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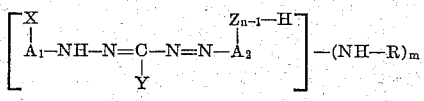
3,202,650

METAL-CONTAINING REACTIVE AZO DYES

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5 Claims. (Cl. 260—146)

The present invention is a continuation-in-part of the application Ser. No. 126,374, filed May 29, 1961 (abandoned since the filing of the present application), and concerns reactive dyes which are 1.1 copper and nickel complex compounds of a dyestuff of the formula



(I)

wherein:

A_1—X represents a first monocyclic aryl group in which the substituent

X is either —OH or —COOH, in ortho-position to the —NH—N= bridge;

A_2—Z_{n-1}—H

represents a second, different, monocyclic or dicyclic aryl group in which the substituent

Z is either —O— or —COO—, in ortho-position to the —N=N— bridge;

n is one of the integers 1 and 2;

Y represents either a (lower alkyl)-CO—, a phenyl-SO_2—, a (lower alkyl)-SO_2—, a naphthyl-SO_2—, a tetrahydronaphthyl-SO_2— or a diphenylyl-SO_2— radical;

R represents a reactive group which is a mono-, di- or trihalogenopyrimidyl, or a mono- or di-halogeno-1,3,5-triazinyl radical, a lower alkenoyl radical, a lower halogenoalkanoyl radical, a lower dihalogenoalkanoyl radical, a lower halogenalkenoyl radical or a lower dihalogenoalkenoyl radical, the halogen having an atomic weight between 35 and 81, i.e. being either chlorine or bromine;

m is one of the integers 1 and 2;

and wherein the dye molecule bears from one to four —SO_3H groups, and the group or groups —(NH—R) is or are linked each to one of the arene nuclei of the bracket-enclosed moiety in the above formula.

The invention yields dyes of high tinctorial strength and of dark hue, which at the same time are of relatively small molecular weight and also of good solubility in water, whereas the known dyes employed for obtaining heavy dyeing of dark shade are metallized polyazo dyes with a large molecular weight and a rather limited solubility in water. Owing to the presence of a reactive grouping in their molecule, the new dyes can be fixed on the substrate and their dyeing possess excellent wet fastness properties.

The metallized reactive dyes conforming to the invention are suitable for dyeing leather; for dyeing, padding and printing fibers of animal origin, e.g. wool and silk; synthetic polyamide fibers, e.g. nylon; cellulosic fibers, e.g. cotton and linen; regenerated cellulose fibers, e.g. viscose staple fiber, viscose filment yarn and cuprammonium rayon; and mixtures and/or other articles of these fibers in red, blue, olive or brown shades. The optimum conditions of application vary with the type of fiber and the dyes used. Animal fibers and synthetic polyamide fibers are dyed, printed or fixed preferably in acid, neutral or weakly alkaline medium, e.g. in presence of acetic acid, formic acid, sulfuric acid, ammonium sulfate, sodium metaphosphate, etc. Dyeing can be carried out in acetic acid to neutral baths in presence of levelling agents, e.g. polyoxethylated fatty amines or mixtures of these and alkylpolyglycol ethers, and the bath adjusted to a neutral or weakly alkaline reaction at the end of dyeing by the addition of small amounts of an agent of alkaline reaction, e.g. ammonia, sodium bicarbonate, sodium carbonate, etc. or compounds which react alkaline on heating, e.g. hexamethylene tetramine, urea. The dyed goods are then well rinsed and if necessary soured with a little acetic acid. The dyeings thus obtained are fast to light, washing, milling, perspiration, water, rubbing and dry cleaning.

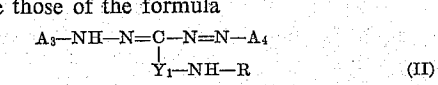
The dyes which contain 3 or 4 water-solubilizing groups (carboxylic acid groups which do not take part in metal complex formation and/or sulfonic acid groups), e.g. two or three sulfonic acid groups and one to two carboxylic acid groups or three or four sulfonic acid groups, possess good solubility in water and yield stable printing pastes and padding liquors, so that they are especially suitable for the printing or padding of cellulosic fibers, whereas the dyes with 1 to 2 water-solubilizing groups which are less water-soluble can be employed for the dyeing of cellulosic fibers according to the exhaustion dyeing process.

The dyeing, padding and printing of the dyes on cellulosic fibers is carried out preferably in alkaline medium, e.g. in presence of sodium bicarbonate, sodium carbonate, sodium hydroxide solution, potassium hydroxide solution, sodium metasilicate, sodium borate, trisodium phosphate, ammonia etc. To preclude reduction effects during dyeing, padding or printing, a mild oxidizing agent such as sodium 1-nitrobenzene-3-sulfonate is often added. The dyes are usually fixed on cellulose fibers by heating. A number of the dyes can be dyed or fixed at low temperature, e.g. 20–40° C., depending on the reactivity of the reactive groupings.

The addition of certain quaternizable amines such as trimethylamine, triethylene-diamine or of asymmetric dimethylhydrazine, preferably in stoichiometric amounts, accelerates the fixation of the dye on the fiber, so that the fixation temperature can be lowered and/or the fixation time shortened.

The dyeings and prints on cellulosic fibers are characterized by outstanding wet fastness properties (fastness to water, sea water, washing, perspiration, wet rubbing and boiling with sodium carbonate solution) due to the formation of a stable chemical linkage between the dye molecule and the cellulose molecule. They also posses good fastness to light and to dry cleaning (organic solvents). Often the total amount of dye does not take part in the reaction, in which case the unreacted dye is removed by suitable treatments such as washing and/or soaping, if necessary with heating. For this purpose synthetic detergents can be used, e.g. alkylarylsulfonates, sodium laurylsulfate, sodium laurylpolyglycol ether sulfate, optionally carboxymethylated alkylpolyglycol ethers, mono- and dialkylphenylpolyglycol ethers.

Among the copper- and nickel-metallized dyes of the above Formula I, dyestuffs of particularly valuable properties are those of the formula



(II)

wherein

A_3 is a first monocyclic aryl group bearing a —OH or —COOH group in ortho-position to the —NH—N= bridge;

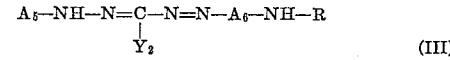
A_4 is a second, different monocyclic or dicyclic aryl group the ortho-position of which relative to the —N=N— bridge is either free from or is substituted with a —COOH or —OH group;

Y_1 is a (monocyclic or dicyclic aryl)-SO_2— radical; and

R is a reactive group as defined in Formula I above.

The copper- and nickel-metallized dyestuffs of Formula II described above have the same advantageous properties common to all copper- and nickel-metallized dyestuffs of Formula I and are further distinguished by particularly excellent fastness to wet treatments, to light and dry cleaning.

Among the aforesaid metallized dyes of the Formula I, a further subclass of dyes particularly distinguished by the fastness of their dyeings on cellulosic fibers to wet treatments, to light and to dry cleaning are the copper- and nickel-complex compounds of the dyestuffs of the formula



(III)

wherein

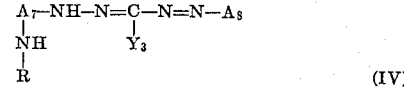
A_5 is a first monocyclic aryl group bearing a —OH or a —COOH group in ortho-position to the —NH—N= bridge;

A_6 is a second monocyclic or dicyclic aryl group the ortho-position of which is either free from or is substituted with a —COOH or a —OH group;

Y_2 is either a (lower alkyl)-CO— group in which the alkyl radical has from 1 to 4 carbon atoms, or a (monocyclic aryl)-SO_2—, a naphthyl-SO_2—, a tetrahydronaphthyl-SO_2—, a diphenylyl-SO_2—, or a (lower alkyl)-SO_2— group, in which latter group the alkyl radical has from 1 to 5 carbon atoms; and

R is a reactive group as defined in Formula I above.

A third subclass of dyes possessing the same excellent properties comprises the copper- and nickel-complex compounds of the dyestuffs of the formula



(IV)

wherein

A_7 is a first monocyclic aryl group bearing a —OH or a —COOH group in ortho-position to the —NH—N= bridge;

A_8 is a second monocyclic or dicyclic aryl group the ortho-position of which is free from —COOH or —OH;

Y_3 is either a (lower alkyl)-CO— group in which the alkyl radical has from 1 to 4 carbon atoms, or a (monocyclic aryl)-SO_2—, a naphthyl-SO_2—, a tetrahydronaphthyl-SO_2—, a diphenylyl-SO_2—, or a (lower alkyl)-SO_2— group, in which latter group the alkyl radical has from 1 to 5 carbon atoms; and

R is a reactive group as defined in Formula I above.

Each of the benzene nuclei of aryl groups A_1 to A_8 can be further substituted with from one to two —SO_3H groups, each of the naphthalene nuclei of aryl groups A_2, A_4, A_6 or A_8 is preferably substituted by 1 to 3 —SO_3H groups, the total of —SO_3H groups in the molecule of the new dyestuffs ranging from at least one to maximally four.

The aforesaid aryl nuclei bear preferably from one to two substituents, other than the above-mentioned —OH or —COOH groups participating in metal complex formation, at least one of which is the preferably aforesaid —SO_3H group. The second substituent can be a chlorine or bromine atom, a nitro, an acylamino group with from 1 to about 7 carbon atoms such as an acetylamino, a formylamino, a propionylamino, a butyrylamino, a n-pentanoylamino, a benzoylamino, a 2-, 3- or 4-methylbenzoylamino, a 2- or 4-chloro-benzoylamino, a 3- or 4-nitrobenzoylamino, a 2-carboxy-benzoylamino, a carbomethoxyamino or a carbethoxyamino group.

In compounds according to the invention in which the benzene nucleus of A_1, or A_3 or A_5 or A_7 is substituted with at least one —SO_3H group, the benzene or naphthalene nucleus of the other aryl group can bear the last-mentioned second substituent, i.e. either chlorine, or bromine, or nitro, etc., as the only substituent, or as the only substituent besides a —OH or —COOH group in ortho-position to the —N=N— bridge, or vice versa.

In Formula II Y_1 is a benzene or naphthalene nucleus which besides the group —NH—R can bear one to two substituents identical with or different from each other (e.g. lower alkyl or alkoxy groups, i.e. having up to 4 carbon atoms, or a carboxy group, etc.).

In Formulae III or IV the substituent Y_2 or Y_3, when it represents a monocyclic radical, is preferably a phenyl, a lower alkyl phenyl, a lower alkoxyphenyl, a chloro phenyl, a carboxyphenyl or nitrophenyl radical.

The following reactive groups R shall be mentioned as particularly effective in the metallized dyestuff molecules according to the invention:

(α) Di-or trihalogenopyrimidyl;

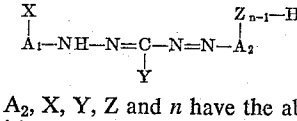
(β) 4,6-dihalogeno-1,3,5-triazinyl-2-,4-amino - 6 - halogeno-1,3,5-triazinyl-2-, where the amino group in 4-position can be substituted with 1 to 2 optionally substituted lower alkyl groups, (e.g. methyl, ethyl, 2-hydroxyethyl, 2- or 3-hydroxypropyl, 2-methoxy- or 2-ethoxy-ethyl, 3-methoxy-propyl, carboxymethyl, 2-carboxyethyl, 2-sulfoethyl etc.), one carboxyphenyl or one sulfo- or disulfo-phenyl- or -naphthyl group;

(γ) halogenoacetyl, β-halogenopropionyl, α,β-dihalogenopropionyl, α-halogenoacrylyl, α,β-dihalogenocrylyl; and γ-halogeno-crotonyl-amino;

Halogen in the reactive groups can be either bromine or chlorine.

Particularly good dyeings or cellulosic fibers with excellent fastness to light, also after a grease finishing treatment, can be obtained with the compounds accordings to the invention which bear as metalcomplex forming substituents 1 to 2 —OH groups, whereas the acid stability of the compounds is maximum when the compounds bear two —OH groups or one —OH and one —COOH group as metal-complex forming substituents.

The process for the production of these dyes consists in reaching the copper and nickel complex compounds of dyes which contain at least one amino group having a reactive hydrogen atom and combined directly or through a bridge and in the metal-free state correspond to the formula



wherein A_1, A_2, X, Y, Z and n have the above-mentioned meanings, with compounds which are condensible with a compound have an exchangeable hydrogen atom and in addition contain at least one substituent which can be split off as an anion and/or an unsaturated radical whose multiple linkage is capable of addition.

(I) The copper or nickel complex compounds of the dyes used as starting materials in the present process are obtained by twofold and stepwise coupling of diacylmethanes with two diazotized amines different from each other, of which at least one must contain in ortho position to the amino group a substituent capable of metal complex formation, with cleavage of an acyl group in each diacylmethane radical in the intermediate formed by the first coupling reaction, and subsequent treatment with a copper or nickel yielding agent, and, where necessary, conversion of a suitable substituent (nitro or acylamino group, mobile halogen atom) into an amino group. The diacylmethanes used may contain two identical or two different acyl groups in the molecule. Particularly suitable compounds of this type are those derived from aliphatic, cycloaliphatic or aromatic monocarboxylic acids or the corresponding sulfonic acids. This number of cyclically arranged carbon atoms in these acids generally amounts to about 10, and those in the aliphatically bound to 6, but the radicals may be of higher molecular weight. The hydrocarbon radicals of the acyl group may contain substituents which are water-solubilizing and/or do not in-

crease or even reduce the water-solubility of the dyes, in particular sulfonamide groups whose hydrogen atoms may be replaced by hydrocarbon radicals which may themselves be substituted, or nitro groups, sulfonic acid, carboxy, alkylsulfonyl, arylsulfonyl, alkylsulfonylamino- or arylsulfonylamino groups.

These diacylmethanes are coupled with diazotized amines. It is possible, for example, to couple 1 mol of a diacylmethane with 1 mol of a diazo compound and subsequently with 1 mol of a diazo compound different from the first or with half a mol of a tetrazo compound. Again, 2 mols of diacylmethane can be coupled in either order with 1 mol of a tetrazo compound and 2 mols of a diazo compound.

All the diazotized monoamines and tetrazotized diamines belonging to the aromatic series, especially the benzene and naphthalene series, or the series of heterocyclic compounds of aromatic character and commonly used in the chemistry of azo dyes can be employed as diazo or tetrazo compounds provided that at least one half of the diazo or tetrazo compounds to be coupled with the diacylmethane contains in ortho position to the diazonium group or diazonium groups a substituent which is capable of forming complex compounds with metals, e.g. a hydroxyl or carboxyl group or a group which can be converted into such a substituent before or during the metallizing reaction, e.g. an alkoxy group in addition to these substituents other substituents which increase and/or do not increase or even diminish water-solublility may be contained in the diazotised or tetrazotized amines, for example those named in the foregoing description of the diacylmethanes.

After the first coupling reaction, one acyl radical in each molecule of the diacylmethane must be split off to render the diacylmethane capable of coupling with a second molecule of a diazotized compound. In many cases this cleavage of acyl radicals takes place of itself during the second coupling reaction. A quicker and more reliable method of effecting cleaving of the acyl radicals is to saponify with alkaline agents, e.g. basic salts or hydroxides of alkali or alkaline earth metals. Often an addition of ammonia, magnesium oxide, sodium bicarbonate or sodium carbonate is sufficient.

The optimum pH for the cleavage of the aryl radicals lies between about 9.5 and 13. An addition of an anti-oxidizing agent to the reaction medium is beneficial, e.g. sodium sulfite or sodium thiosulfate or, generally, the alkaline salts of sulfurous acid or of thiosulfuric acid.

The coupling reactions are carried out under the usual conditions, e.g. at temperatures from about −10° to +35° C. and at pH values between about 5 and 10 for the first coupling reaction and between 7 and 13 for the second coupling reaction. In the second coupling reaction there is no danger of saponification of acyl radicals so that no precautionary measures must be taken. The reaction is effected in aqueous-alkaline medium without the addition of an organic solvent, but organic solvents and/or dispersing agents can also be used. Specially suitable solvents are e.g. dimethylformamide and formamides generally, also substituted hydrocarbons, e.g. chlorobenzene, and pyridine. They are used e.g. in amounts 1 to 5 times greater by weight than the coupling component.

The resulting dyes are metallized by reaction with solutions of copper or nickel salts, e.g. solutions of copper sulfate, copper formate, copper acetate or the corresponding nickel compounds, preferably at high temperatures from about 40° to 70° C. The metal salt is employed in such an amount that the resulting complex compounds contain one copper or nickel atom for each formazane structure.

The metallizing reaction can be carried out in aqueous, weakly acid to alkaline medium, if necessary with pressure and/or in presence of ammonia and/or organic bases, or in concentrated aqueous solutions of alkaline salts of low molecular aliphatic monocarboxylic acids, or in organic solvents, e.g. mixtures containing formamides, acetamides or glycols or mixtures of these with water. Metallization can also be effected simultaneously with the second coupling reaction by coupling in presence of solutions of metal salts. If the dyes contain alkoxy groups, metallization must be carried out with cleavage of these groups.

(II) The metal complex dyes thus obtained must contain at least one amino group with reactive hydrogen, combined either directly or through a bridge. They may of course contain further substituents.

At least one of the diazo components and/or the diacylmethane used for the synthesis of the dyes contains such a group or a substituent convertible into such a group. In the latter case the conversion of the substituent into the amino group (e.g. by reducetion of a nitro group, hydrolysis of an acylamino group or replacement of a mobile halogen atom) must be carried out under such mild conditions that the dye molecule is not affected.

The amino group or the substituent convertible into this group can be attached to the dye molecule either directly or indirectly through a bridge, e.g. an aliphatic chain and if desired a bridge member.

The following are examples of aliphatic chains:

$$-CH_2-,\ -CH_2-CH_2-,\ -CH_2-CH_2-CH_2-,$$
$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\ \text{and}\ -CH_2-CH_2-CH_2-CH_2-$$

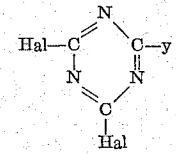
Examples of suitable bridge members are:

$$-SO_2-,\ -CO-,\ -O-,\ -S-,\ -SO_2-\overset{\displaystyle R'}{\overset{|}{N}}-$$

$$-CO-\overset{\displaystyle R'}{\overset{|}{N}}-,\ -\overset{\displaystyle R'}{\overset{|}{N}}-,\ -NH-CO-NH-\ \text{or}\ -\overset{\displaystyle R''}{\overset{|}{N}}-$$

wherein R′ stands for hydrogen, low molecular alkyl or hydroxyalkyl, cycloalkyl, aralkyl or aryl, and R″ for acyl.

(III) In accordance with the invention, these metallized dyes, which contain at least one amino group with reactive hydrogen attached directly or through a bridge, are reacted with compounds which are condensible with a compound containing an exchangeable hydrogen atom plus at least one substituent which can be split off as an anion and/or an unsaturated radical whose multiple linkage is capable of addition. Examples of such compounds are functional derivatives of chloroacetic acid, bromoacetic acid, β-chloro- and β-bromo-propionic acid, α,β-dichloro- or α,β-dibromopropionic acid, acrylic acid, methacrylic acid, α-chloro-, and α-bromo-acrylic acid, α,β-dichloro- and α,β-dibromo- acrylic acid, γ-bromo- and γ-chlorocrotonic acid, and the following heterocyclic compounds: cyanuric chloride, cyanuric bromide, primary condensation products of a cyanuric halide of the composition



where Hal represents chlorine or bromine, and y represents the radical, which may be further substituted, of a primary or secondary aliphatic, alicyclic, aromatic or heterocyclic amine, an aliphatic, alicyclic, aromatic or heterocyclic hydroxy or thiol compound, but more especially the radical of aniline, its alkyl and sulfonic acid or carboxylic acid derivatives, or of low mono- or dialkylamines, or the radical of ammonia.

Further compounds are 2,4,6-trichloropyrimidine and 2,4,6-tribromopyrimidine, their derivatives which contain in the 5 position e.g. methyl, ethyl, carbomethoxy carbethoxy, carboxy, carboxy-methyl, bromomethyl or chloromethyl, 2,4,6-tetrachloro- or -tetrabromopyrimidine, 2,6-dichloro- or -dibromopyrimidine-4-carboxylic acid ethyl or methyl ester, 2,4,5-trichloropyrimidine, 2,4,5-tribromopyrimidine, 2,4-dichloro- or -dibromopyrimidine, 2,5,6-tri-

chloro-4-methylprimidine, 2,4-dichloro-5-chloromethyl-6-methyl-pyrimidine, 2,4-dibromo-5-bromomethyl-6-methylpyrimidine, 2,4-dichloro-5-chloromethylpyrimidine, 2,4-dibromo-5-bromomethylpyrimidine or 2,6-dichloro - 4-trichloromethylpyrimidine.

The introduction of the acid radicals is, as a rule, most easily accomplished by the use of the corresponding acid halides, or in some cases the acid anhydrides. It is preferably to work at low temperatures, e.g. 0° to 20° C., and in presence of acid binding agents such as sodium carbonate, sodium hydroxide, calcium hydroxide or sodium acetate at a weakly acid, neutral or weakly alkaline reaction, for example in the pH region of 4 to 9. For acylation the carboxylic acid chlorides are used as such or in solution in two to five times their amount of benzene, chlorobenzene, methylbenzene, dimethylbenzene or acetone, and are added dropwise to the aqueous, well buffered solution of the substance containing the amino group at a temperature of e.g. 2–5° C. Acylation with the anhydrides can be effected in the same way. The introduction of a dihalogenocyanuric radical is best carried out in aqueous medium at about 0° C. and at a weakly acid reaction, e.g. at pH values from 1.5 to 5. The cyanuric halide is employed as such in solid form or in solution in an organic solvent, e.g. acetone. In the case of the primary condensation products of a cyanuric halide it is best to choose a temperature of 30° to 60° C. and a pH value of 4 to 6, while for the di-, tri- and tetrahalogenopyrimidines temperatures from 40° to 100° C. and pH values between 9 and 3 are most suitable, the condensation being carried out advantageously in the presence of acid-binding agents, e.g. buffer mixtures and/or substances of alkaline reaction which are added gradually to the condensation mixture.

In the following examples the parts and percentages are by weight and the temperatures in degrees centigrade.

EXAMPLE 1

2000 parts of an aqueous neutral solution of 75.8 parts of the copper complex compound of N-(2-hydroxy-5-nitro - 3 - sulfophenyl) - N' - (2' - hydroxy - 3',5' - disulfophenyl)-ms-4''-aminophenylsulfonylformazane are used. The formazane can be obtained by cleavage of the acetyl group attached to carbon in the dye produced from 2-diazo-1-hydroxy-4-nitrobenzene-6-sulfonic acid and 4-acetylamino-phenylsulfonyl-acetylmethane with subsequent coupling with the equimolecular amount of 2-diazo-1-hydroxybenzene-4,6-disulfonic acid in present of copper-yielding agents and subsequent saponification of the acetylamino group in alkaline solution, e.g. in 5–10% sodium or potassium hydroxide solution at 70–100°. This solution is run at an even rate into 230 parts of a 10% aqueous suspension at 0° of finely dispersed cyanuric chloride. The suspension is stirred at 0° and pH 1.8–2.5 until no further free amino groups are indicated, then the dye is salted out with sodium chloride, filtered off, washed with sodium chloride solution and dried.

Cotton is padded at room temperature with an aqueous solution containing 1% of this dye and 2.5% of sodium carbonate, rolled up and stored for a few hours, then rinsed and soaped for 25 minutes at the boil. It is dyed a brilliant fast blue.

If one of the diazo components employed contains an acylamino group (e.g. an acetylamino, formylamino, carbethoxyamino group), the formazane dye serving as starting substance contains two amino groups which are condensed with two molecular proportions of cyanuric chloride. The reactive dye obtained, owing to the presence of two reactive groups in the molecule, gives fixation yields of 100%.

EXAMPLE 2

120 parts of a 20% acetonic solution of 2,4,5,6-tetrachloropyrimidine are added dropwise at 50° in the course of 2 hours to 1800 parts of a neutral aqueous solution of 75.4 parts of the copper complex compound of N-(2-hydroxy - 3,5 - disulfophenyl) - N' - (4' - amino - 2' - sulfophenyl) - ms-4''-methylphenylsulfonylformazane. The pH of the reaction solution is maintained at 6 by simultaneous addition of sodium carbonate. When no more free amino groups are indicated, the dye is salted out with sodium chloride, filtered off, washed with sodium chloride solution and dried. It dissolves in water with a clear blue coloration.

Cotton is padded with a 2% solution of this dye, thickened with alginate and containing 2% sodium carbonate and 20% urea. It is then dried, steamed in neutral steam for 10 minutes, soaped in a warm bath, rinsed and dried. A bright blue dyeing fast to washing is obtained.

The formazane used is obtained by coupling 2-diazo-1-hydroxybenzene-4,6-disulfonic acid with 4-methylphenylsulfonyl-acetylmethane, splitting off the acetyl group, coupling with 1-diazo-4-acetylaminobenzene - 2 - sulfonic acid in presence of copper-yielding agents and saponifying the acetylamino group.

EXAMPLE 3

27.5 parts of the sodium salt of the copper complex compound of N-(2-carboxy-4-aminophenyl)-N'-(2'-carboxy-5'-sulfophenyl)-ms-methylsulfonyl - formazane (obtained by coupling 1-diazo-4-nitrobenzene-2-carboxylic acid with the saponified dye from 1-diazo-2-carboxybenzene-5-sulfonic acid and methylsulfonyl-acetylmethane, reducing to the aminoformacyl compound and coppering the product) are dissolved in 650 parts of water. To the aqueous aminoformacyl solution cooled to 0° so much of a 40% chlorobenzenic chloroacetyl chloride solution is added dropwise in the course of several hours that no further free amino groups are indicated. During the operation a 20% aqueous solution of crystallized sodium acetate is added dropwise so that the pH value of the reaction solution does not fall below 2,3. On completion of chloroacetylation the chlorobenzene is removed under reduced pressure and the dye precipitated with sodium chloride, filtered off, washed with aqueous sodium chloride solution, carefully dried and ground. A dark powder is obtained which dissolves in water with a blue coloration.

A dyebath is prepared with 5000 parts of water, 2 parts of the above-described dye and 2 parts of glacial acetic acid. 100 parts of wool fabric are entered at 50°, the bath heated to 100° in 45 minutes and maintained at this temperature for a further 45 minutes. It is then neutralized with ammonium hydroxide and maintained for 20 minutes at 90°. After rinsing and drying, a reddish blue dyeing of good wet and light fastness is obtained.

EXAMPLE 4

71.1 parts of the copper complex compound of N-(2-carboxy-4-aminophenyl) - N' - (2'-hydroxy-3',5'-disulfophenyl) - ms - naphthyl-(2'')-sulfonyl-formazane (produced by coupling 1-diazo-4-nitrobenzene-2-carboxylic acid with the saponified dye produced from 1-diazo-2-hydroxybenzene-3,5-disulfonic acid and naphthyl-(2)-sulfonyl-acetylmethane, reduction to the aminoformacyl compound and coppering this compound) are dissolved in 1500 parts of water with the necessary amount of sodium hydroxide. In the course of several hours this solution is run at an even rate into an ice-cold, fine suspension of 21.5 parts of cyanuric chloride in 215 parts of water with continuous stirring at 0° until no more aminoformacyl is indicated. The pH value is maintained between 4 and 3 by the addition of dilute sodium carbonate solution. Subsequently, sodium carbonate is added to increase the pH value of the reaction solution to 5. The reaction product is then precipitated with sodium chloride, filtered off, washed with an aqueous sodium chloride solution, and dissolved in 1500 parts of water. 24 parts of sodium 3-aminobenzene-1-sulfonate are added to the solution, the pH value maintained between 4.5 and 5.5 with dilute sodium carbonate solution, and stirring continued at 50° until the hydrogen ion con-

centration of the reaction mass no longer increases. As soon as this is the case, the dye is precipitated with potassium chloride, filtered off and washed with aqueous potassium chloride solution, carefully dried and ground. It is a blue-black powder giving blue solutions in water.

Cotton is padded at 60° with a 1% aqueous solution of this dye containing 18 grams per liter of calcined sodium carbonate and 200 parts of urea. The cotton is dried, heated for 5 minutes at 160° and soaped for 30 minutes at the boil. It is dyed a fast blue shade.

When in place of the copper complex the nickel complex of the formazane mentioned above is reacted with cyanuric chloride and 3-aminobenzene-1-sulfonic acid according to the procedure of this example, a somewhat redder but equally fast dye is obtained.

EXAMPLE 5

125 parts of the copper complex compound obtained by demethoxylating coppering of N-(2-methoxy-5-sulfophenyl)-N'-(2' - methoxy-5'-nitrophenyl)-ms-3''-acetylamino-4''-methoxyphenylsulfonyl-formazane are dissolved in 900 parts of 6% sodium hydroxide solution. The solution is heated at 85° until the acetylamino group is completely hydrolysed, diluted with water to 2500 parts by volume, and neutralized with aqueous acetic acid to a pH value of 7. This aminoformacyl solution is cooled to 35° and in the course of 2½ hours a 30% chlorobenzenic solution of β-chloropropionic acid chloride is added at an even dropwise rate until no more free amino groups are indicated. During this operation 10% sodium carbonate solution is dropped into the reaction solution so that its pH value does not fall below 4.5. On completion of acylation, the dye is salted out with sodium chloride, filtered off, washed with an aqueous sodium chloride solution, carefully dried and ground. The dye is a blue-black powder which gives blue solutions in water.

Cotton is padded with a 1% aqueous solution of this dye thickened with sodium alginate and containing 200 grams per liter of urea and 20 grams per liter of sodium hydrogen carbonate. It is dried, heated for 5 minutes at 160°, soaped at the boil for 30 minutes, rinsed and dried. A blue dyeing fast to washing is obtained.

When in place of the copper complex compound of the formacyl dye, the nickel complex compound is used and the procedure of this example followed, a somewhat redder but equally fast dye is obtained.

EXAMPLE 6

71.1 parts of the copper complex compound of N-(2-carboxy - 4 - sulfophenyl)-N'-(2'-hydroxy-5'-sulfophenyl)-ms-5''-aminonaphthyl-(2'')-sulfonyl-formazane (produced by coupling 1-diazo-2-methoxybenzene-5-sulfonic acid with the saponified dye from 1-diazo-2-carboxybenzene-4-sulfonic acid and 5-acetylaminonaphthyl-(2)-sulfonylacetylmethane, demethoxylating coppering and saponification of the acetylamino group) are dissolved in 1200 parts of water. The dye solution is heated to 75°, its pH value decreased to 5.5 with a little acetic acid, and 23 parts of 2,4,5,6-tetrachloropyrimidine added. The mass is stirred at 75°, with slow addition of dilute sodium carbonate solution to maintain the pH between 5 and 6, until no more amino groups are indicated. On cooling to 40° the precipitated formacyl dye is filtered off, washed with an aqueous sodium chloride solution, carefully dried and ground. The new dye is a blue-black powder which dissolves in water with a blue coloration. The nickel complex of this formacyl dye produced in an analogous manner gives slightly more reddish blue solutions in water.

2 parts of the copper-containing dye, 7 parts of ammonium sulfate and 10 parts of anhydrous sodium sulfate are dissolved in 4000 parts of water at 30°. 100 parts of wool are entered in this solution, the temperature raised to the boil in 30 minutes and the bath boiled for 1 hour. After cooling to 90°, 4 parts of 25% aqueous ammonia solution are added and dyeing continued for 30 minutes at 90°. The wool is then rinsed with water and finally with 0.5% formic acid. It is dyed in a blue shade fast to washing.

The following Table 1 contains further 1:1 metal complex compounds of dyes of the formula

$$A_3\text{—NH—N=C(—Y}_1\text{—NH—R)—N=N—A}_4$$

which can be obtained according to the details of Examples 1, 5 and 6 and are characterized by the amines from which A_3— and A_4— are derived (columns I and II), the amino radical from which

$$\text{—Y}_1\text{—NH—}$$

is derived (column III) the reactive component from which R is derived (column IV) the metal employed for the complex formation (column V) and the shade of the dyeing on cotton or wool (column VI).

Table 1

Ex. No.	A_3—NH_2 (I)	H_2N—A_4 (II)	—Y_1—NH_2 (III)	R—:derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
7	2-amino-1-hydroxy-4-nitrobenzene-6-sulfonic acid.	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	4-aminophenyl-1-sulfonyl	Cyanuric chloride	Ni	Red.
8	do	do	do	Cyanuric bromide	Cu	Blue.
9	do	2-amino-1-hydroxybenzene-4-sulfonic acid.	4-amino-2,5-dimethoxyphenyl-1-sulfonyl.	2-amino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
10	2-amino-1-hydroxy-4-chlorobenzene-6-sulfonic acid.	do	do	2-(2'-hydroxyethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
11	do	do	3-amino-4-methoxyphenyl-1-sulfonyl.	2,4,6-trichloropyrimidine	Cu	Do.
12	2-amino-1-hydroxy-4-phenylbenzene-6-sulfonic acid.	do	4-amino-2-methylphenyl-1-sulfonyl.	2-(2'-sulfoethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
13	2-amino-1-hydroxy-6-nitrobenzene-4-sulfonic acid.	2-amino-1-hydroxy-5-chlorobenzene-4-sulfonic acid.	do	do	Cu	Do.
14	do	2-amino-1-hydroxybenzene-5-sulfonic acid.	4-amino-2,5-dimethylphenyl-1-sulfonyl.	2-(4'-sulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
15	2-amino-1-hydroxy-4-methylsulfonylamino-benzene-6-sulfonic acid.	do	do	do	Cu	Do.
16	2-amino-1-hydroxybenzene-4-sulfonic acid.	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	3-amino-4-methoxyphenyl-1-sulfonyl.	2,4,5,6-tetrachloropyrimidine.	Cu	Do.
17	do	do	do	2,4,6-tribromo-5-carboxypyrimidine.	Ni	Blue-red.
18	do	do	5-amino-napthyl-2-sulfonyl	2,4,6-trichloropyrimidine	Cu	Blue.
19	2-amino-1-carboxybenzene-5-sulfonic acid.	do	do	2,4,6-trichloro-5-chlorovinylpyrimidine α-bromoacrylyl chloride.		Do.
20	do	do	do	α-Bromoacrylyl chloride	Cu	Do.
21	do	do	do	α-Chlorocrotonylchloride	Cu	Do.
22	do	do	do	2-dimethylamino-4,6-di-	Cu	Do.

Table 1—Continued

Ex. No.	$A_3—NH_2$ (I)	$H_2N—A_4$ (II)	$—Y_1—NH_2$ (III)	R—:derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
				chloro-1,3,5-triazine.		
23	2-amino-1-carboxybenzene	2-amino-1-hydroxy-5-chlorobenzene-4-sulfonic acid.	4-aminophenyl-1-sulfonyl	2-amino-4,6-dibromo-1,3,5-triazine.	Cu	Blue.
24	do	2-amino-1-hydroxybenzene-4-sulfonic acid.	do	2-(2′,5′-disulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
25	2-amino-1-hydroxy-4-nitrobenzene.	do	do	2-(2′,4′-disulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
26	2-amino-1-hydroxy-4-chlorobenzene.	do	do	2-(3′-sulfo-2′-hydroxypropylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
27	do	do	do	Chloracetyl chloride	Cu	Do.
28	2-amino-1-hydroxy-6-chlorobenzene-4-sulfonic acid.	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	4-amino-3-carboxyphenyl-1-sulfonyl.	2,4,5,6-tetrachloropyrimidine.	Cu	Do.
29	do	do	do	2,4-dichloro-5-chloromethyl-6-methylpyrimidine.	Ni	Bluish-red.
30	2-amino-1-hydroxybenzene-4-sulfonic acid.	do	3-aminophenyl-1-sulfonyl	2,4,5,6-tetrabromopyrimidine.	Cu	Blue.
31	do	do	4-aminophenyl-1-sulfonyl	2,4,6-tribromo-5-allylpyrimidine.	Cu	Do.
32	do	do	do	2,4-dibromo-5-bromomethylpyrimidine.	Cu	Do.
33	do	do	do	α,β-Dibromopropionyl chloride.	Cu	Do.
34	do	do	do	β-Bromopropionylchloride	Cu	Do.
35	2-amino-1-carboxybenzene-4-sulfonic acid.	2-amino-1-carboxybenzene	do	Chloracetyl chloride	Cu	Red.
36	do	2-amino-1-carboxybenzene-5-sulfonic acid.	do	2,4,6-trichloro-4-carboethoxypyrimidine.	Ni	Green.
37	2-amino-1-carboxybenzene	do	do	2-(3′-sulfophenylamino)-4,6-dibromo-1,3,5-triazine.	Cu	Red.
38	do	do	do	2-methylamino-4,6-dichloro-1,3,5-triazine.	Cu	Red.
39	2-amino-1-hydroxybenzene-5-sulfonic acid.	do	do	Bromacetyl chloride	Cu	Red-blue.
40	2-amino-1-hydroxy-4-chlorobenzene-6-sulfonic acid.	2-amino-1-carboxybenzene-5-sulfonic acid.	4-aminophenyl-1-sulfonyl	β-Chloropropionylchloride	Cu	Do.
41	do	do	do	2,4,6-tribromopyrimidine	Cu	Do.
42	do	2-amino-1-carboxybenzene-4-sulfonic acid.	do	2,4,5-trichloropyrimidine	Cu	Do.
43	do	do	do	2-carboxymethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
44	do	2-amino-1-carboxybenzene	do	2-N-methyl-N-2′-sulfoethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
45	do	1-amino-benzene-4-sulfonic acid.	do	2-(2′-ethoxyethylamino)-4,6-dichloro-1,3,5-triazine.	Ni	Red.
46	do	do	do	α,β-Dichloropropionyl chloride.	Cu	Red-blue.
47	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	1-aminobenzene-2-sulfonic acid.	3-amino-4-methoxyphenyl-1-sulfonyl.	α,β-Dichloracrylylchloride	Cu	Blue.
48	do	do	do	2,4,6-tribromo-5-ethylpyrimidine.	Cu	Do.
49	do	2-aminonaphthalene-6-sulfonic acid.	do	2,4,6-trichloro-5-methylpyrimidine.	Cu	Do.
50	do	2-aminonaphthalene-5-sulfonic acid.	4-aminophenyl-1-sulfonyl	2,4,6-trichloro-5-carboxymethylpyrimidine.	Cu	Do.
51	do	2-amino-1-hydroxybenzene-4-sulfonic acid.	do	do	Cu	Do.
52	2-amino-1-hydroxybenzene-4-sulfonic acid.	1-aminobenzene-2,5-disulfonic acid.	4-amino-2-methylphenyl-1-sulfonyl.	2,4,5-tribromopyrimidine	Ni	Red.
53	2-amino-1-carboxybenzene-4-sulfonic acid.	do	6-aminonaphthyl-1-sulfonyl	2,4,6-tribromomopyrimidine.	Cu	Red.
54	do	do	6-aminonaphthyl-2-sulfonyl	2,4-dichloro-5-chloromethylpyrimidine.	Ni	Red.
55	do	1-aminobenzene-3-sulfonic acid.	do	α-Bromocrotonyl chloride	Ni	Red.
56	2-amino-1-hydroxybenzene-4-sulfonic acid.	do	do	2-di-(2′-hydroxyethyl)-amino-4,6-dichloro-1,3,5-triazine.	Cu	Red.
57	do	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	do	2-(3′-methoxypropylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Blue.
58	do	do	4-aminonaphthyl-1-sulfonyl	2,4,6-tribromo-5-carboethoxypyrimidine.	Cu	Do.
59	do	do	do	α,β-Dibromoacrylyl chloride.	Cu	Blue.
60	do	do	do	2-diethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Blue.
61	2-amino-1-carboxybenzene	do	5-aminonaphthyl-1-sulfonyl.	2-(2′-sulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Blue.
62	do	do	4-aminophenyl-1-sulfonyl	2-(2′-sulfoethylamino)-4,6-dibromo-1,3,5-triazine.	Cu	Blue.
63	do	do	do	2,4,6-tribromo-5-carboxymethylpyrimidine.	Cu	Blue.
64	do	do	do	α-chloroacrylyl chloride	Cu	Blue.
65	2-amino-1-hydroxy-4-chlorobenzene-6-sulfonic acid.	1-aminobenzene-2,4-disulfonic acid.	4-aminophenyl-1-sulfonyl	2,4,6-trichloro-5-ethylpyrimidine.	Cu	Red-blue.
66	do	do	do	2-(4′-carboxyphenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Red-blue.
67	do	1-aminonaphthalene-4-sulfonic acid.	do	2,4-dichloro-6-methylpyrimidine.	Cu	Red-blue.
68	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	1-aminonaphthalene-5-sulfonic acid.	do	2,4,6-trichloro-5-chloromethylpyrimidine.	Ni	Brown-red.
69	do	1-aminonaphthalene-6-sulfonic acid.	do	2,4,6-tribromo-5-carbomethoxypyrimidine.	Cu	Red.
70	do	1-aminonaphthalene-7-sulfonic acid.	do	2-(2′-hydroxypropylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Red.
71	do	2-aminonaphthalene-4,8-disulfonic acid.	do	2,4,6-tribromo-5-bromomethylpyrimidine.	Cu	Red.
72	2-amino-1-carboxybenzene-5-sulfonic acid.	do	do	2,4-dibromo-6-carboethoxypyrimidine.	Cu	Red.

Table 1—Continued

Ex. No.	$A_5—NH_2$ (I)	$H_2N—A_4$ (II)	$—Y_1—NH_2$ (III)	R—:derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
73	2-aminhnaphthalene-4,8-disulfonic acid.	2-aminonaphthalene-5,7-disulfonic acid.	4-aminophenyl-1-sulfhnyl	2,4,6-trichloro-5-carbomethoxy-pyrimidine.	Cu	Red.
74	2-amino-1-hydroxybenzene-4-sulfonic acid.	2-aminonaphthalene-6,8-disulfonic acid.	3-aminophenyl-1-sulfonyl	2,4-dichloro-6-carboethoxy-pyrimidine.	Cu	Red.
75	do	1-aminonaphthalene-3,8-disulfonic acid.	do	2,4-dibromo-5-bromomethyl-6-methylpyrimidine.	Cu	Red.
76	do	1-aminonaphthalene-4,8-disulfonic acid.	do	2,4,6-trichloro-5-carboxy-pyrimidine.	Cu	Red.
77	2-amino-1-carboxy-benzene-4-sulfonic acid.	2-aminonaphthalene-1-sulfonic acid.	4-aminophenyl-1-sulfonyl	2-(2'-carboxyethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Red.
78	do	2-aminonaphthalene-1,5-disulfonic acid.	do	2,4,6-tribromo-5-methyl-pyrimidine.	Cu	Red.
79	2-amino-1-hydroxybenzene-4-sulfonic acid.	1-aminonaphthalene-3,6,8-trisulfonic acid.	do	2,4,6-tribromo-5-bromovinyl-pyrimidine.	Cu	Red.
80	do	2-aminonaphthalene-3,6,8-trisulfonic acid.	4-aminonaphthyl-1-sulfonyl	2,4-dichloro-6-trichloromethylpyrimidine.	Cu	Red.
81	do	1-aminonaphthalene-3,6-disulfonic acid.	do	2-phenylamino-4,6-dichloro-1,3,5-triazine.	Cu	Red.
82	2-amino-1-hydroxy-4-chlorobenzene.	2-aminonaphthalene-4,6,8-trisulfonic acid.	4-amino-phenyl-1-sulfonyl	2-(2'-carboxyphenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Red.

The following Table 2 contains further 1:1 metal complex compounds of dyes of the formula

$$A_5—NH—N=C(Y_2)—N=N—A_6—NH—R$$

which are obtainable according to the particulars of Examples 2 to 4 and are characterized in the table by the amine from which A_5— is derived (column I), the amino radical from which —A_6—NH— is derived (column II), the radical Y_2— (column III), the compound from which —R is derived (column IV), the metal employed for the complex formation (column V) and the shade of the dyeings on cotton or wool (column VI).

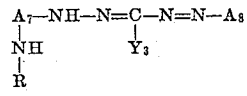
Table 2

Ex. No.	$A_5—NH_2$ (I)	$—A_6—NH_2$ (II)	$Y_2—$ (III)	R—: derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
83	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	4-amino-2-sulfophenyl	4-methylphenyl-1-sulfonyl	2,4,5,6-tetrabromopyrimidine.	Cu	Blue.
84	do	do	do	2,4,6-trichloropyrimidine	Cu	Do.
85	do	do	do	2,4-dichloro-5-chloromethyl-6-methylpyrimidine.	Cu	Do.
86	2-amino-1-hydroxy-4-chlorobenzene-6-sulfonic acid.	do	Phenylsulfonyl	2-dimethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
87	do	do	do	Chloroacetyl chloride	Cu	Do.
88	do	5-amino-2-sulfophenyl	do	2,4-dichlorophyrimidine	Cu	Do.
89	2-amino-1-hydroxy-4-nitrobenzene-6-sulfonic acid.	do	4-chlorophenyl-1-sulfonyl	2-(3'-sulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Ni	Brownish red.
90	do	do	do	β-Chloropropionyl chloride	Ni	Do.
91	2-amino-1-hydroxybenzene-4-sulfonic acid.	do	do	2,4-dibromo-6-carbomethoxypyrimidine.	Cu	Blue.
92	do	2-carboxy-4-aminophenyl	do	2-(2'-sulfoethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
93	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	do	2-chlorophenyl-1-sulfonyl	2-(3'-methoxybutylamino)-4-6-dichloro-1,3,5-triazine.	Cu	Blue.
94	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	2-hydroxy-3-amino-5-sulfophenyl.	2-methylphenyl-1-sulfonyl	2,4,6-tribromopyrimidine	Cu	Do.
95	do	do	do	2,4,6-trichloro-5-allyl-pyrimidine.	Ni	Red.
96	2-amino-1-hydroxybenzene-5-sulfonic acid.	do	do	2-(3'-hydroxypropylamino)-4-6,dichloro-1,3,5-triazine.	Cu	Blue.
97	do	do	Ethylsulfonyl	2-(N-2'-hydroxyethyl-N-phenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
98	do	do	do	α-Bromoacrylyl chloride	Cu	Do.
99	do	do	do	Bromoacetyl chloride	Cu	Do.
100	do	do	n-Propylsulfonyl	2,4-dichloro-6-carbomethoxypyrimidine.	Cu	Do.
101	2-amino-1-carboxy-benzene-5-sulfonic acid.	do	n-Butylsulfonyl	β-Chloropropionyl chloride	Cu	Reddish blue.
102	do	do	Methylsulfonyl	α,β-Dichloropropionyl chloride.	Cu	Do.
103	do	4-amino-2-carboxyphenyl	do	2,4,6-trichloro-5-carboxy-methylpyrimidine.	Ni	Olive.
104	do	do	do	2-carboxymethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Red.
105	do	do	Acetyl	α-Chloroacrylyl chloride	Cu	Red.
106	do	do	do	β-Bromopropionyl chloride	Cu	Red.
107	2-amino-1-carboxybenzene-4-sulfonic acid.	2-carboxy-4-aminophenyl	3-carboxyphenyl-1-sulfonyl	α,β-Dibromopropionyl chloride.	Cu	Red.
108	do	do	do	2-di-(2'-hydroxyethyl)-amino-4,6-dibromo-1,3,5-triazine.	Cu	Red.
109	do	do	do	2,4-dichloro-5-chloromethyl-6-methylpyrimidine.	Cu	Red.
110	do	do	Acetyl	do	Cu	Red.
111	do	4-amino-2-sulfophenyl	Propionyl	2-(N-methyl-N-phenyl-amino)-4,6-dichloro-1,3,5-triazine.	Cu	Red.
112	2-amino-1-carboxybenzene-5-sulfonic acid.	do	Butyryl	2,4,6-trichloropyrimidine	Cu	Red.
113	do	do	Acetyl	Cyanuric chloride	Cu	Red.
114	do	5-amino-2-sulfophenyl	do	Cyanuric bromide	Cu	Red.
115	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	do	3-nitrophenyl-1-sulfonyl	2,4,6-trichloro-5-carboxy-pyrimidine.	Cu	Olive.

Table 2—Continued

Ex. No.	A_5—NH_2 (I)	—A_6—NH_2 (II)	Y_2— (III)	R—: derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
116	2-amino-1-hydroxybenezene-4,6-disulfonic acid.	5-amino-2-sulfophenyl	3-nitrophenyl-1-sulfonyl	2-amino-4,6-dichloro-1,3,5-triazine.	Cu	Olite.
117	do	do	do	2,4,6-trichloro-5-methyl-pyrimidine.	Cu	Do.
118	2-amino-1-hydroxybenzene-4-sulfonic acid.	2-hydroxy-3-amino-5-sulfo-phenyl.	n-Propylsulfonyl	2-(2'-hydroxyethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Blue.
119	do	do	4-ethoxyphenyl-1-sulfonyl	2,4,6-trichloropyrimidine	Cu	Do.
120	do	do	4-methoxyphenyl-1-sulfonyl	do	Cu	Do.
121	do	do	Propionyl	2,4-dibromo-5-bromo-methyl-6-methylpyrimi-dine.	Cu	Do.
122	do	do	Naphthyl-1-sulfonyl	2,4,6-tribromo-5-carboxy-methylpyrimidine.	Cu	Do.
123	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	do	5,6,7,8-tetrahydronaphthyl-1-sulfonyl.	2,4,6-trichloropyrimidine	Cu	Do.
124	do	do	1,1'-diphenylyl-4-sulfonyl	do	Cu	Do.
125	2-amino-1-hydroxy-6-chloro-benzene-4-sulfonic acid.	4-amino-2-carboxyphenyl	4-methylphenyl-1-sulfonyl	2-(N-methyl-N-3'-sulfo-2'-hydroxypropylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
126	2-amino-1-hydroxy-6-nitro-benzene-4-sulfonic acid.	do	4-ethylphenyl-1-sulfonyl	2-(4'-sulfophenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
127	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	4-aminophenyl	Methylsulfonyl	2-(2',5'-disulfophenyl-amino)-4,6-dichloro-1,3,5-triazine.	Ni	Reddish brown.
128	2-amino-1-hydroxy-4-carboxybenzene-6-sulfonic acid.	do	Acetyl	2,4,6-trichloropyrimidine	Ni	Do.
129	do	3-aminophenyl	2-chlorophenyl-1-sulfonyl	do	Cu	Blue.
130	2-amino-1-hydroxybenzene-4,6-disulfonic acid.	do	Ethylsulfonyl	2,4,6-tribromopyrimidine	Cu	Do.
131	do	3-amino-4-methyl-phenyl	Methylsulfonyl	2,4,5-trichloropyrimidine	Cu	Do.
132	do	3-amino-6-methylphenyl	n-Butylsulfonly	2,4,6-trichloro-5-carboxy-methylpyrimidine.	Cu	Do.
133	2-amino-1-hydroxybenzene-4-sulfonic acid.	4-amino-2-carboxyphenyl	n-Amylsulfonyl	2-(2',4'-disulfophenyl-amino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
134	do	do	4-methylphenyl-1-sulfonyl	2-(2'-sulfoethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
135	2-amino-1-carboxybenzene-5-sulfonic acid.	2-hydroxy-3-amino-5-sulfo-phenyl.	do	2-(2'-carboxyphenylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
136	do	do	do	2-(carbosymethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.

In Table 3 are listed 1:1 metal complex compounds of the formula



which are obtainble according to the particulars of Examples 2 to 4 and are characterized in the Table by the amino radical from which —A_7—NH is derived (column I), the amine from which A_8— is derived (column II), the radical Y_3— (column III), the compound from which —R is derived (column IV), the metal employed for the complex formation (column V) and the shade of the dyeing on cotton or wool (column VI).

Table 3

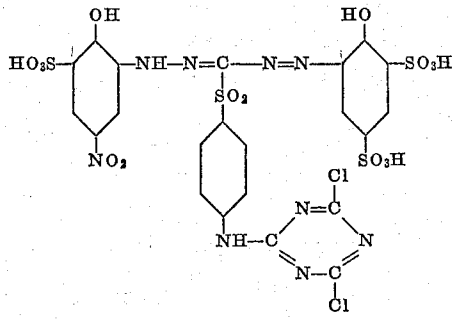
Ex. No.	—A_7—NH (I)	A_8—NH_2 (II)	Y_3— (III)	R=derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
137	2-hydroxy-3-amino-5-sulfo-phenyl.	1-aminobenzene-4-sulfonic acid.	Methylsulfonyl	2,4,5,6-tetrachloropyrimi-dine.	Ni	Reddish gray.
138	do	1-aminonaphthalene-4-sulfonic acid.	4-methylphenyl-1-sulfonyl	2-(4'-sulfo-phenylamino)-4,6-dichloro-1,3,5-triazine.	Ni	Do.
139	do	2-aminonaphthalene-4,8-disulfonic acid.	Phenylsulfonyl	Chloracetyl chloride	Cu	Blue.
140	do	1-aminobenzene-2-sulfonic acid.	Acetyl	2,4,6-trichloropyrimidine	Cu	Reddish blue.
141	2-hydroxy-3-sulfo-5-amino-phenyl.	do	Propionyl	2-amino-4,6-dichloro-1,3,5-triazine.	Cu	Gray.
142	do	1-aminonaphthalene-3,6-disulfonic acid.	Butyryl	β-Chloropropionyl chloride	Cu	Do.
143	do	2-aminonaphthalene-3,6-disulfonsaure.	Ethylsulfonyl	2,4-dichloro-5-chloromethyl-6-methylpyrimidine.	Cu	Bluish gray.
144	2-hydroxy-5-amino-phenyl	2-aminonaphthalene-3,6,8-trisulfonic acid.	do	2-methylamino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
145	do	1-aminobenzene-3-sulfomic acid.	4-chlorophenyl-1-sulfonyl	2-(2',5'-disulfo-phenyl-amino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
146	do	2-aminonaphthalene-5,7-disulfonic acid.	Naphthyl-1-sulfonyl	2-(2'-sulfo-ethylamino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
147	2-carboxy-4-amino-phenyl	2-aminonaphthalene-6,8-disulfonic acid.	Naphthyl-2-sulfonyl	2-(N-methyl-N-2'-sulfo-ethyl-amino)-4,6-di-chloro-1,3,5-triazine.	Cu	Red.
148	do	1-aminonaphthalene-3,6,8-trisulfonic acid.	n-Propylsulfonyl	β-Chloropropionyl	Cu	Red.
149	do	1-aminobenzene-2,5-disulfonic acid.	Methylsulfonyl	2,4,6-trichloro-5-carboxy-methylpyrimidine.	Cu	Red.
150	2-hydroxy-5-amino-phenyl	do	4-methoxyphenyl-1-sulfonyl	Chloracetyl chloride	Cu	Blue.
151	do	do	Phenylsulfonyl	Cyanuric chloride	Cu	Do.
152	do	do	do	2,4,5,6-tetrachloropyrimi-dine.	Cu	Do.

Table 3—Continued

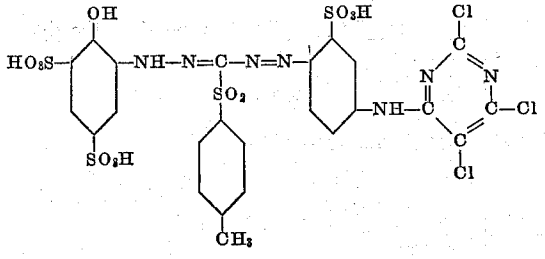
Ex. No.	—A_7—NH (I)	A_8—NH_2 (II)	Y_3— (III)	R=derived from— (IV)	Metal (V)	Shade of Dyeing on Cotton or Wool (VI)
153	2-hydroxy-3-sulfo-5-amino-phenyl.	1-aminobenzene-2,5-disulfonic acid.	5,6,7,8-tetrahydro-napthyl-1-sulfonyl.	2,4,6-trichloropyrimidine	Cu	Blue.
154	2-hydroxy-3-amino-5-sulfo-phenyl.	do	1,1'-diphenylyl-4-sulfonyl	do	Cu	Do.
155	do	2-aminonaphthalene-2,6,8-trisulfonic acid.	5,6,7,8-tetrahydro-naphthyl-2-sulfonyl.	2,4,5,6-tetrabromo-pyrimidine.	Cu	Do.
156	do	2-aminonaphthalene-6-sulfonic acid.	4-methylphenyl-1-sulfonyl	2-(2'-hydroxyethyl-amino)-4,6-dichloro-1,3,5-triazine	Cu	Do.
157	do	1-aminonaphthalene-5-sulfonic acid.	do	α-Chloracrylyl chloride	Cu	Do.
158	do	1-aminonaphthalene-6(7)-sulfonic acid.	do	2-carboxymethylamino-4,6-dichloro-1,3,5-triazine.	Cu	Do.
159	2-hydroxy-3-sulfo-5-amino-phenyl.	Aminobenzene	Methylsulfonyl	2,4,6-trichloropyrimidine	Cu	Do.
160	do	1-aminonaphthalene	do	2-(3'-sulfo-phenyl-amino)-4,6-dichloro-1,3,5-triazine.	Cu	Do.
161	do	2-aminonaphthalene-5-sulfonic acid.	n-Butylsulfonyl	2,4,6-tribromopyrimidine	Cu	Do.
162	do	1-aminobenzene-2,4-disulfonic acid.	n-Amylfulfonyl	Cyanuric bromide	Ni	Reddish gray.
163	do	1-aminobenzene-3-sulfonic acid.	2-chlorophenyl-1-sufonyl	2-amino-4,6-dibromo-1,3,5-triazine.	Cu	Blue.
164	do	do	4-ethylphenyl-1-sufonyl	2-(3'-sulfophenylamino)-4,6-dibromo-1,3,5-triazine	Cu	Do.
165	do	do	4-methylphenyl-1-sulfonyl	Bromoacetyl chloride	Cu	Do.
166	do	do	do	β-Bromopropionyl chloride	Cu	Do.
167	do	do	do	2,4-dichloro-6-carbomethoxy pyrimidine.	Cu	Do.
168	do	do	do	2,4-dichloro-5-chloromethyl-pyrimidine.	Cu	Do.

Formulae of representative dyes of the foregoing examples are as follows:

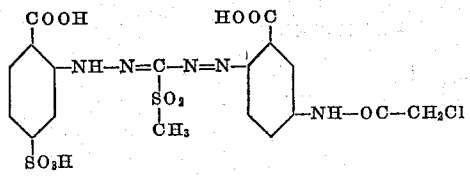
Example 1.—The 1:1 copper complex compound of



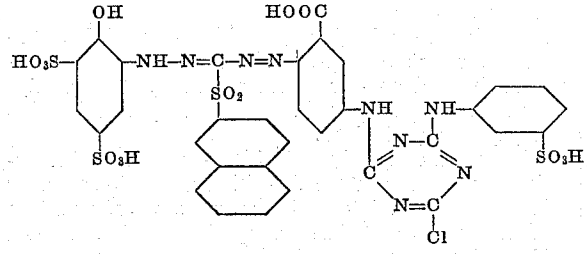
Example 2.—The 1:1 copper complex compound of



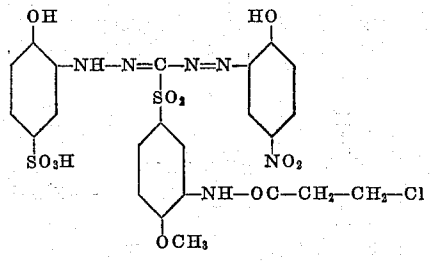
Example 3.—The 1:1 copper complex compound of



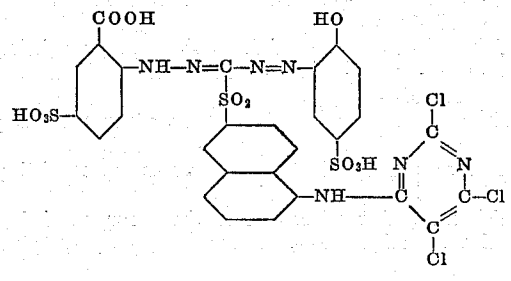
Example 4.—The 1:1 copper complex compound of



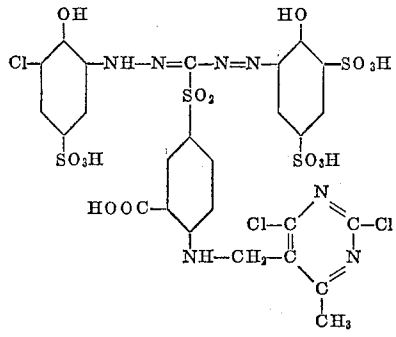
Example 5.—The 1:1 copper complex compound of



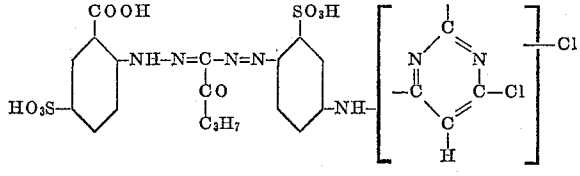
Example 6.—The 1:1 copper complex compound of



Example 29.—The 1:1 nickel complex compound of



Example 112.—The 1:1 copper complex compound of



The formula of Example 112 indicates that the dye is a mixture of the 4,6-dichloro-pyrimidyl-2-amino dye and of the 2,6-dichloro-pyrimidyl-4-amino dye.

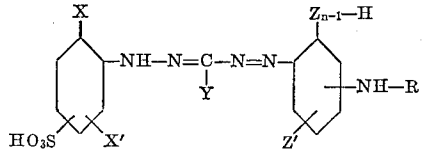
On condensing 2,4,5-trichloro- or 2,4,5-tribromopyrimidine with an amino dye, a mixture of the 2,5-dichloro- or 2,5-dibromopyrimidyl-4-amino dye and of the 4,5-dichloro- or 4,5-dibromopyrimidyl-2-amino dye is very probably obtained.

Similarly on condensing 2,6-dichloro- or 2,6-dibromopyrimide or their derivatives with an amino dye, a mixture of the 2-chloro- or 2-bromopyrimidyl-6-amino dye and of the 6-chloro- or 6-bromopyrimidyl-2-amino dye is very probably obtained.

The derivatives of 2,4,6-trichloro- or 2,4,6-tribromopyrimidine bearing in the 5-position a substituent other than halogen give mixtures similar to those produced with 2,4,6-trichloro- or 2,4,6-tribromopyrimidine (cf. formula of Example 112), whereas 2,4,6-trichloro-5-chloromethyl-pyrimidine and 2,4,6-tribromo-5-bromomethyl-pyrimidine react in the same manner as 2,4-dichloro-5-chloromethyl-pyrimidine and 2,4-di-chloro-5-chloromethyl-6-methyl-pyrimidine (cf. formula of Example 29).

Having thus disclosed the invention what I claim is:

1. A dyestuff selected from the group consisting of the 1:1-copper and 1:1 nickel complex compounds of dyestuffs of the formula



wherein

X is a member selected from the group consisting of —OH and —COOH in ortho position to the —NH—N= bridge,

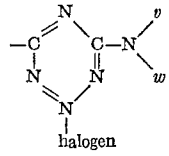
Z is a member selected from the group consisting of —O— and —COO— in ortho position to the —N=N— bridge,

X′ is a member selected from the group consisting of H, —SO_3H, Cl, —NO_2 and —COOH,

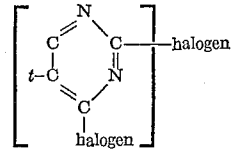
Z′ is a member selected from the group consisting of H, —CH_3 and —SO_3H,

Y is a member selected from the group consisting of lower alkyl-CO—, lower alkyl-SO_2—, phenyl-SO_2—, chlorophenyl-SO_2—, lower alkylphenyl-SO_2—, nitrophenyl-SO_2—, carboxyphenyl-SO_2—, lower alkoxyphenyl-SO_2— and naphthyl—SO_2—.

R is a member selected from the group consisting of halogenoacetyl, halogenopropionyl, dihalogenopropionyl, halogenoacrylyl, 4,6-dihalogeno-1,3,5-triazinyl-2-, 2,4-dihalogeno-6-methyl-pyrimidyl-5-methylene, monohalogeno-1,3,5-triazinyl of the formula



and dihalogenopyrimidyl of the formula



wherein

halogen has an atomic weight between 35 and 81,

v is a member selected from the group consisting of hydrogen, lower alkyl, and lower hydroxyalkyl,

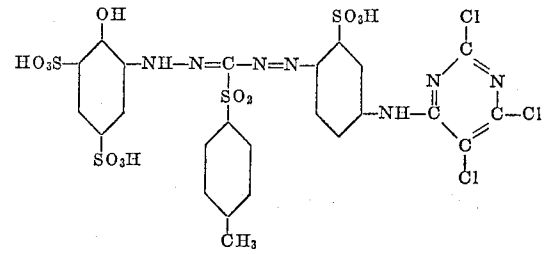
w is a member selected from the group consisting of hydrogen, lower alkyl, lower hydroxyalkyl, lower alkoxyalkyl, lower carboxyalkyl, lower sulfoalkyl, lower hydroxysulfoalkyl, phenyl, carboxyphenyl, sulfophenyl and disulfophenyl,

t is a member selected from the group consisting of hydrogen, chlorine, bromine, methyl, allyl, carboxy and carboxymethyl,

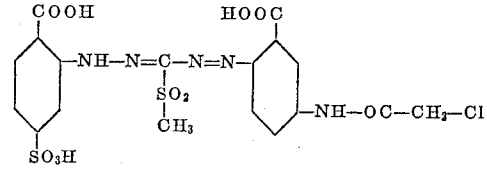
n is one of the integers 1 and 2,

and the whole dye molecule bears one to four SO_3H groups.

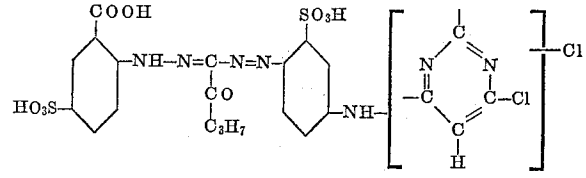
2. The 1:1 copper complex compound of the dyestuff of the formula



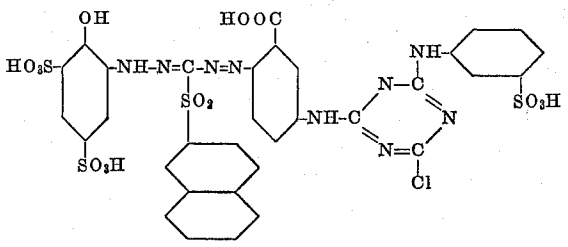
3. The 1:1 copper complex compound of the dyestuff of the formula



4. The 1:1 copper complex compound of the dyestuff of the formula



5. The 1:1 copper complex compound of the dyestuff of the formula



References Cited by the Examiner

UNITED STATES PATENTS

3,041,328	6/62	Kraus et al.	260—146
3,068,219	12/62	Beffa et al.	260—146

FOREIGN PATENTS

246,475 9/47 Switzerland.

OTHER REFERENCES

Nineham: Chem. Review, vol. 55, No. 2, April 1955, pp. 355–483.

Wegmann: Textile Praxis, October 1958, pp. 1056–1058.

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