

UNITED STATES PATENT OFFICE

2,193,998

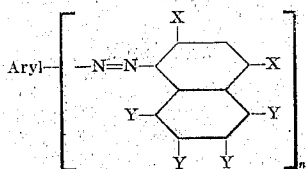
DIAZONIUM COMPOUND

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No Drawing. Application December 30, 1937,
Serial No. 182,469

3 Claims. (Cl. 260—141)

This invention relates to aryl-azo-naphthol-diazonium compounds and especially to air-stable and readily soluble diazonium compounds from amines which have the general formula



in which Aryl is a radical from the group consisting of benzene, naphthalene, carbazole, anthracene, diphenyl and azo-benzene compounds, one X is hydroxy and the other X is hydrogen, one Y is amino and the other Y's are hydrogen, and n is an integer 1 or 2, depending upon whether the coupling is made to a diazotized arylamine or diamine. In these compounds Aryl may be substituted by any group which does not impart water solubility to the aryl-azo-naphthol-amine or it may be unsubstituted. It may not be substituted by the water solubilizing groups carboxy or sulfonic acid.

Heretofore dyeings with ice colors have been made by coupling suitable diazotized arylamines to coupling components on the fibre. Because of the instability of the diazonium compounds they were generally used either in the form of freshly prepared diazotized solutions, freshly prepared solutions of metal salts of the diazonium compounds or in the form of some stabilized composition of the diazonium compound, such as an antidiazotate or a diazoimino compound. The stabilized diazonium compounds are stable in the dry form and in solution and can be conveniently used in printing pastes. The metal salts of diazonium compounds, such as the zinc chloride complexes are generally stable when dry but they are unstable to storage when wet.

Such soluble diazo salts as can be precipitated from solution are obtainable by salting out with sodium chloride. These compounds heretofore produced are usually less stable than the zinc chloride complexes and when they are dry they are so unstable as to involve explosion hazards during preparation and upon storage. A great many diazo solutions cannot be salted out, and the most of them which can be salted out cannot be dried without decomposition. It was therefore desirable to provide dry soluble diazo compounds which would be stable when they were salted out from solution and dried.

The diazo salts are used both for dyeing and for printing. In dyeing, a variety of shades are obtainable without difficulty inasmuch as numerous selections among coupling components as well as among diazo components can be made, but in printing it is necessary to pad the goods with

one coupling component and then vary the shade solely by selection among diazo salts. Consequently in printing, it was not possible to obtain all different shades. For example, it was not possible to obtain a yellow from Naphthol AS or ASD with any one diazo salt, nor was it possible to produce brown shades with any one diazo salt. It was therefore desirable to provide stable and soluble diazo salts instead of stabilized diazo compounds which would produce browns in printing processes.

It was also desirable to provide brown producing stable diazo salts from the standpoint of cost since the stabilization of diazo compounds in general adds to the cost of production.

It was a surprising discovery that the products of the invention were highly soluble and stable as zinc complexes and in the form in which they were salted out of solution with sodium chloride. In the form of solutions the products also had remarkable stability. That the diazo salts of the invention produce brown shades in printing processes from Naphthol AS is an important, novel and remarkable advance in the art, both from the standpoint of the ability to produce new colors by printing processes and from cost considerations.

Certain highly soluble diazonium compounds which will produce printings in brown shades from Naphthol AS have now been found which are stable in dry form and are remarkably stable in solution.

It is among the objects of this invention to provide diazonium compounds which are characterized firstly by high stability in air, both when they are separated as solids from the media in which they are formed and when they are made into water solutions, secondly by good solubility in water, and thirdly by their ability to couple readily with ice color coupling components. Another object of the invention is to provide air-stable diazonium salts from the aryl-azo-naphthol-amines heretofore described and processes for manufacturing the same. Another object of the invention is to provide diazonium salts which can be economically produced in the form of dry soluble products which are stable in air so that they can be stored over long periods, in condition for immediate use.

The objects of the invention are attained generally by diazotizing a primary aryl amine from the group heretofore described by any of the methods well known in the art, as for example, by the action of sodium nitrite on the primary arylamine in mineral acid medium, such as hydrochloric or sulfuric acid. Coupling with the indicated naphthol amine must be done in alkaline medium so that coupling will take place on the benzene ring of the naphthol radical which is substituted by hydroxy. This may be done

conveniently by neutralizing the mineral acidity of the diazotized solution with sodium acetate just before coupling and then pouring the solution of diazotized arylamine at a suitable temperature into a sodium hydroxide solution of the coupling component, salting out the product of coupling and then filtering to separate the precipitated product of coupling from the reaction medium, but many variations of this general method can be used.

If desired the aryl-azo-naphthol-amine can be refined by recrystallization from a suitable organic solvent or by stirring the product in a strong mineral acid solution under proper conditions of acidity, temperature and volume, the principles of which are well understood in the art. Thus in one method of purification the desired product is caused to dissolve in the acid solution while the impurities are insoluble. The mixture is filtered and the purified product is recovered from the filtrate by precipitation with alkali, filtration, washing and drying. Hydrochloric acid is suitable for this purpose.

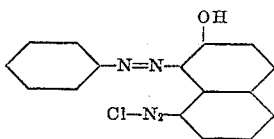
The stable and soluble diazo salts of the aryl-azo-naphthol-amines of the invention are prepared in general by making a suspension or solution of the above described amine in hydrochloric acid solution and adding sufficient sodium nitrite for diazotization, the diazotization medium being held at a suitable diazotization temperature, say about 0° to 30° C. Temperatures in excess of 30° C. are rarely if ever desirable but temperatures higher than about 30° C. can sometimes be used. The diazo salts are precipitated in the diazotization medium by salting with a suitable salting compound, such as sodium chloride, sodium sulfate or zinc chloride, and the precipitate is filtered off and dried.

The invention will be more fully set forth in the following more detailed description which includes examples that are given as illustrative embodiments of the invention and not as limitations thereof.

Example 1

Aniline (9.3 parts) was diazotized at 0°-2° C. in the usual manner, using 6.9 parts of sodium nitrite as a 30% solution and 25 parts hydrochloric acid of 20° Bé. The diazo solution was neutralized with soda ash using Congo red as an indicator and immediately added to a solution containing 19.0 parts of 1-amino-7-naphthol which solution had been made alkaline using Brilliant Yellow as an indicator. The precipitate which was formed was filtered and washed free of alkali with water. The cake was reslurried, acidified with hydrochloric acid, diazotized at about 30° C. for 15 minutes using 6.9 parts of sodium nitrite as a 30% solution, filtered and the filtrate salted at 20%. The brick red precipitate which was formed was filtered, washed with 10 parts of acetone and dried at 50-60° C.

12 parts of a bright, brick red powder represented by the following formula were obtained.

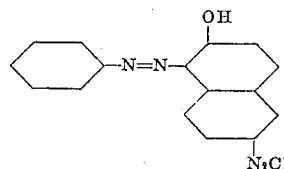


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The product is very soluble in water and most surprisingly stable in both dry form and in solution.

Example 2

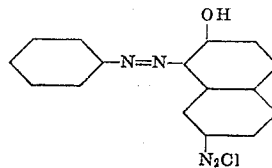
9.3 parts of aniline were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium as described in Example 1. The precipitate of the aryl-azo-naphthol amine was filtered, washed free of alkali with water and treated as in Example 1. 12.0 parts of a brick red powder represented by the following formula were obtained.



The product was soluble in water and it had high stability in air both in the dry state and when it was in solution.

Example 3

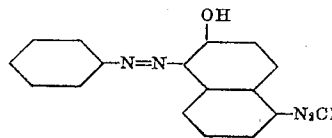
9.3 parts of aniline were diazotized and coupled to 19.0 parts of 2-amino-7-naphthol in alkaline medium as described in Example 1. The precipitate of the aryl-azo-naphthol amine was filtered, washed free of alkali with water and treated as in Example 1. 9 parts of a brick red powder represented by the following formula were obtained.



This product had the soluble and stable properties of the products of the preceding examples.

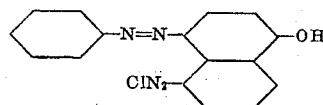
Example 4

9.3 parts of aniline were diazotized in the usual manner, then coupled to 19.0 parts of 1-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 13 parts of a brick red powder represented by the following formula were obtained.



Example 5

9.3 parts of aniline were diazotized and coupled to 19 parts of 1-amino-5-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. A dark powder represented by the following formula was obtained.



Example 6

9.3 parts of aniline were diazotized and coupled to 19 parts of 1-amino-3-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Exam-

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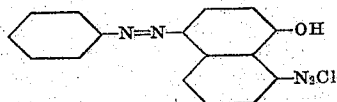
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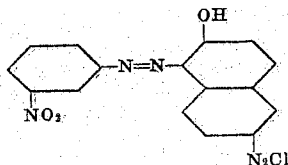
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ple 1. A dark powder represented by the following formula was obtained.



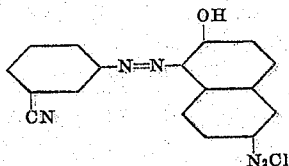
Example 7

9.3 parts of meta-nitro-aniline were diazotized and coupled to 19.0 parts of 2-formyl-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkalinity with water and the formyl group saponified off with diluted hydrochloric acid in the usual manner. The amine was then diazotized and treated further as in Example 1. 10 parts of a brick red powder represented by the following formula were obtained.



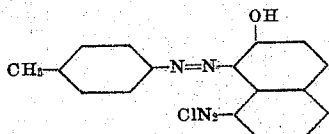
Example 8

12.0 parts of meta-amino-benzonitrile were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 6 parts of a dark powder represented by the following formula were obtained.



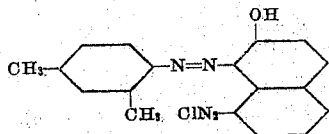
Example 9

11 parts of para-toluidine were diazotized and coupled to 19 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 13.0 parts of a red powder represented by the following formula were obtained.



Example 10

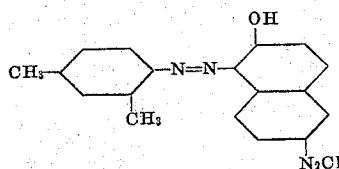
12.0 parts of meta-xylydine were diazotized and coupled to 19.0 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 16 parts of a dark red powder represented by the following formula were obtained.



Example 11

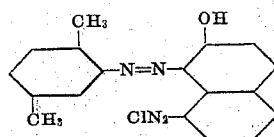
12.0 parts of meta-xylydine were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 9.0 parts of a dark red powder

represented by the following formula were obtained.



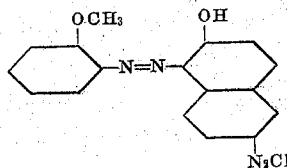
Example 12

12.0 parts of para-xylydine were diazotized and coupled to 19.0 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 14.5 parts of a red powder represented by the following formula were obtained.



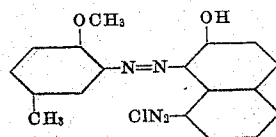
Example 13

12 parts of o-anisidine were diazotized in the usual manner, then coupled to 19 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 11 parts of a dark red powder represented by the following formula were obtained.



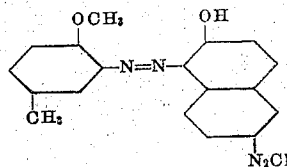
Example 14

13.0 parts of cresidine were diazotized and coupled to 19.0 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 20.0 parts of a dark powder represented by the following formula were obtained.



Example 15

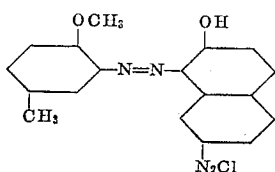
13.0 parts of cresidine were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 14 parts of a red powder represented by the following formula were obtained.



Example 16

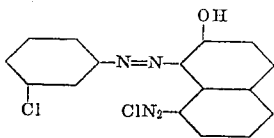
13.0 parts of cresidine were diazotized and coupled to 19.0 parts of 2-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as

in Example 1. 9.0 parts of a powder represented by the following formula were obtained.



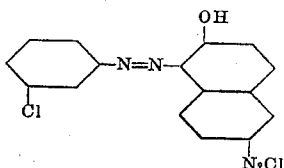
Example 17

13.0 parts of meta-chlor-aniline were diazotized and coupled to 19.0 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 12.0 parts of a red powder represented by the following formula were obtained.



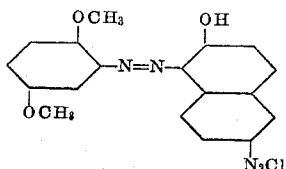
Example 18

13.0 parts of meta-chlor-aniline were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 7.0 parts of a red powder represented by the following formula were obtained.



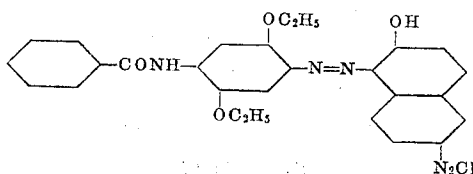
Example 19

16 parts of 2:5-dimethoxy-aniline were diazotized and coupled to 19 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. 8 parts of a dark powder represented by the following formula were obtained.



Example 20

30 parts of 4-benzoylamino-2:5-diethoxy-aniline were diazotized and coupled to 19 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 1. A dark powder represented by the following formula was obtained.

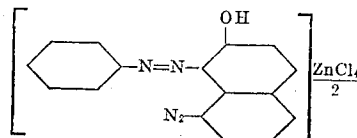


Example 21

9.3 parts of aniline were diazotized and coupled to 19.0 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered and

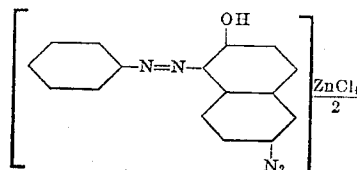
washed free of alkali with water and diazotized as described in Example 1.

Instead of salting out this diazonium salt as described in Example 1, 6.8 parts of zinc chloride were added to the filtered diazo solution. This was followed with an addition of 10% sodium chloride. The red precipitate which was formed was filtered off, washed with 10 parts of acetone and dried at 50-60° C. 20.0 parts of a brick red powder represented by the following formula were obtained.



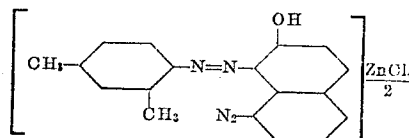
Example 22

9.3 parts of aniline were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 21. 18.0 parts of a brick red powder represented by the following formula were obtained.



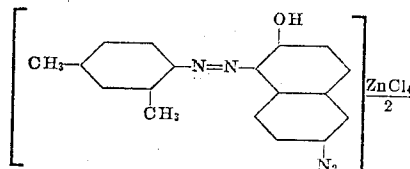
Example 23

12.1 parts of meta-xylylidine were diazotized in the usual manner, then coupled to 19 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 21. 19.0 parts of a brick red powder represented by the following formula were obtained.



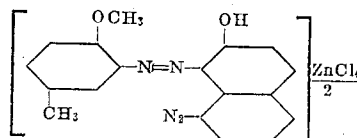
Example 24

12.1 parts of meta-xylylidine were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 21. 18.0 parts of a powder represented by the following formula were obtained.



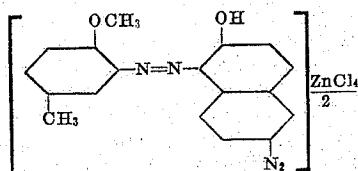
Example 25

13.0 parts of cresidine were diazotized in the usual manner, then coupled to 19 parts of 1-amino-7-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 21. 16 parts of a dark red powder represented by the following formula were obtained.



Example 26

13.0 parts of cresidine were diazotized and coupled to 19.0 parts of 2-amino-6-naphthol in alkaline medium. The precipitate was filtered, washed free of alkali with water and treated as in Example 21. 15 parts of a red powder represented by the following formula were obtained.



In the preparation of the aryl-azo-naphthol-amine, the primary arylamine may be diazotized by any of the methods known to the art, a convenient method being diazotization in mineral acid medium by the addition of an alkali metal nitrite. A suitable medium for this purpose is one acidified with hydrochloric or sulfuric acid, but other mineral acids and other methods of diazotization can be used. Sodium nitrite is a convenient nitrite for this purpose. The coupling with the amino-naphthol may be done conveniently by neutralizing the mineral acidity with sodium acetate and immediately adding the diazo solution to a basic solution of the amino-naphthol which contains sufficient base to provide an alkaline coupling medium when the required amount of diazo solution has been added. Suitable bases for this purpose are caustic soda and soda ash but other bases can be used.

In the preparation of the diazonium compounds from the aryl-azo-naphthol-amines and the zinc salts thereof, reaction media acidified with hydrochloric acid are desirably used. As in diazotization processes known to the art a wide variation in the acid concentration can be used for diazotization.

The presence of the formyl group in the amino naphthol does not materially vary the methods of coupling, the formyl group being present to force an alkaline type coupling. In saponifying the formyl group of the aryl-azo-naphthol-formylamine, the compound is desirably treated in a dilute hydrochloric acid solution, say about 10% solution and boiled until transformation of the formylamine to the amino is attained. A wide variation in acid concentration, say 5% to 25% can be used.

The foregoing examples illustrate only a few of the many new azo-arylamines which can be used in making the compounds of the present invention. The arylamines which are free from the water solubilizing carboxyl and sulphonic acid groups, may be diazotized and coupled with amino-naphthols to produce the new azo-arylamines according to the present invention. The aryl nucleus of the diazo component may be a benzene or a naphthalene nucleus which is unsubstituted or is substituted by groups other than carboxy and sulphonic acid. In general from 1 to 3 substituent groups in this component are satisfactory but more can be used. The substituents from the groups alkyl, alkoxy, aryloxy, aralkyl, aralkoxy, aryl, hydro-aryloxy, acylamina, halogen, nitro, cyanogen, trifluoromethyl, and even others, except carboxy and sulphonic acid can be used. Alkyl refers to aliphatic groups generally, such as aliphatic straight and branched chains. As examples of alkyl, methyl, ethyl,

propyl and butyl are mentioned, but longer chain as well as branched chain groups can be used. From the standpoint of high solubility of the diazo salts of the compounds, those which contain 1 or 2 alkyl and alkoxy groups give excellent results.

Among suitable amines which can be used besides those illustrated in the above examples the following are mentioned:

Ortho-toluidine	10
Meta-toluidine	
Ortho-anisidine	
Para-anisidine	
Ortho-phenetidine	15
Para-phenetidine	
Ortho-xylydine	
Para-xylydine	
2:5-dichlor-aniline	
2:5-dimethoxy aniline	20
2:5-diethoxy aniline	
Para-chlor-aniline	
Ortho-chloro-aniline	
p-Nitro-aniline	
4-nitro-2-amino-anisole	25
4-chloro-2-amino-anisole	
3-amino-benzo-trifluoride	
Ortho-phenetidine	
4-benzoylamino-2:5-diethoxy-aniline	
Alpha-naphthylamine	30
1-amino-2-methoxy-naphthalene	
Amino-azo-benzene	
Benzidine	
4:4'-diamino-diphenylamine	
4:4'-diamino-diphenyl-ether	35
4:4'-diamino-azo-benzene	

All the amino-naphthols may be utilized generally as second components in the preparation of the new compounds. These amino-naphthols include 1:5-, 1:6-, 1:7-, 1:8-, 2:5-, 2:6-, 2:7- and 2:8-amino-naphthols.

The general methods of preparing the compounds of the invention as well as numerous variations in the details of these methods are understood in the art. However, the coupling of the diazotized arylamines or tetrazotized arylene-diamines must be carried out under alkaline conditions in order to obtain products consisting chiefly of the compounds in which coupling has taken place in the nucleus of the amino-naphthol bearing the hydroxyl substituent.

The diazonium compounds of the present invention have a wide range of usefulness. Because of their stability both when dry and in solution, they can be kept for use in either form over long periods of time, and they can be used in the broad field of dyeing processes where stabilized products are used. The preparation of the new stable products does not involve the use of stabilizing agents which would otherwise add to their cost. They are highly soluble and can be used to produce ice colors having good fastness properties. The compounds can be used to produce a wide variety of shades of reds, wines, browns, blues and blacks.

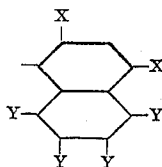
This application is a continuation in part of my copending application, Serial No. 149,888, filed June 23, 1937.

Since from the foregoing description of the invention it will be apparent to those skilled in the art that various other embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that no limitations are intended except

those which are specifically recited in the annexed claims or are imposed by the prior art.

I claim:

1. A compound represented by the formula
 $\text{Aryl}-\text{N}=\text{N}-\text{Aryl}'-\text{N}_2\text{R}$ in which Aryl is one of the group consisting of radicals of benzene, naphthalene, carbazole, anthracene, diphenyl and azo-benzene series which are devoid of carboxy and sulfonic acid, Aryl' is the radical

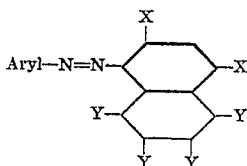


- in which one X is hydroxy and the other is hydrogen, one Y is $-\text{N}_2\text{R}$ wherein R is one of a group consisting of Cl and



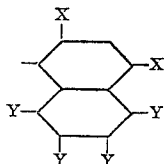
- and the other Y's are hydrogen, said compound being a solid and having only one hydroxy group and characterized by relatively high stability in air and by solubility in water.

2. A compound represented by the formula



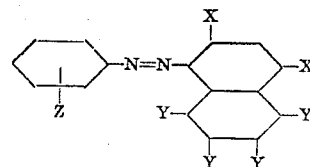
- in which Aryl is one of the group consisting of the radicals of the benzene, naphthalene, carbazole, anthracene, diphenyl and azo-benzene series which are devoid of carboxy and sulfonic acid, one X is hydroxy and the other X is hydrogen, and one Y is one of the group consisting of $-\text{N}_2\text{Cl}$ and the metal-complex radical obtainable by reacting zinc chloride with said aryl-azo-naphthol-diazonium chlorides, and the other Y's are hydrogen, said compound being a solid and having only one hydroxy group and characterized by relatively high stability in air and by solubility in water.

3. A compound represented by the formula
 $\text{Aryl}-\text{N}=\text{N}-\text{Aryl}'-\text{N}_2\text{R}$ in which Aryl is one of the group consisting of radicals of benzene, naphthalene, carbazole, anthracene, diphenyl and azo-benzene series which are devoid of carboxy and sulfonic acid, Aryl' is the radical



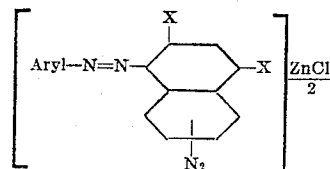
- in which one X is hydroxy and the other is hydrogen, one Y is $-\text{N}_2\text{Cl}$ and the other Y's are hydrogen, said compound being a solid and having only one hydroxy group, and characterized by relatively high stability in air and by solubility in water.

4. A compound represented by the formula



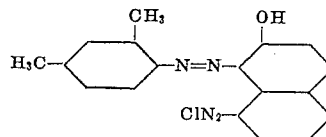
- in which one X is hydroxy and the other X is hydrogen, one Y is the group $-\text{N}_2\text{Cl}$ and the other Y's are hydrogen, and Z is one of the group consisting of hydrogen, alkyl, alkoxy, aryloxy, aralkyl, aralkoxy, aryl, hydro-aryloxy, acylamino, halogen, nitro, cyanogen and trifluoromethyl, said compound being a solid and stable in air.

5. A compound represented by the formula



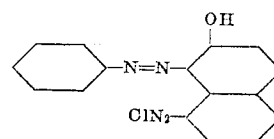
- in which Aryl is one of the group consisting of the radicals of benzene, naphthalene, carbazole, anthracene, diphenyl and azo-benzene compounds which are devoid of carboxy and sulfonic acid groups, one X is hydroxy and the other X is hydrogen, said compound being characterized by being a solid and by stability in air when dry.

6. A compound represented by the formula



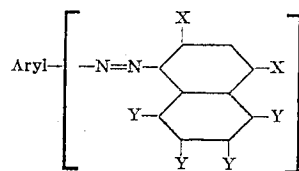
- said product being a solid and characterized by relatively high stability in air when dry and by solubility in water.

7. A compound represented by the formula



- said product being a solid and characterized by relatively high stability in air when dry and by solubility in water.

8. The process which comprises diazotizing a compound represented by the formula



- in which Aryl is a radical from the group consisting of benzene, naphthalene, carbazole, anthracene, diphenyl, and azo-benzene compounds, one X is hydroxy and the other X is hydrogen, one Y is amino and the other Y's are hydrogen, and n is an integer not greater than 2, separating the diazo salt from the reaction mixture and drying, said product being characterized by relatively high stability and by solubility in water.

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