2. Reaction with 2,3-diaminonaphthalene (1924-48)

a. Schiff base formation

Two gram 2,3-diaminonaphthalene, 5.6g 2,4-dihydroxy-3-formylquinoline and 225 ml butanol were maintained at reflux for five hours. The hot slurry was filtered, and the presscake washed with ethanol, and dried at 60°C. The yield was 6.5g.

b. Chelation

One gram of the above Schiff base, 0.65g nickel acetate, and dimethylformamide were heated at reflux for four hours. At the end of this time, the hot slurry was filtered, and the presscake washed with ethanol, water and ethanol and dried at 60°C. The yield was 0.48g.

Analysis Calculated for $C_{30}H_{18}N_4O_4Ni$	Found
Ni = 10.43	Ni = 9.33
N = 10.06	N = 9.22, 9.27
C = 64.38	C = 61.59
H = 3.23	H = 3.51

3. Reaction with 4,5-diamino-2,6-dihydroxypyrimidine 1924-34

a. Schiff base formation

Two hundred ml butanol, 2g, 4,5-diamino-2,6-dihydroxy-pyrimidine dihydrochloride, 5g, 2,4-dihydroxy-3-formylquinoline and 0.3g sodium acetate were heated at reflux for five hours. The hot slurry was filtered, and the presscake washed with alcohol and dried at 60°C. The yield was 4.1g.

b. Nickel Chelate

Two grams of the above Schiff base, 1.2g, nickel acetate, and 250 ml dimethylformamide were heated to reflux for four hours. At the end of this period, the hot slurry was filtered, and the presscake washed with alcohol, water and alcohol, but no solid remained on top of the filter paper. In the filterate, there was some solid.

Analysis Calculated for $C_{26}H_{14}N_6O_6Ni$	Found
N = 17.77	N = 17.05
C = 53.33	C = 52.57
H = 2.59	H = 4.03

4. Reaction with 3,6-dimethoxy-o-phenylenediamine (1924-47)

A. Synthesis of 3,6-dimethoxy-o-phenelenediamine:

a. Nitration of 1,4-dimethoxybenzene

To a solution of 50g 1,4-dimethoxybenzene in 250 ml acetic acid, 250 ml of 70% nitric was added over a period of 20 minutes. After completion of the addition, the reaction mixture was stirred at 30-35°C for 40 minutes. The slurry was filtered, and the presscake washed with water, and dried at room temperature. The solid was recrystallized from 2200 ml ethanol. The yield was 39.2g.

b. Reduction of the nitro groups.

A mixture of 15.2g 1,4-dimethoxy-2,3-dinitrobenzene, 1.5g palladium on charcoal (10%) and 100 ml ethanol were hydrogenated under a pressure of 55 lbs. of hydrogen at room temperature for four hours. At the end of this period, the slurry was filtered into a flask containing hydrochloric acid. Upon contact of the filterate with the hydrochloric acid, a white solid formed. The solid slurry was filtered, and the presscake washed with ethanol and dried at room temperature. The yield was 5.3g.

B. Formation of Schiff base:

Two grams 3,6-dimethoxy-o-phenylenediaminedihydrochloride, 3.6g 2,4-dihydroxy-3-formylquinoline, 1g sodium acetate and 200 ml

butanol were heated at reflux for four hours. The hot slurry was filtered, and the presscake washed with ethanol and dried at 60°C. The yield was 2.8g.

c. Chelation

One and a half grams of the above Schiff base, 0.8g, nickel acetate, and 200 ml dimethylformamide were heated at reflux for four hours. The hot slurry was filtered, and the presscake washed with ethanol, water and ethanol and dried at 60°C. The yield was 1.26g.

Analysis Calculated for $C_{28}H_{20}N_4O_6Ni$.	Found
Ni = 10.24	Ni = 9.19
N = 9.89	N = 9.87,10.02
C = 59.36	C = 57.99
H = 3.53	H = 3.71

5. Reaction with 5,6-Diamino-1,3-dimethyluracil (1924-49)

a. Schiff base formation

Three grams 5,6-Diamino-1,3-dimethyluracil, 7g. 2,4-dihydroxy-3-formylquinoline, and 250 ml butanol were heated at reflux for four hours. The hot slurry was then filtered, and the presscake washed with ethanol, water and ethanol and dried at 60°C. The yield was 5.8g.

b. Chelation

1.00g of the above Schiff base, 0.55g nickel acetate and 300 ml DMF were heated at reflux for four hours. The slurry was filtered hot, and the presscake washed with alcohol, water and alcohol and dried at 60°C. The yield was 0.19g.

Analysis Calculated for $C_{26}H_{18}N_6O_6Ni$.	Found
Ni = 10.21	Ni = 8.84
N = 14.78	N = 11.83,11.96
C = 54.93	C = 42.94
H = 3.16	H = 3.90

6. Reaction with 2,3-Diaminoquinoxaline (1924-39)

a. Schiff base formation

One gram 2,3-Diaminoquinoxaline 2.8g 2,4-dihydroxy-3-formyl-quinoline and 200 ml butanol were heated at reflux for five hours. The hot slurry was filtered, washed with ethanol and dried at 60°C. The yield was 1.47g.

b. Chelation

The above Schiff base(1.0g), nickel acetate(0.65g) and dimethylformamide(200ml)were heated to reflux and maintained at reflux for four hours. At the end of this time, the hot slurry was filtered, and the presscake washed with DMF, ethanol, water and ethanol and dried at 60°C. The yield was 0.81g.

Analysis Calculated for $C_{28}H_{16}N_6O_4Ni$	Found
Ni = 10.39	Ni = 8.82
N = 15.05	N = 13.45, 13.42
C = 60.21	C = 54.43, 54.75
H = 2.86	H = 3.06,3.08

7. Reaction with Diaminomaleonitrile (1924-44)

a.Schiff base formation

One gram Diaminomaleonitrile, 3.8g, 2,4-dihydroxy-3-formylquinoline and 150 ml butanol were heated at reflux for five hours. At the end of this period, the hot slurry was filtered, and the presscake washed with ethanol and dried at 60°C. The yield was 3.2g.

b. Chelation

Two grams of the above Schiff base, 1.2g, nickel acetate and 200 ml dimethylformamide were heated at reflux for four hours. At the end of this period, the hot slurry was filtered and the presscake washed with alcohol and dried at 60°C. The yield was 0.77g.

c. DMF Extraction

Eight tenths of a gram of the above chelate and 100 ml dimethylformamide were heated at reflux for 20 minutes. The hot slurry was filtered, and the presscake washed successively with alcohol, water and alcohol and dried at 60°C. The yield was 0.55g.

Analysis Calculated for $C_{24}H_{12}N_6O_4Ni$	Found
Ni = 11.46	Ni = 9.14
N = 16.66	N = 16.24

8. Reaction with 3,6-dichloro-o-phenylenediamine (1945-51E)

a Schiff base formation and chelation

One and six tenths grams 3,6-Dichloro-o-phenylenediamine, 1.6g 2,4-dihydroxy-3-formylquinoline and 100 ml butanol were heated at reflux for five hours. At the end of this time 3.8g nickel acetate and 200 ml dimethylformamide was added and the butanol distilled off. Upon completion of the butanol distillation, the reaction mixture was maintained at 150-155°C for four hours. The hot slurry was filtered, and the presscake washed with ethanol and dried at 60°C. The yield was 3.0g.

b. DMF Extraction

Three grams of the above chelate and 150 ml dimethylformamide were heated at reflux for 20 minutes. The hot slurry was filtered, and the presscake washed with ethanol, water and ethanol and dried at 60°C. The yield was 2.5g.

Analysis Calculated for $C_{26}H_{14}Cl_2N_4O_4Ni$	Found
Ni = 10.08	Ni = 8.88
N = 9.74	N = 9.72
C = 54.2	C = 51.2
H = 2.44	H = 2.86
Cl = 13.6	Cl = 11.7

9. Reaction with 3,4,5,6-Tetramethyl-o-phenylenediamine - 1945-40D

a. Synthesis of Tetramethyl-o-phenylenediamine

1. Reduction of 3,4,5,6 tetramethyl-1,2-dinitrobenzene

3,4,5,6-Tetramethyl-1,2-dinitrobenzene eleven grams, and 94 ml isopropyl alcohol were heated to reflux. One hundred ten grams stannous chloride dissolved in 100 ml concentrated hydrochloric was added dropwise over a period of 25 minutes, while maintaining the reaction at reflux. The slurry was allowed to cool, water added and the reaction mixture cooled in ice and filtered. The presscake was washed with hydrochloric acid and dried at room temperature. The yield was 10.5g.

b. Schiff base formation

Five grams 3,4,5,6-tetramethyl-o-phenylenediamine dihydrochloride, 8.2g 2,4-dihydroxy-3-formylquinoline and 300 ml butanol were heated at reflux for five hours. The hot slurry was filtered, and the presscake washed with ethanol and dried at 60°C. The yield was 10.0g.

c. Chelation

Ten grams of the above Schiff base, 7.5g nickel acetate and 400 ml dimethylformamide were heated at reflux for four hours. The hot slurry was filtered, and the presscake washed with alcohol, water and alcohol and dried at 60°C. The yield was 11.0g.

Analysis Calculated for $C_{30}H_{24}N_4O_4Ni$	Found
Ni = 10.32	Ni = 13.94
N = 9.99	N = 8.09
C = 64.05	C = 53.64
H = 4.27	H = 3.64

Reaction of Schiff base (I) with Other Metals

1. Reaction with Cupric Acetate 1924-28

Two and a half grams of the Schiff base (I), 1.1g cupric acetate, and 250 ml dimethylformamide were heated at reflux for four hours. The hot slurry was filtered, and the presscake was washed successively with ethanol, water, and ethanol and dried at 60°C. The yield was 2.5g.

a. DMF Extraction

Two and a half grams of the above chelate and 300 ml dimethylformamide were heated at reflux for 20 minutes. At the end of this time, the hot slurry was filtered, and the presscake washed successively with alcohol, water and alcohol and dried at 60°C. The yield was 0.99g.

Analysis Calculated for $C_{34}H_{20}N_4O_4Cu$	Found
Cu = 10.31	Cu = 13.10
N = 9.16	N = 8.74,8.49
C = 66.77	C = 63.31
H = 3.27	H = 3.39

2. Reaction with Cobaltous (II) Acetate NB 1930-24

Cobaltous acetate (1.33g), the Schiff base (I) (2.0g), and 300 ml dimethylformamide were heated at reflux for four hours. At the end of this time, the hot slurry was filtered and the presscake washed with ethanol, water and ethanol and dried at 60°C. The yield was 1.85g.

3. Reaction with Zinc Acetate 1924-29

Half a gram zinc acetate, 1g of the Schiff base (I) and 100 ml dimethylformamide were heated at reflux for four hours. At the end of this time, the reaction mixture was filtered hot, but no solid was retained on the filter. No insoluble chelate formed.

Attempts to find an economic method for the Production of Phenanthrene-9,10-diamine are described in several experiments in notebooks 1924,1930, and 1945.