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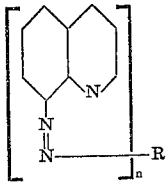
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COMPLEX METAL COMPOUNDS OF WATER-INSOLUBLE AZO-DYESTUFFS

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The present invention relates to new complex metal compounds of water-insoluble azo-dyestuffs; more particularly it relates to complex metal compounds of dyestuffs corresponding to the following general formula



wherein the quinoline radical may be substituted by halogen atoms, trifluoromethyl, alkyl, alkoxy, aryloxy, sulfonic acid ester, sulfonic acid amide, carboxylic acid ester, carboxylic acid amide, cyano, acylamino, alkylsulfonic, arylsulfonic or acyl groups, R stands for the radical of an arylamide of an aromatic or heterocyclic ortho-hydroxycarboxylic acid or of an acylacetic acid being free from water-soluble groups, and *n* represents the integer 1 or 2.

We have found that new water-insoluble metalliferous azo-dyestuffs are obtained by coupling in substance, on the fiber or on another substratum the diazonium compounds of 8-aminoquinolines with arylides of aromatic or heterocyclic ortho-hydroxycarboxylic acids or of acrylacetic acids, the components being selected so that they are free from groups imparting solubility in water such, for example, as sulfonic acid or carboxylic acid groups, and treating the dyestuffs so obtained with agents yielding metal.

The treatment of the water-insoluble azo-dyestuffs obtainable according to the process of this invention with the agents yielding metal may be carried out by known methods during or after the coupling in substance or on the fiber. When the dyestuffs are produced on the fiber, the metallization may be carried out by adding the agents yielding metal to the developing bath or to the impregnation bath. The treatment of the dyestuffs with agents yielding metal after the coupling may be carried out in a second bath which is neutral, weakly alkaline or weakly acid and may contain dispersing agents or detergents, such, for example, as a fatty alcohol polyglycol ether, an alkylphenol polyglycol ether, an alkylnaphthol polyglycol ether, a fatty acid polyglycol ester or a fatty acid amide polyglycol ether.

As agents yielding metal, there are preferably used for the process of the present invention compounds yielding copper, cobalt, nickel, manganese, zinc, cadmium or iron which may be used in the form of their inorganic or organic salts such, for example, as chlorides, bromides, sulfates, nitrates, formates or acetates, or as complex compounds of these metals, especially with hydroxyalkylamines, such, for example, as triethanolamine, with amino acids such as aminoacetic acid or nitrilotriacetic acid, with hydroxycarboxylic acids, such as citric acid or tartaric acid, or with alkali metal phosphates, such, for example, as alkali pyrophosphates or alkali polyphosphates. When an agent yielding cobalt is used, the addition of compounds of hexavalent chormium or other oxidizing agents,

for example alkali metal perborates or alkali metal persulfates, has an advantageous effect on the metallization. On vegeatable fibers, including fibers of regenerated cellulose, there are obtained by the ice colour method known for dyeing and printing dyestuffs which possess, in addition to good general properties of fastness a very good fastness to light. The claret tints which are obtained by using arylides of 2,3-hydroxynaphthoic acid as coupling components and nickel compounds as agents yielding metal are particularly valuable.

The production of the dyestuffs on vegetable fibers may be carried out at a long goods-to-liquor ratio. Piece goods, warps or bands may be dyed in a continuous manner, or printed by the base or naphtholate printing process.

The new dyestuffs can also be produced on animal fibers such as wool or silk, or on synthetic fibers such as polyamide, acetylcellulose, or polyvinyl alcohol fibers, by the dyeing processes usual for these fibers, and valuable dyeings possessing good properties of fastness are obtained.

The dyestuffs can also be prepared in substance and converted into complex metal compounds by a treatment with agents yielding metal. The complex metal compounds so obtained are suitable for dyeing synthetic fibers, or for colouring plastic masses of high molecular weight.

As diazo components there can be used for the process of the present invention the 8-aminoquinoline or substitution products, thereof, as substituents being used groups which do not impart solubility in water such, for example, as halogen atoms, trifluoromethyl, alkyl, alkoxy, aryloxy, sulfonic acid ester, sulfonic acid amide, carboxylic acid ester, carboxylic acid amide, cyano, acylamino, alkylsulfonic, arylsulfonic, or acyl groups.

As coupling components for the process of the present invention, there can be used arylides of aromatic or heterocyclic ortho-hydroxycarboxylic acids or of acylacetic acids such, for example, as arylides of 2,3-hydroxynaphthoic acid or its derivatives substituted in the 6-position, or arylides of 2-hydroxyanthracene-3-carboxylic acid, 3-hydroxydiphenylene oxide-2-carboxylic acid, 2-hydroxycarbazole-3-carboxylic acid, 5-hydroxy-1,2,1',2'-benzocarbazole-4-carboxylic acid, acetoacetic acid, benzoylacetic acid or terephthaloyl-bis-acetic acid.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the parts being by weight unless otherwise stated, and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the liter.

Example 1

Cotton yarn is treated for 45 minutes at 35° C. at a goods-to-liquor ratio of 1:20 in the impregnation bath prepared as described below, then centrifuged, and while wet, developed first for some minutes at 20° C. and then, after being slowly heated to 85° C. to 95° C., for 20 to 30 minutes at 90° C. to 95° C. in the developing bath prepared as described below. The yarn is then rinsed with a solution containing, per liter of water, 3 cc. of hydrochloric acid of 20° Bé., soaped first for 15 minutes at 60° C. and then for 15 minutes at 95° C. with a solution containing, per liter of water, 1 g. of a reaction product of about 10 mols of ethylene oxide with 1 mol of isododecylphenol and 3 grams of sodium carbonate, rinsed and dried.

Impregnation bath.—1.75 grams of 2-(2',3'-hydroxynaphthoylamino)-naphthalene are dissolved in 3.5 cc. of denatured ethyl alcohol, 0.9 cc. of sodium hydroxide solution of 38° Bé., 2 cc. of warm water and 0.9 cc. of a formaldehyde solution of 33% strength. The solution so obtained is then made up to 1 liter with water of 35° C., 3 grams of a condensation product of fatty acids of high

molecular weight and protein degradation products, and 10 cc. of sodium hydroxide solution of 38° Bé.

Developing bath.—1.4 grams of 8-aminoquinoline in the form of a diazonium compound prepared in the usual manner are dissolved in 1 liter of water containing 2 grams of a reaction product of about 20 mols of ethylene oxide with 1 mol of octadecyl alcohol, 3 cc. of acetic acid of 50% strength, 10 grams of sodium acetate and 2.5 grams of copper sulfate.

A red brown dyeing having a very good fastness to light is obtained.

By using in the above example 2.4 grams of cobaltous chloride instead of 2.5 grams of copper sulfate, a bluish black brown dyeing is obtained. By using 2.8 grams of nickel sulfate there is obtained an erica dyeing and with 1.6 grams of ferric chloride there is obtained a rust-red dyeing.

Example 2

Cotton fabric is padded on the foulard with the following solution and dried:

3.5 grams of 2,3-hydroxynaphthoylaminobenzene are dissolved with 30 grams of Monopol Brilliant Oil, 15 cc. of sodium hydroxide solution of 38° Bé. and made up to 1 liter with boiling water. The dried fabric is developed on the foulard with a solution containing, per liter of water, 2.8 grams of 8-aminoquinoline in the form of a diazonium compound prepared in the usual manner, 2 grams of a reaction product of about 20 mols of ethylene oxide with 1 mol of ocetadecyl alcohol and 10 cc. of acetic acid of 50% strength. After passing through air for 30 seconds and hot water, the fabric is soaped for 5 minutes at 60° C. with a solution containing, per liter of water, 5 grams of soap, rinsed and dried. The dried fabric is then printed with a printing paste containing, per kilogram, 200 grams of sodium-formaldehyde-sulfoxylate, 25 grams of the sodium salt of benzylsulfanilic acid, 25 grams of potassium carbonate, 30 grams of anthraquinone paste of 30% strength, 25 grams of potassium salt of the disulfonic acid of the dimethyl-benzyl-phenyl-ammonium chloride and starch tragacanth as thickening agent. After drying, the fabric is then treated for 7 minutes with steam at 102° C. to 103° C., washed with hot dilute sodium carbonate solution, rinsed and aftertreated for 15 minutes at 90° C. to 95° C. with a solution containing, per liter of water, 1 gram of a reaction product of about 10 mols of ethylene oxide with 1 mol of isododecyl phenol, 1 gram of sodium carbonate, 1 gram of aminoacetic acid and 0.7 gram of nickel sulfate. The material is then rinsed and dried.

A white discharge on claret ground is obtained.

Example 3

Cotton fabric is padded on the foulard with the following solution and dried:

6.4 grams of 2,3-hydroxynaphthoylaminobenzene are dissolved with 15 cc. of sodium hydroxide solution of 38° Bé., 20 grams of Monopol Brilliant Oil and 50 cc. of water of 80° C. and made up to 1 liter with boiling water.

The dried fabric is developed on the foulard with a solution containing, per liter of water, 4 grams of 8-aminoquinoline in the form of a diazonium compound prepared in the usual manner, 2 grams of a reaction product of about 20 mols of ethylene oxide with 1 mol of octadecyl alcohol and 10 cc. of acetic acid of 50% strength. After passing through air for 30 seconds, the fabric is treated for 15 minutes at 98° C. with a solution containing, per liter of water, 2.5 grams of copper sulfate. It is then rinsed hot and cold, soaped with a solution containing, per liter of water, 1 gram of a reaction product of about 10 mols of ethylene oxide with 1 mol of isododecylphenol and 3 grams of calcined sodium carbonate, rinsed and dried.

A red brown dyeing having good properties of fastness is obtained.

By using in this example 2.4 grams of cobaltous chloride, instead of 2.5 grams of copper sulfate, a bluish brown dyeing is obtained; by using 2.8 grams of nickel sulfate, a claret dyeing having the same good properties of fastness is obtained.

Example 4

Wool yarn is treated for 45 minutes at 55° C. at a goods-to-liquor ratio of 1:30 in the impregnation bath described below and then rinsed for 5 minutes at 18° C. in a solution containing, per liter of water, 40 grams of sodium chloride and 3 grams of sodium carbonate. The excess liquor is then allowed to drain off the material, and the latter is treated first for 20 minutes at 18° C. and then, after gradually heating the bath to 95° C. for 20 minutes at 95° C. in the developing bath described below. The yarn is soaped for 20 minutes at 40° C. with a solution containing, per liter of water, 1 gram of a reaction product of about 20 mols of ethylene oxide with 1 mol of octadecyl alcohol and 1 cc. of ammonia of 25% strength, and then for 20 minutes at 85° C. with a solution containing, per liter of water, 1 gram of a condensation product from an aminoalkyl-sulfonic acid and a fatty acid of high molecular weight and 0.5 cc. of acetic acid of 50% strength, rinsed and dried.

Impregnation bath.—1 gram of 1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-chlorobenzene and 0.2 gram of sodium hydroxide are dissolved in 4 cc. of denatured ethyl alcohol, 4 cc. of water of 60° C., 0.5 gram of a condensation product from fatty acids of high molecular weight and protein degradation products, and 1.5 cc. of a formaldehyde solution of 33% strength. The solution so obtained is made up to 1 liter with water of 60° C., 2.5 grams of a condensation product from fatty acids of high molecular weight and protein degradation products, and 3 grams of sodium carbonate.

Developing bath.—0.6 gram of 8-aminoquinoline in the form of a diazonium compound prepared in the usual manner are dissolved in 1 liter of water containing 2 grams of a reaction product of about 20 mols of ethylene oxide with 1 mol of octadecyl alcohol, 2 cc. of acetic acid of 50% strength, 10 grams of sodium acetate and 1.75 grams of copper sulfate.

A brown dyeing having good properties of fastness is obtained.

By using in the above example 1.65 grams of cobaltous chloride, instead of 1.75 grams of copper sulfate, a grey brown dyeing is obtained; by using 2.1 grams of nickel sulfate, a claret dyeing having the same good properties of fastness is obtained.

Example 5

Natural silk is treated for 45 minutes at 25° C. at a goods-to-liquor ratio of 1:30 in the impregnation bath prepared as described below, centrifuged and then developed in the developing bath for 15 minutes at 20° C. and, after slowly heating the bath to 95° C. for 20 minutes at this temperature. The material is then rinsed, acidified with a solution containing, per liter of water, 3 cc. of hydrochloric acid of 20° Bé., rinsed and soaped for 15 minutes at 95° C. with a solution containing, per liter of water, 5 grams of soap, rinsed again and dried.

Impregnation bath.—3 grams of 2,3-hydroxynaphthoylaminobenzene are dissolved in 6 cc. of denatured ethyl alcohol, 1.5 cc. of sodium hydroxide solution of 38° Bé., 3 cc. of hot water and 1.5 cc. of a formaldehyde solution of 33% strength. This solution is made up to 1 liter with water of 25° C., 5 grams of a condensation product from fatty acids of high molecular weight and protein degradation products, 4 cc. of sodium hydroxide solution of 38° Bé. and 10 grams of sodium chloride.

Developing bath.—0.8 gram of 8-aminoquinoline in the form of a diazonium compound prepared in the usual manner are dissolved in 1 liter of water containing 2 grams of a reaction product of about 20 mols of ethylene oxide with 1 mol of octadecyl alcohol, 3 cc. of acetic

acid of 50% strength, 10 grams of sodium acetate and 1.75 grams of copper sulfate.

A red brown dyeing having good properties of fastness is obtained.

By using in the above example 1.65 grams of cobaltous chloride, instead of 1.75 grams of copper sulfate, a brown currant dyeing is obtained; by using 2.1 grams of nickel sulfate, a claret dyeing having the same good properties of fastness is obtained.

Example 6

Polyamide yarn is treated for 1 hour at 80° C. at a goods-to-liquor ratio of 1:20 in a solution containing, per liter of water, 1 gram of 1-(2',3'-hydroxynaphthoylamino)-2-methoxybenzene, 0.5 cc. of sodium hydroxide solution of 38° Bé., 10 cc. of denatured ethyl alcohol, 2 grams of Monopol Brilliant Oil and 0.4 gram of 8-aminoquinoline. The material is then rinsed and treated for 30 minutes at 20° C. in a solution containing, per liter of water, 2 grams of sodium nitrite and 3 cc. of hydrochloric acid of 20° Bé. The excess liquor is then allowed to drop off the material and the latter is treated in a solution containing, per liter of water, 0.5 cc. of concentrated ammonia, 2 grams of sodium acetate, 2.5 grams of copper sulfate and 6 grams of triethanolamine. The bath is slowly heated from 35° C. to 95° C. and maintained for 20 minutes at 95° C. The material is then rinsed, soaped for 15 minutes at 90° C. with a solution containing, per liter of water, 1 gram of a reaction product of about 10 mols of ethylene oxide with 1 mol of isododecylphenol and 3 grams of sodium carbonate, rinsed and dried.

A reddish brown dyeing having good properties of fastness is obtained.

By using in the above example 2.4 grams of cobaltous chloride and 3 grams of aminoacetic acid, instead of 2.5 grams of copper sulfate and 6 grams of triethanolamine, a brown dyeing having the same good properties of fastness is obtained.

Example 7

Polyvinyl alcohol yarn is treated for 1 hour at 90° C. to 95° C. at a goods-to-liquor ratio of 1:25 in the following solution:

1 gram of 2,3-hydroxynaphthoylaminobenzene and 0.4 gram of 8-aminoquinoline are dissolved with 0.5 cc. of sodium hydroxide solution of 38° Bé., 5 cc. of denatured ethyl alcohol, 5 cc. of dimethylformamide and 2 cc. of hot water and the solution is introduced into a bath containing, per liter of water, 2 grams of Monopol Brilliant Oil and 5 cc. of sodium hydroxide solution of 38° Bé. The material is then rinsed and treated for 30 minutes at 65° C. in a solution containing, per liter of water, 2 grams of sodium nitrite and 3 cc. of hydrochloric acid of 20° Bé. The excess liquor is then allowed to drain off the material, and the latter is treated for 15 minutes at 95° C. with a solution containing, per liter of water 5 grams of sodium acetate, 1 gram of a reaction product of about 10 mols of ethylene oxide with 1 mol of isododecylphenol, 1.25 grams of copper sulfate and 3 grams of triethanolamine. The material is then rinsed and dried.

A red brown dyeing having good properties of fastness is obtained.

By using in the above example 1.2 grams of cobaltous chloride and 1.5 grams of aminoacetic acid, instead of 1.25 grams of copper sulfate and 3 grams of triethanolamine, a brown dyeing having the same good properties of fastness is obtained.

Example 8

16.2 parts of 1-(2'.3' - hydroxynaphthoylamino)-2-methylbenzene are dissolved in 100 parts of hot water and 75 parts by volume of 2 N-sodium hydroxide solution. The solution is diluted with water to about 400 parts by volume and ice is added in such an amount that the temperature amounts to 0° C. To this solution there is added a mixture of 6.5 parts of crystalline copper sulfate, 30 parts by volume of water, 10 parts of triethanolamine and 25 parts by volume of a 2 N-sodium hydroxide solution, and a diazo solution prepared in usual manner from 7.2 parts of 8-aminoquinoline is added dropwise, while vigorously stirring, the temperature being maintained at 0° C. by the addition of ice. After the coupling, the complex copper compound is filtered off with suction, washed and dried. The dyestuff so obtained is a dark red powder.

By using in the above example 6 parts of crystalline nickel chloride, instead of 6.5 parts of crystalline copper sulfate, the complex nickel compound of the dye-stuff is obtained.

Example 9

7.2 parts of 8-aminoquinoline are dissolved in 88 parts by volume of 2 N-hydrochloric acid. The red orange solution is cooled below 0° C. by the addition of about 100 parts of ice. Into this solution there are poured, while rapidly stirring, 25 parts by volume of a 2 N-sodium nitrite solution. A limpid pale yellow diazo solution is obtained which, while stirring well, is added dropwise, at 0° C., to the mixture described below:

16.1 parts of 1-(2',3'-hydroxynaphthoylamino)-2-methoxybenzene are dissolved at 80° C. in 75 parts by volume of a 2 N-sodium hydroxide solution and 200 parts by volume of water. After cooling the solution to room temperature, a solution of 6.5 parts of crystalline copper sulfate, 30 parts by volume of water, 10 parts of triethanolamine and 25 parts by volume of a 2 N-sodium hydroxide solution is added and the whole is cooled to 0° C. by the addition of ice.

The coupling with the diazo solution dropped in takes place immediately and the red complex copper compound of the azo-dyestuff separates.

After the coupling, the compound is filtered off and washed with water until neutral.

After drying at 60° C., the complex copper compound is obtained in the form of a dark red powder.

In same manner there is obtained the complex nickel compound of the dyestuff by using 6 parts of crystalline nickel chloride ($NiCl_2 \cdot 6H_2O$) instead of 6.5 parts of crystalline copper sulfate.

The dyestuff is a dark red powder.

In the following table are given further components which can be used in the process of the invention, and the tints produced by forming the metalliferous azo-dyestuffs from these components on the fiber, which tints possess good fastness properties.

Diazo component	Coupling component	Tint			
		Copper-complex	Cobalt-complex	Nickel-complex	Iron-complex
8-aminoquinoline	2-(2',3'-hydroxynaphthoylamino)-3-methoxy-diphenylene oxide.	Brownish garnet	Bluish brown	Erica	Red brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2,4-dimethoxy-5-chlorobenzene.	Garnet	do	do	Do.
Do	1-(2'-hydroxycarbazole-3'-carboylamino)-4-chlorobenzene.	Brown	Brown	Brown	Yellowish brown.
Do	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene.	Black	Greenish black	Blue black	Currant.
Do	Terephthaloyl-bis-(1-acetylamino-2-methoxy-4-chloro-5-methylbenzene).	Yellowish brown	Yellow brown	Yellow brown	

Diazo component	Coupling component	Tint			
		Copper-complex	Cobalt-complex	Nickel-complex	Iron-complex
8-aminoquinoline	1-(2',3'-hydroxynaphthoylamino)-2-methoxybenzene.			Erica	Rust coloured.
Do	1-(2',3'-hydroxynaphthoylamino)-3-nitrobenzene.			do	Red brown.
Do	1-(2',3'-hydroxynaphthoylamino)-naphthalene.			do	Rust coloured.
Do	1-(2',3'-hydroxynaphthoylamino)-4-methoxybenzene.			do	Yellowish brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2-methoxy-4-chloro-5-methylbenzene.			do	Rust coloured.
Do	1-(2',3'-hydroxynaphthoylamino)-2-methylbenzene.			do	Do.
Do	1-(2',3'-hydroxynaphthoylamino)-4-chlorobenzene.			do	Red brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-methoxybenzene.			do	Yellowish brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2,5-dimethoxy-4-chlorobenzene.			do	Red brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2,5-dimethoxybenzene.			do	Do.
Do	4,4'-bis-(2'',3''-hydroxynaphthoylamino)-3,3'-dimethoxydiphenyl.			do	Do.
Do	1-(2',3'-hydroxynaphthoylamino)-2-ethoxybenzene.			do	Do.
Do	1-(6'-bromo-2',3'-hydroxynaphthoylamino)-2-methoxybenzene.			do	Do.
Do	1-(2',3'-hydroxynaphthoylamino)-2-methoxy-5-chlorobenzene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-4-methylbenzene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-4-ethoxybenzene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-2,4-dimethylbenzene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-2,3-dimethylbenzene.			do	
Do	1-(2'-hydroxyanthracene-3'-carboylamino)-2-methylbenzene.			Blue grey	Bluish brown.
Do	2,3-hydroxynaphthoylaminobenzene				Red brown.
Do	1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-chlorobenzene.				Do.
2-methyl-8-aminoquinoline	2,3-hydroxynaphthoylaminobenzene	Garnet	Bluish brown	Claret	
Do	1-(2',3'-hydroxynaphthoylamino)-naphthalene.	do			
Do	2-(2',3'-hydroxynaphthoylamino)-naphthalene.	do	Bluish brown	Claret	
Do	1-(2',3'-hydroxynaphthoylamino)-2-methoxybenzene.	do		do	
Do	1-(2',3'-hydroxynaphthoylamino)-2-methylbenzene.	do	Bluish brown		
Do	1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-chlorobenzene.	do	do		
Do	1-(2',3'-hydroxynaphthoylamino)-2,4-dimethoxy-5-chlorobenzene.	do	do		
Do	1-(2',3'-hydroxynaphthoylamino)-2,5-dimethoxy-4-chlorobenzene.	do	Blue brown		
Do	4-4'-bis-(2'',3''-hydroxynaphthoylamino)-3,3'-dimethoxydiphenyl.	do	do		
Do	1-(2'-hydroxycarbazole-3'-carboylamino)-4-chlorobenzene.	Brown	Brown	Brown	
Do	2-(2',3'-hydroxynaphthoylamino)-3-methoxydiphenylene oxide.	Garnet	Blue brown		
Do	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene.	Olive	Olive	Greenish blue	
Do	1-(2',3'-hydroxynaphthoylamino)-2-methyl-5-chlorobenzene.	Garnet			
Do	1-(2',3'-hydroxynaphthoylamino)-2-methoxy-5-chlorobenzene.	do			
Do	1-(2',3'-hydroxynaphthoylamino)-2,5-dimethoxybenzene.		Bluish brown		
Do	Terephthaloyl-bis-(1-acetylamino)-2,4-dimethoxy-5-chlorobenzene.		Yellow brown		
Do	1-(2',3'-hydroxynaphthoylamino)-3-nitrobenzene.			Claret	
Do	1-(2'-hydroxyanthracene-3'-carboylamino)-2-methylbenzene.			Bluish brown	
6-chloro-8-aminoquinoline	2-(2',3'-hydroxynaphthoylamino)-3-methoxydiphenylene oxide.	Brown			
Do	4,4'-bis-(2'',3''-hydroxynaphthoylamino)-3,3'-dimethoxydiphenyl.		Bluish brown		
Do	2,3-hydroxynaphthoylaminobenzene			Erica	
Do	2-(2',3'-hydroxynaphthoylamino)-naphthalene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-4-chlorobenzene.			do	
6-methyl-8-aminoquinoline	2,3-hydroxynaphthoylaminobenzene			Claret	
Do	1-(2',3'-hydroxynaphthoylamino)-3-nitrobenzene.	Red brown		do	
Do	2-(2',3'-hydroxynaphthoylamino)-naphthalene.			do	
Do	1-(2',3'-hydroxynaphthoylamino)-2,5-dimethoxybenzene.			do	
Do	2-(2',3'-hydroxynaphthoylamino)-3-methoxydiphenylene oxide.			do	
Do	1-(5'-hydroxy-1',2',1'',2''-benzocarbazole-4'-carboylamino)-4-methoxybenzene.			Currant	
Do	Terephthaloyl-bis-(1-acetylamino-2-methoxy-4-chloro-5-methylbenzene).			Yellow brown	
Do	1-(2',3'-hydroxynaphthoylamino)-4-methoxybenzene.		Currant		
Do	1-(2',3'-hydroxynaphthoylamino)-2-methoxy-4-chloro-5-methylbenzene.		do		
Do	1-(2',3'-hydroxynaphthoylamino)-2-methyl-4-methoxy-benzene.		do		

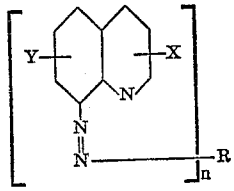
Diazo component	Coupling component	Tint			
		Copper-complex	Cobalt-complex	Nickel-complex	Iron-complex
6-methyl-8-aminoquinoline	1-(2'-hydroxycarbazole-3'-carboylamino)-4-chlorobenzene.		Brown		
Do	1-(2',3'-hydroxynaphthoylamino)-2-ethoxybenzene.		Currant		
Do	1-(6'-bromo-2',3'-hydroxynaphthoyl-amino)-2-methoxybenzene.		do		
Do	1-(2',3'-hydroxynaphthoylamino)-4-methylbenzene.		do		
Do	1-(2',3'-hydroxynaphthoylamino)-2-methylbenzene.	Red brown			
Do	4,4'-bis-acetoacetylamino-3,3'-dimethyl-diphenyl.	Yellow brown			
Do	1-(2',3'-hydroxynaphthoylamino)-2,4-dimethylbenzene.	Red brown			
6-methoxy-8-aminoquinoline	2,3-hydroxynaphthoylaminobenzene	do	Currant	Bluish claret	
Do	1 - (2',3' - hydroxy - naphthoylamino) - 3 - nitrobenzene	do			
Do	1 - (2',3' - hydroxy - naphthoylamino) - naphthalene	do			
Do	1 - (3' - hydroxydiphenylene oxide - 2' - carboylamino)-2-ethoxybenzene	do			
Do	1 - (2',3' - hydroxy - naphthoylamino) - 4 - methoxybenzene		Currant	Bluish claret	
Do	2 - (2',3' - hydroxynaphthoylamino) - naphthalene		do	do	
Do	1 - (2',3' - hydroxynaphthoylamino) - 2 - methyl-4-chlorobenzene		do	Garnet	
Do	1 - (2',3' - hydroxynaphthoylamino) - 2,4 - dimethoxy-5-chlorobenzene		do	Bluish claret	
Do	Terephthaloyl - bis - (1 - acetylamino - 2 - methoxy-4-chloro-5-methylbenzene)		Yellowish-brown	Yellow brown	
Do	4,4' - bis - (2'',3'' - hydroxynaphthoyl-amino)-3,3'-dimethoxydiphenyl			Bluish brown	
Do	1 - (2' - hydroxycarbazole - 3' - carboyl-amino)-4-chlorobenzene			do	
Do	1 - (5' - hydroxy - 1',2',1'',2'' - benzocarba-zole - 4' - carboylamino) - 2 - methyl - 4 - methoxybenzene			Black blue	
2-methyl-6-methoxy-8-aminoquinoline.	2,3-hydroxynaphthoyl-aminobenzene	Garnet	Currant	Claret	
Do	2 - (2',3' - hydroxynaphthoylamino) - naphthalene	do	do	do	
Do	1 - (2',3' - hydroxynaphthoylamino) - 2 - methoxybenzene	do	Garnet	do	
Do	1 - (2',3' - hydroxynaphthoylamino) - 2 - methyl-4-chlorobenzene	do	do	Red brown	
Do	1 - (2',3' - hydroxynaphthoylamino) - 2,4 - dimethoxy-5-chlorobenzene	do	do	Claret	

Diazo component	Coupling component	Tint, manganese complex
8-aminoquinoline.	2,3 - hydroxynaphthoylaminobenzene	Bluish red.
Do	1 - (2',3' - hydroxynaphthoylamino) - 4-methoxybenzene.	Claret.
Do	2 - (2',3' - hydroxynaphthoylamino) - naphthalene.	Do.
Do	1 - (2',3' - hydroxynaphthoylamino) - 4-chlorobenzene.	Do.
Do	1 - (2',3' - hydroxynaphthoylamino) - 2-methyl-4-methoxybenzene.	Do.
Do	1 - (2',3' - hydroxynaphthoylamino) - 4-methylbenzene.	Do.
Do	1 - (2',3' - hydroxynaphthoylamino) - 4-ethoxybenzene.	Do.

Diazo component	Coupling component	Tint, zinc-complex
8-aminoquinoline.	2 - (2',3' - hydroxynaphthoylamino) - 3-methoxydiphenylene oxide.	Garnet.

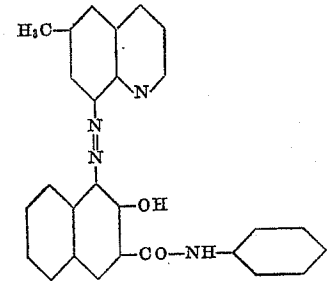
We claim:

1. A complex metal compound containing a metal selected from the group consisting of copper, cobalt, nickel and manganese, of a water-insoluble azo-dyestuff having the following general formula



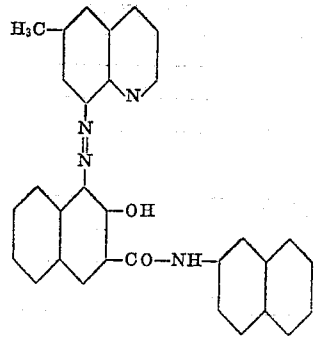
wherein X and Y represent members selected from the group consisting of hydrogen, methyl, methoxy and chlorine, *n* means one of the integers of 1 or 2 and R represents the radical of a coupling component selected from the group consisting of arylamides of 2-hydroxy-naphthalene-3-carboxylic acid, the arylamide components being selected from the group consisting of radicals of the benzene, naphthalene, diphenyl and diphenylene oxide series, and arylamides of 6-bromo-2-hydroxynaphthalene-3-carboxylic acid, 2-hydroxyanthracene - 3 - carboxylic acid, 2-hydroxycarbazole - 3 - carboxylic acid, 5-hydroxy-1,2,1',2'-benzocarbazole - 4 - carboxylic acid, 3-hydroxy-dipheylene oxide - 2 - carboxylic acid, aceto-acetic acid and terephthaloyl-bis-acetic acid, the arylamide components being radicals of the benzene series, and being free from groups imparting solubility in water.

2. The complex nickel compound of the water-insoluble azo-dyestuff corresponding to the following formula:

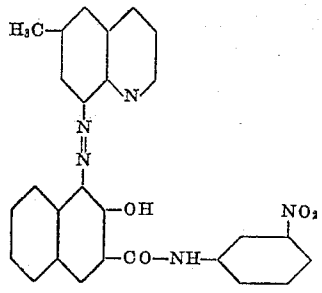


3. The complex nickel compound of the water-in-

soluble azo-dyestuff corresponding to the following formula:

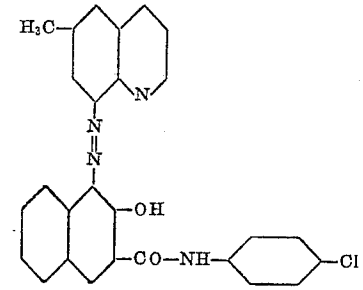


4. The complex nickel compound of the water-insoluble azo-dyestuff corresponding to the following formula:

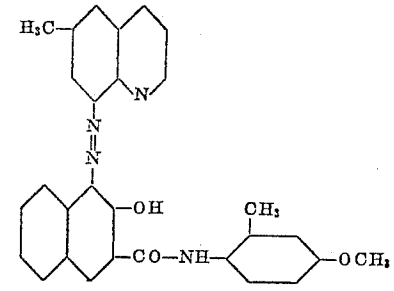


5. The complex nickel compound of the water-in-

soluble azo-dyestuff corresponding to the following formula:



6. The complex nickel compound of the water-insoluble azo-dyestuff corresponding to the following formula:



References Cited in the file of this patent

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443,163 Great Britain ---------- Feb. 24, 1946