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PROCESS FOR THE PRODUCTION OF FAST TINTS ON CELLULOSIC FIBERS

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8 Claims. (Cl. 8—42)

This invention is based on the observation that fast tints on cellulose fibers, for instance cotton and artificial silk consisting of regenerated cellulose, which are produced by dyeing with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble or insoluble in water and in dilute alkalies, and after-treating the dyeings with agents that yield metal in complex union, can be so produced by dyeing and after-treating the material in one and the same bath.

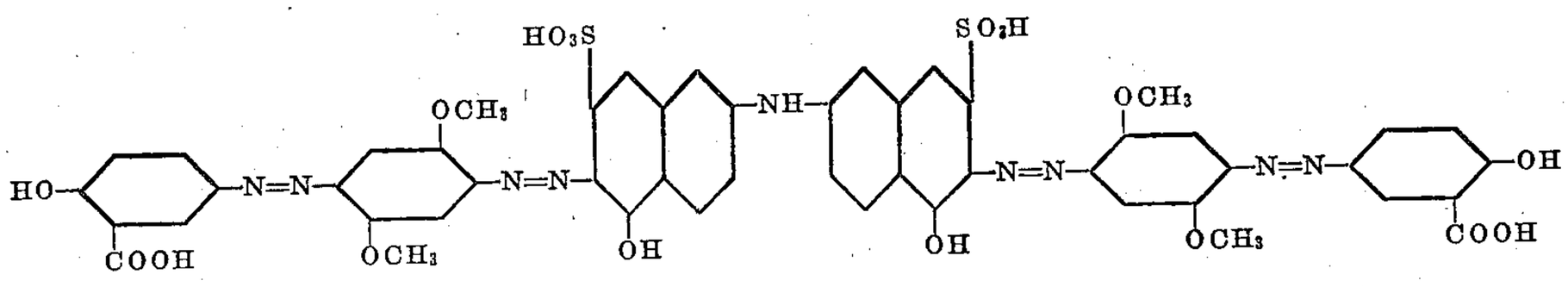
For the purpose of this invention the expression "direct cotton azo-dyestuffs" includes dis- and polyazo-dyestuffs which have affinity for cellulosic fibers. Such dyestuffs are obtainable from diazotized aromatic amines which lend dyestuffs affinity for cellulose fibers and any coupling component, for instance phenols, naphthols and amines of the benzene or naphthalene series; or they may be obtained by coupling any diazotized aromatic amine with a coupling component which lends dyestuffs affinity for cellulosic fibers. Moreover, such direct cotton dyestuffs are produced by using a diazo-component which imparts to the dyestuffs affinity for cellulosic fibers and a coupling component which has the same effect. The choice of the components used in making the direct cotton dyestuffs should be such that the direct cotton dyestuff contains at least one group capable of binding metal in complex union. Components of this kind are, for example, the diazo-compounds which contain in ortho-position to the diazo-group a hydroxyl-, carboxyl- or alkoxy-group, or which contain the salicyclic acid grouping, or coupling components which carry the salicylic acid grouping as substituents. The direct cotton dyestuffs which serve as parent materials in the invention must fulfill the condition that their complex metal compounds are sparingly soluble or insoluble in water and in dilute alkalies. This condition is, for example, fulfilled if the direct cotton dyestuff contains only a few or no groups which impart solubility, for example sulfonic acid or carboxylic acid groups, and therefore is already sparingly soluble or insoluble as such, or if it contains groups imparting solubility, such as the salicylic acid group, if desired in addition to sulfonic acid groups, which unite with the metal and thereby lose their property of imparting solubility.

It will be seen from the foregoing statement that for the construction of the direct cotton dyestuffs, in addition to the usual aromatic amines of the benzene and naphthalene-series which may contain groups capable of binding metal in complex union, as diazo-components and, besides the usual phenols, naphthols and amines, as coupling components there come particularly into consideration direct-dyeing components, such as benzidine and stilbene derivatives, as well as ureas and thioureas of arylene-diamines, also acetoacetic acid arylides, pyrazolones, amino-naphthols and their sulfonic acids.

The dyeing of cellulosic fibers with direct cotton dyestuffs, the complex metal compounds of which are sparingly soluble or insoluble in water and in dilute alkalies, or with mixtures of such dyestuffs, may be conducted in the manner usual for direct cotton dyestuffs, that is to say the dye-bath may contain Glauber's salt, preferably also alkali, such as sodium carbonate, and the dyeing may continue, for example, for 1 to 1½ hours at about 80–100° C. In many cases it has proved to be of advantage to add to the dye-bath a dispersing agent, a wetting agent or an emulsifying agent, that is to say the dyeing may be conducted in presence of capillary active anions or cations or capillary active substances which are not ionized. Such agents or substances are, for example, ammonia and organic derivatives of ammonia, for instance armines of the aliphatic, hydroaromatic and aromatic series, which also may contain hydroxyl-groups or other substituents for example, pyridine, amines, alkylamines, methanolamine, ethanolamine, cyclohexylethanolamine, butylethanolamine), sulfonic acids of the benzene- or naphthalene-series, which may contain alkyl-groups; alcohols, for instance glycerine; alcohol sulfuric ester salts, soluble condensation products from fatty acids of high molecular weight or ethylene oxide, and amines, oxyoleic acids, sulforicinates, glue, sulfite cellulose solution, dextrin, albuminous degradation products, for instance, protalbinic acid or lysalbinic acid; organic compounds of high molecular weight, for instance polymerisation products of aldehydes and soluble degradation products of cellulose.

The after-treatment of the dyeings with agents yielding metal in complex union in the same bath in which the dyeing has occurred may be conducted by the generally usual methods, that is

to say, the agent yielding metal, for instance chromium, cobalt, nickel, aluminium, manganese, zinc, vanadium, titanium and particularly copper,



is added and the bath is maintained for ¼ to 1 hour at about 90–100° C.

When dyestuffs are used which are not fully exhausted in the bath, it is advantageous to use such agents yielding metal in complex union as are stable to weak alkalies, for example the sodium carbonate present in the dye-bath. Agents of this kind are, for example, the products of the reaction of ammonia or an aliphatic amine, such as triethanolamine, diethanolamine or ethylene diamine, with an ordinary agent yielding copper; the heavy metal salts of aminocarboxylic acids, such as the copper salt of glycocoll; and the aqueous solutions of alkaline reaction which are produced by mixing the product of the action of an ordinary agent yielding metal on an aliphatic hydroxycarboxylic acid (for instance lactic acid, tartaric acid, glycocollic acid, tartronic acid, maleic acid, dihydroxytartaric acid, citric acid, saccharic acid, gluconic acid and heptonic acid) with bases, for instance, caustic soda solution, caustic potash solution, ammonia or an ammonia derivative, for instance methanolamine or ethanolamine, until the reaction is alkaline.

When dyeing is conducted with a dyestuff which is practically completely exhausted from the bath, it is of advantage to neutralise the alkali existing in the dye-bath, for instance sodium carbonate, and to conduct the after-treatment with the usual agents yielding metal, for instance a chloride, sulfate, formate, acetate, oxalate, benzene sulfonate or naphthalene sulfonate of the metal in question.

In many cases the same dispersing, wetting or emulsifying agent used during the dyeing may be applied also in the after-treatment.

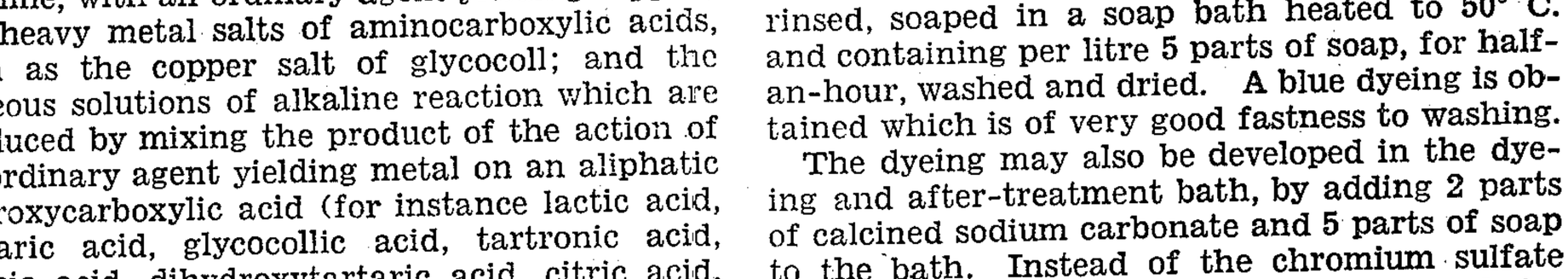
With or without essentially influencing the results of the dyeing it is frequently possible in the process of the invention also to wash or develop the after-treated dyeings with soap or soap and sodium carbonate in the same bath in which the dyeing and after-treatment have been conducted.

The dyeings obtainable by the invention have very good fastness; it is particularly of value that these dyeings, produced in a very simple manner, do not bleed on to undyed cotton washed together with the dyed goods, not merely at 50° C. in a bath containing per litre 5 parts of soap and 2 parts of sodium carbonate, but also when washed at 70° C. or even at 90–100° C.

The following examples illustrate the invention, the parts being by weight.

Example 1

Into a dye-bath consisting of 3000 parts of water, 2 parts of calcined sodium carbonate and 1 part of sodium salt of the dyestuff of the formula

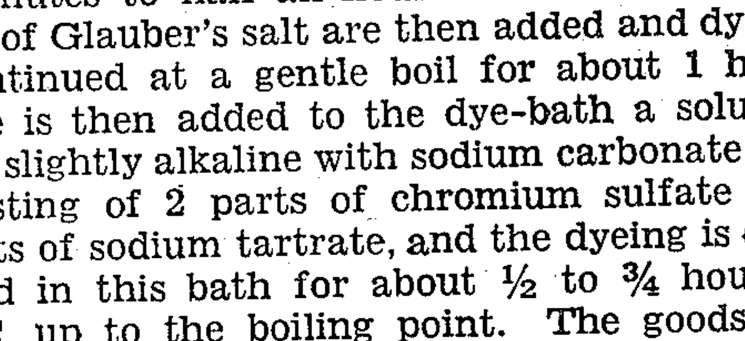


there are entered, at 40–50° C., 100 parts of cotton, the temperature of the bath is raised within 20 minutes to half-an-hour to 90–95° C., 30–40 parts of Glauber's salt are then added and dyeing is continued at a gentle boil for about 1 hour. There is then added to the dye-bath a solution made slightly alkaline with sodium carbonate and consisting of 2 parts of chromium sulfate and 2 parts of sodium tartrate, and the dyeing is continued in this bath for about ½ to ¾ hour at 95° C. up to the boiling point. The goods are rinsed, soaped in a soap bath heated to 50° C. and containing per litre 5 parts of soap, for half-an-hour, washed and dried. A blue dyeing is obtained which is of very good fastness to washing.

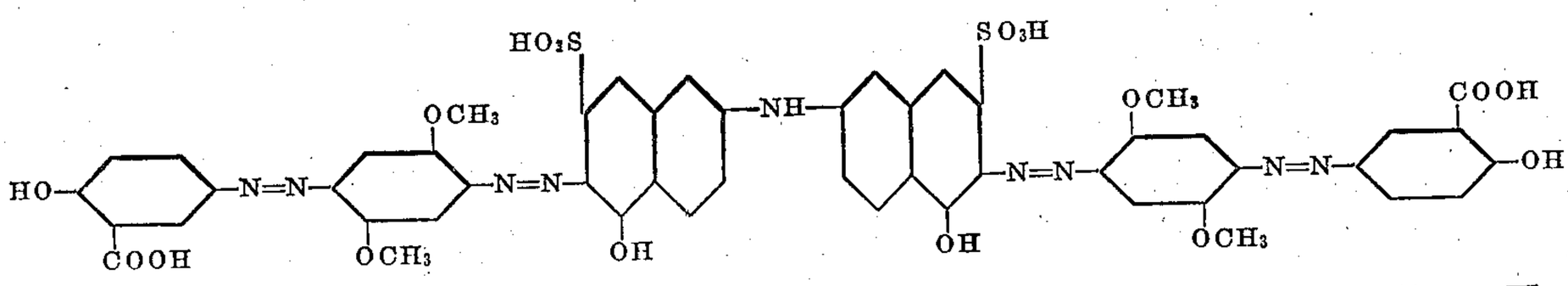
The dyeing may also be developed in the dyeing and after-treatment bath, by adding 2 parts of calcined sodium carbonate and 5 parts of soap to the bath. Instead of the chromium sulfate another soluble chromium salt may be used, for instance chromium acetate, chromium formate, chromium lactate or chromium benzene-sulfonate.

Example 2

Into a dye-bath consisting of 3000 parts of water, 2 parts of calcined sodium carbonate and 0.5 part of the dyestuff of the formula



as well as 0.5 part of the dyestuff of the formula

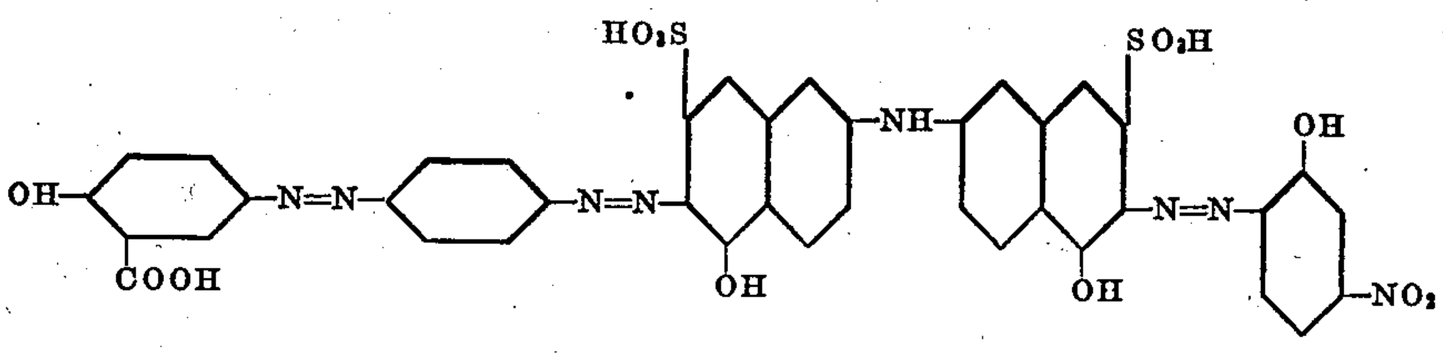


are entered at 40° C. 100 parts of cotton. The temperature is raised within 20 minutes to half-an-hour to 90–95° C., and then 30–40 parts of Glauber's salt are added and dyeing continued at a gentle boil for about 1 hour. There is then added a solution, made feebly alkaline with sodium carbonate, containing 1–2 parts of copper sulfate crystals and 2 parts of sodium tartrate and dyeing is continued in the same bath for about half-an-hour at 95° C. up to the boiling point. The goods are rinsed and soaped in a soap-bath, heated to 50° C. and containing per litre 5 grams of soap, for about half-an-hour. They are then washed and dried. A green dyeing is obtained of excellent fastness to washing.

Example 3

Into a dye-bath consisting of 3000 parts of

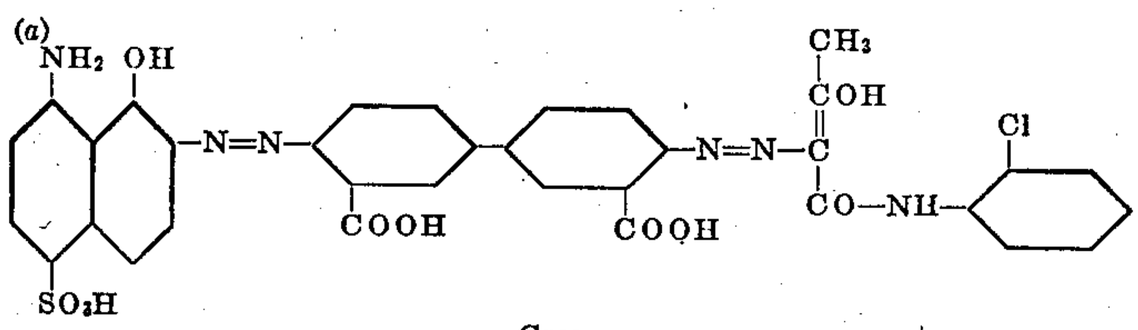
water, 2 parts of calcined sodium carbonate and 1 part of the dyestuff of the formula



are entered, at 40–50° C., 100 parts of cotton; the temperature is raised within 20 minutes to half-an-hour to 90–95° C., 30–40 parts of Glauber's salt are added and dyeing is continued at a gentle boil for about an hour. There are then added to the dyebath a solution feebly alkaline with sodium carbonate containing 1–2 parts of copper sulfate crystals and 2 parts of sodium tartrate, and the goods are treated in the same bath at 95° C. up to the boiling point, for about half-an-hour. At the end of this time the dye-bath is practically completely exhausted. The goods are then handled in a soap bath at 50° C., containing 5 parts of soap per litre, for half-an-hour. Washing and drying follow. The dyeing produced is blue-violet of very good fastness to washing.

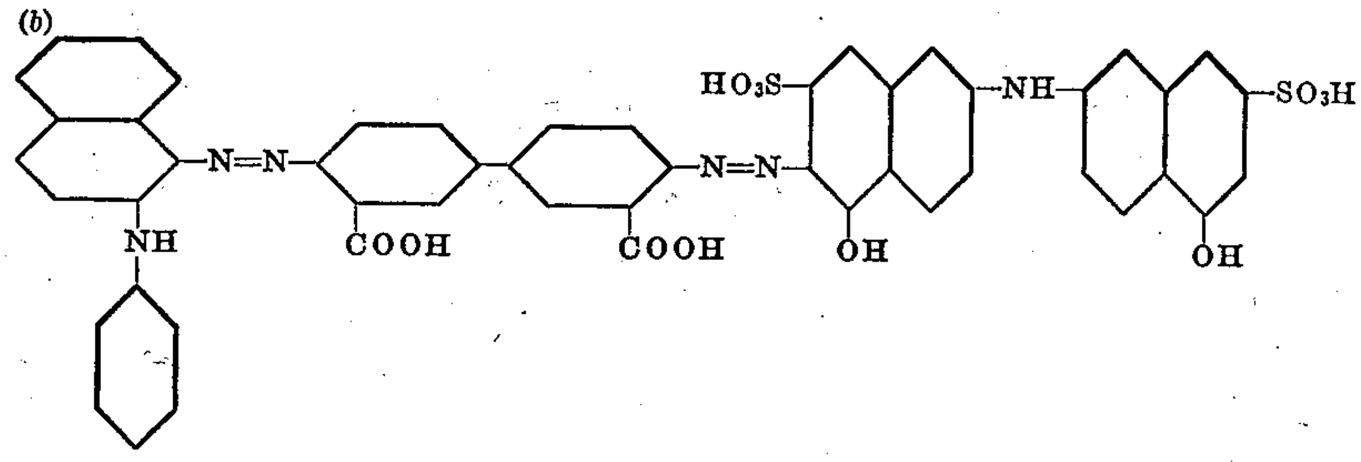
If instead of the dyestuff used in this example there is used one of the dyestuffs represented by the following formulae there are obtained very fast dyeings having the shades indicated:

(a)



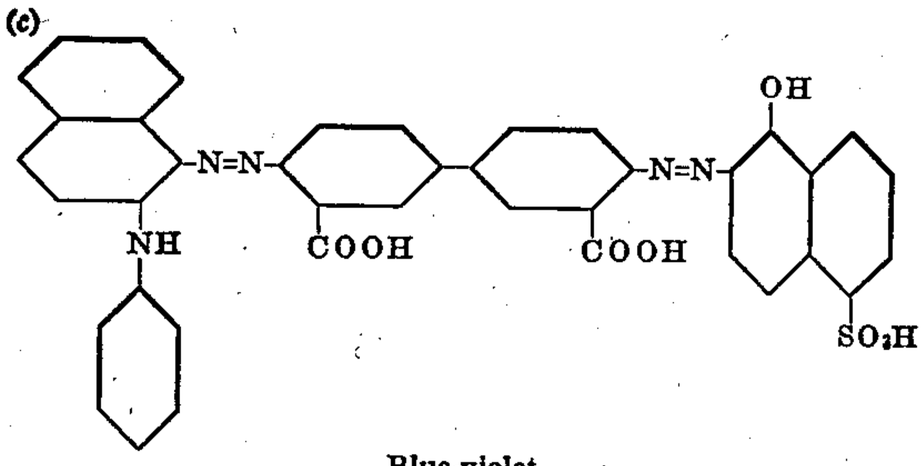
Green.

(b)



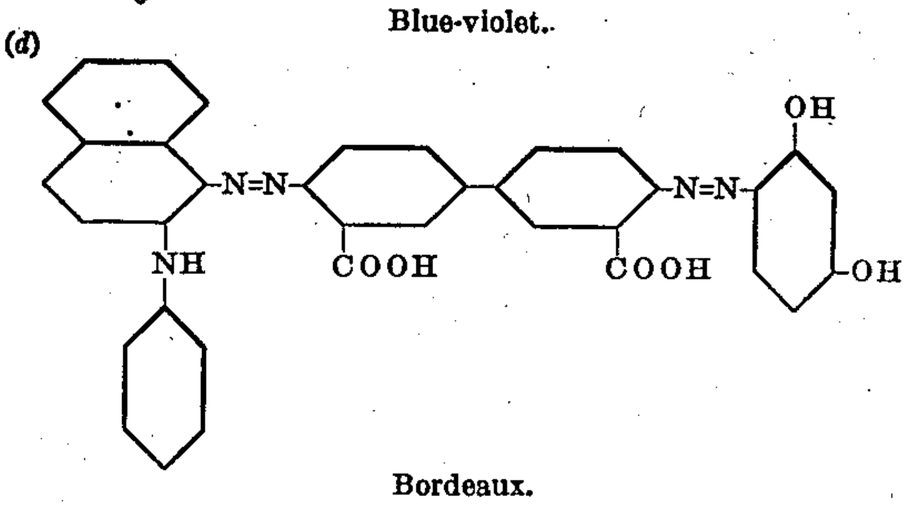
Blue.

(c)



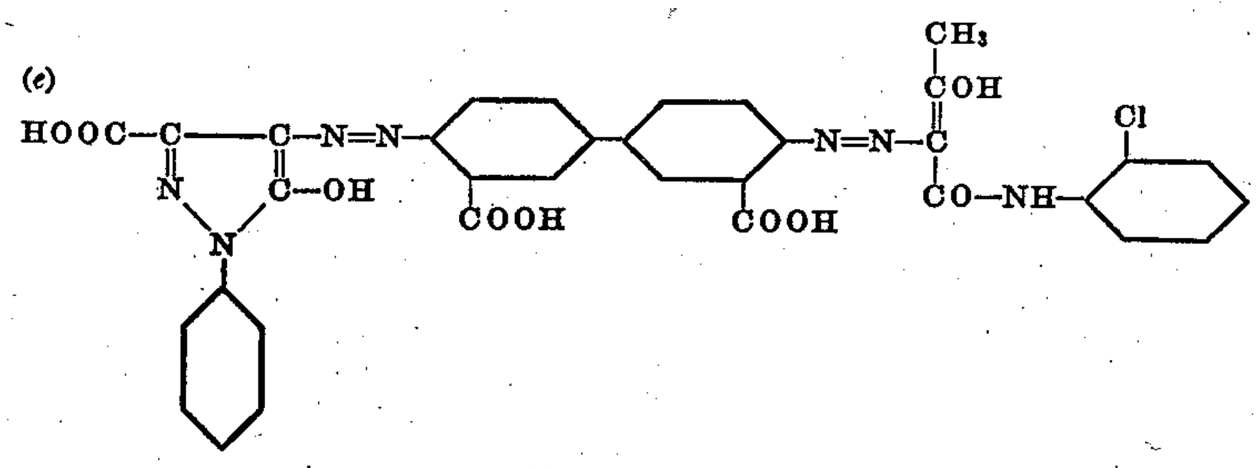
Blue-violet.

(d)



Bordeaux.

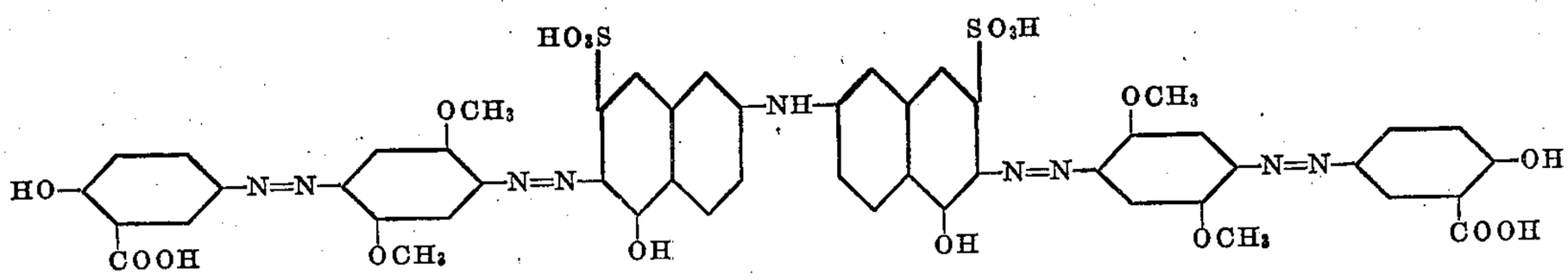
(e)



Yellow-brown.

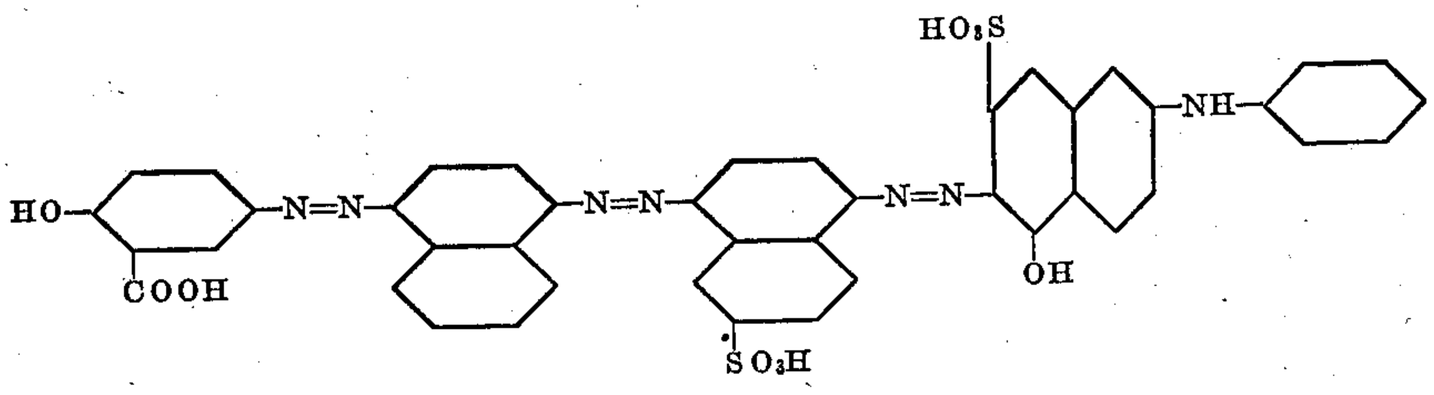
Example 4

Into a dye-bath consisting of 3000 parts of water, 2 parts of calcined sodium carbonate and 0.25 part of the salt-free dyestuff of the formula

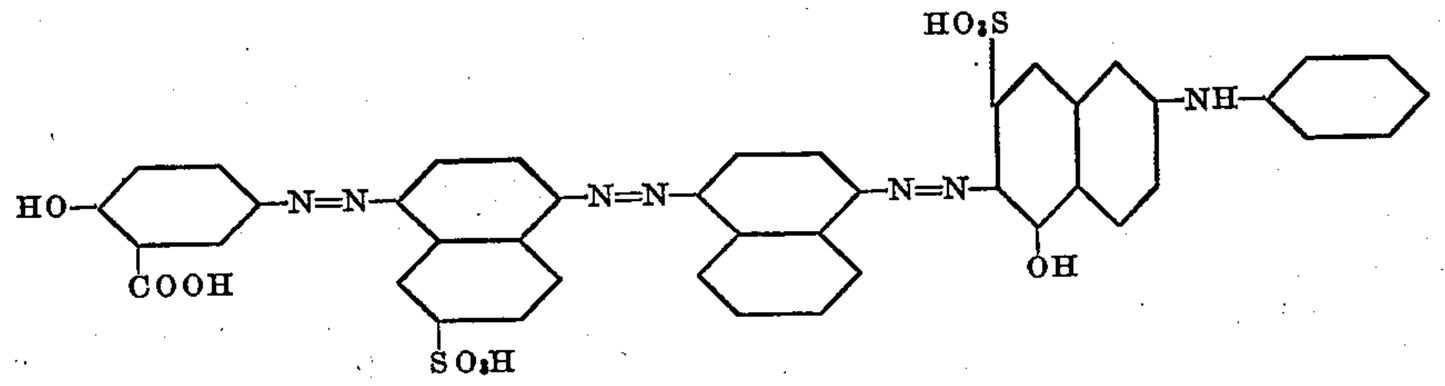


there are introduced, at 40–50° C., 100 parts of cotton; the temperature is raised within 20 minutes to half-an-hour to 90–95° C., 30–40 parts of Glauber's salt are added and dyeing is continued at the gentle boil for about 1 hour. There is then added to the dye-bath a solution made feebly alkaline with sodium carbonate, containing 1–2 parts of copper sulfate crystals and 2 parts of sodium tartrate, and the goods are treated in the same bath for about half-an-hour at 95° C. up to boiling point. They are then rinsed and handled in a soap bath at 50° C., containing 5 parts of soap per litre, for half-an-hour and finally washed and dried. The dyeing is a greenish-blue of very good fastness to washing.

If instead of the dyestuff used in this Example there is used the dyestuff of the formula



or the dyestuff of the formula



there are obtained blue-grey dyeings which are very fast to light.

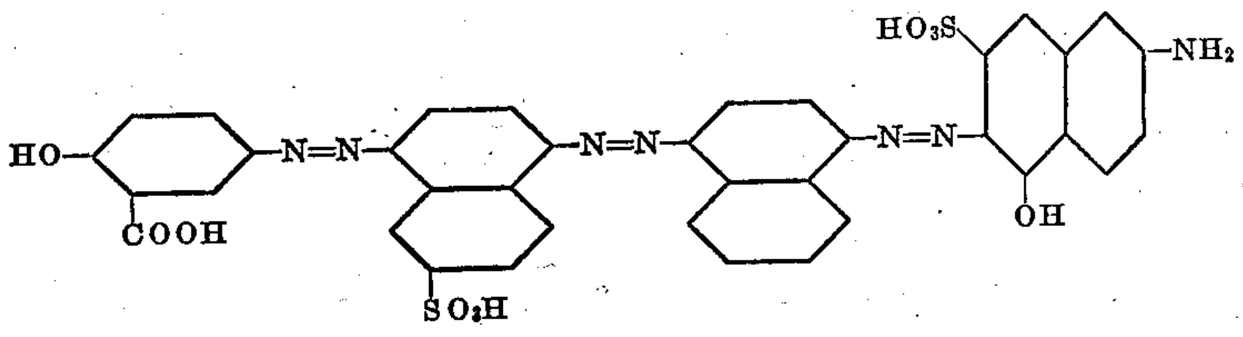
Example 5

1 part of the dyestuff obtainable as described in the first paragraph of Example 9 of U. S. specification No. 1,861,323 is dissolved in 2000 parts of water with the addition of 2 parts of sodium carbonate and 30 parts of Glauber's salt. 100 parts of cotton are introduced at 40° C. and are dyed for 45 minutes at 90–100° C. Then an aqueous solution of 1 part of copper glycocollate is added and dyeing is continued for 15–30 minutes longer at 80–100° C. No flocculation is visible in the dye-bath. After rinsing and drying there is obtained a vivid powerful brown-red dyeing having excellent fastness to washing at 75° C. White effects remain well reserved.

The dyeing can be rendered still brighter by treatment for ½ hour at 50° C. in a bath containing 5 grams of soap per litre.

Instead of copper glycocollate, copper ethylglycocollate or copper diethylglycocollate can be used with the same result.

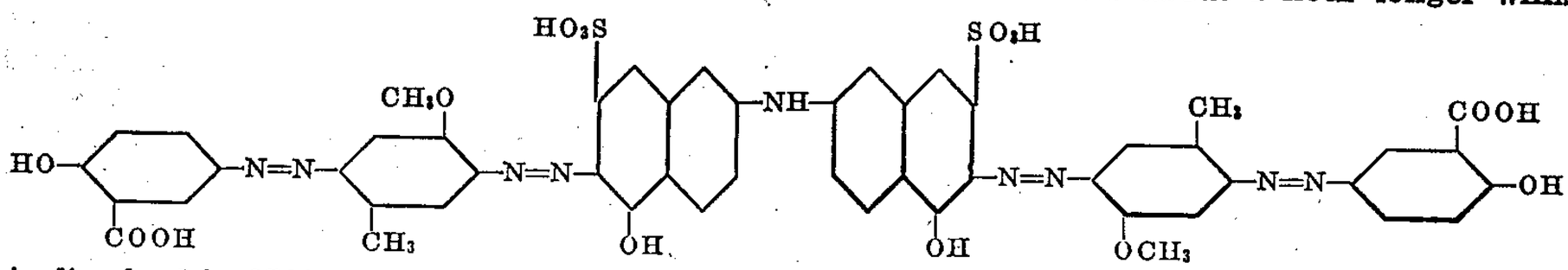
If instead of the dyestuff used in this example there is used the dyestuff obtained by the action of para-amino-salicylic acid on 4:4′-dinitrostilbene-2:2′-disulfonic acid in the presence of caustic alkali solution at a raised temperature, there is obtained a fast orange-brown dyeing. If there is used the dyestuff obtainable in an analogous manner from para-amino-phenylene-azo-ortho-cresotinic acid and 4:4′-dinitrostilbene-2:2′-disulfonic acid or that obtainable from para-amino-salicylic acid→α-naphthylamine and 4:4′-dinitrostilbene-2:2′-disulfonic acid there are obtained brown dyeings. By using the dyestuff of the formula



there is obtained a very fast blue dyeing.

Example 6

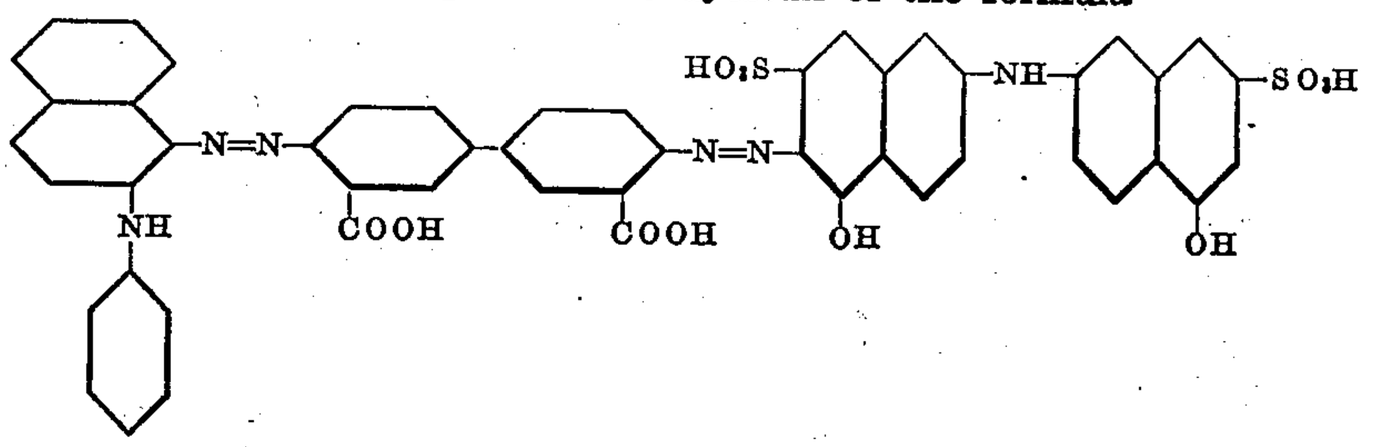
1 part of the tetrakisazo dyestuff of the formula



is dissolved in 2500 parts of water and 2 parts of calcined sodium carbonate and 30 parts of Glauber's salt are added. 100 parts of cotton are introduced at 40° C. and dyed for ¾ hour at 90–100° C. There is then added a copper salt solution prepared by dissolving 1 part of copper sulfate in water, adding 0.8 part of tartaric acid and then neutralizing the whole with sodium carbonate. Dyeing is continued for 15–30 minutes longer and the material is then rinsed in cold water. There is obtained a vivid blue dyeing of very good fastness to washing.

Example 7

0.1 part of the dyestuff Cotton Yellow G



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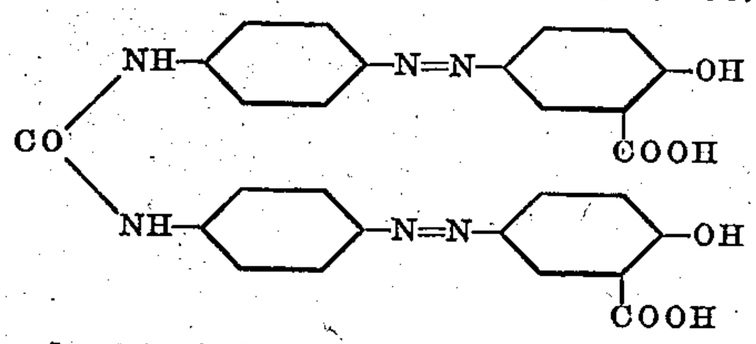


is dissolved in 200 parts of water with the addition of 0.2 part of calcined sodium carbonate and 3 parts of Glauber's salt. 10 parts of cotton are introduced at 30–40° C., the bath is quickly brought to the boil and dyeing is conducted for 45 minutes at 95–100° C. Then there is added a solution of triethanolamino-cupri-sulfate, which is prepared by adding to an aqueous solution of 0.2 part of copper sulfate sufficient triethanolamine to produce a deep blue solution. Dyeing is continued for 20–30 minutes longer at 80–100° C. and the material is then rinsed with cold water. There is obtained a vivid yellow dyeing of very good fastness to light and to washing. White effects remain well reserved when the material is washed at 75° C. The dyeing thus obtained is considerably purer and brighter than one prepared by conducting the after-coppering in a fresh bath with copper sulfate.

Example 8

100 parts of cotton are introduced at 40–50° C. into a dye bath consisting of 3000 parts of water, 2 parts of calcined sodium carbonate and 1.5 part of the dyestuff obtained by the action of para-phenylenediamine→salicylic acid on 4:4′-dinitro-stilbene-2:2′-disulfonic acid in presence of caustic alkali solution at a raised temperature. The temperature of the bath is raised within 20–30 minutes to 90–95° C., 30–40 parts of crystalline Glauber's salt are added and dyeing is continued for about 1 hour longer whilst the bath is maintained gently boiling. Then there is added to the dye bath the quantity of acetic acid required for neutralization of the sodium carbonate, then 2 parts of copper sulfate, and the treatment is continued at about 90–95° C. for 20–30 minutes longer. The material is rinsed, soaped in a fresh bath containing 5 grams of Marseilles soap per litre for about ½ hour at 50° C., rinsed and dried. There is obtained a brown-red dyeing of very good fastness to washing.

Example 9

100 parts of cotton are introduced at 40–50° C. into a dye-bath consisting of 3000 parts of water, 2 parts of calcined sodium carbonate and 1.5 part of the dyestuff of the formula

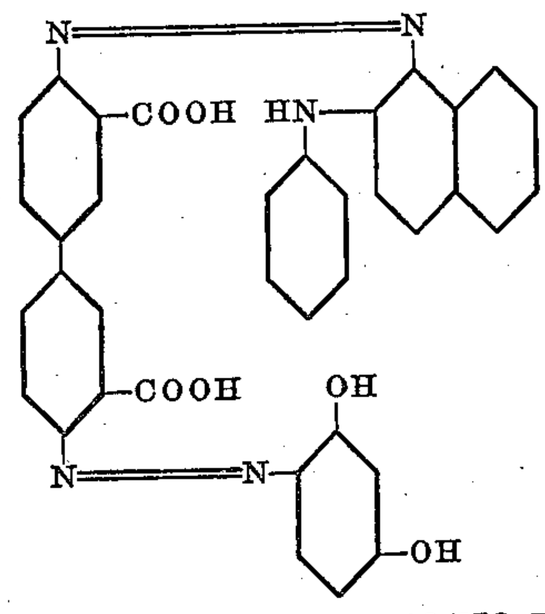
the temperature of the bath is raised within 20–30 minutes to 90° C., 30–40 parts of crystalline Glauber's salt are added and dyeing is continued for about 1 hour longer whilst the bath is maintained gently boiling. Then there is added to the dye bath the quantity of acetic acid required for neutralizing the sodium carbonate and then 2 parts of crystalline copper sulfate; then the goods are reintroduced into the bath and treated therein at about 90–95° C. for about 20–30 minutes, after which they are rinsed in a fresh bath and dried. There is obtained a reddish-blue dyeing of very good fastness to washing.

Example 10

1.5 parts of the azo-dyestuff obtained as described in U. S. specification No. 1,861,323, Example 9, 4th paragraph, are dissolved in 2000–2500 parts of water and 30 parts of Glauber's salt are added. 100 parts of cotton are introduced into the bath, which is brought to the boil within 20 minutes, whereafter dyeing is continued for about ¾ hour. Then the dye liquor is allowed to cool to about 80° C. and there is added a triethanolamino-cupri-sulfate solution which is prepared by dissolving 2 parts of crystalline copper sulfate in 6 parts of water and 6 parts of triethanolamine. Dyeing is continued for 20–30 minutes at 80° C., and the material is then rinsed in a fresh bath. Finally, the material is handled for about ½ hour in a soap bath having a temperature of 50° C. and containing 5 grams of Marseilles soap per litre, then rinsed and dried. There is obtained a brown-red shade of excellent properties of fastness, particularly towards light and washing.

Example 11

1.5 parts of the dyestuff of the formula

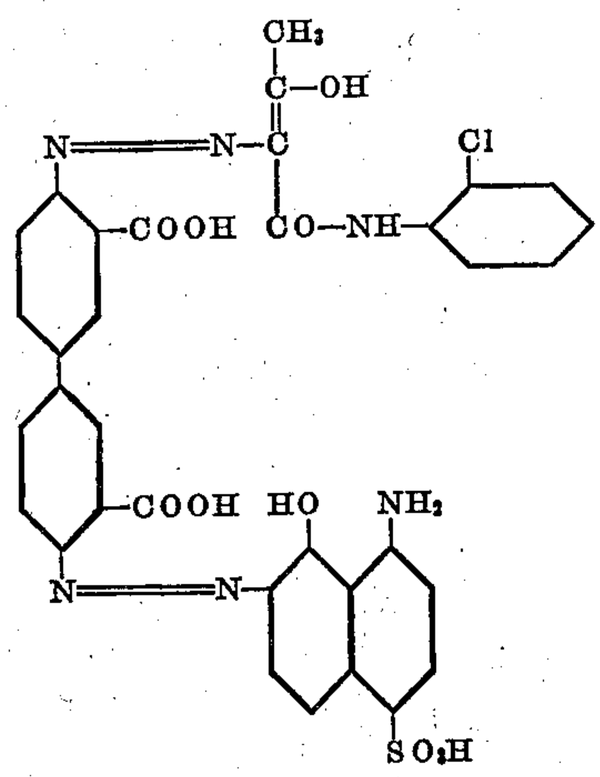


(see German specification No. 410,758, Example 5) are dissolved in 2000 parts of water with addition of 2 parts of sodium carbonate and 1 part of the cyclohexyl ester of sulfophthalic acid. 100 parts of cotton are introduced into the path at 30–40° C., the bath is brought to the boil, 30 parts of crystalline Glauber's salt are added and dyeing is continued for 45 minutes at 90–100° C. Then there are added 200 parts of a copper solution, which is neutral or only weakly alkaline and contains per litre 10 grams of crystallized copper sulfate, 17.6 grams of saccharic acid and 8.64 grams of caustic soda, and dyeing is continued for about 30 minutes longer at 90–100° C. Then the material is rinsed, washed for about 20–30 minutes at 75° C. in a bath containing per litre 2 grams of calcined sodium carbonate and 5 grams of Marseilles soap per litre, again rinsed and dried. There are obtained violet-brown shades of excellent fastness to washing.

Similar results are obtained if in this example trioxyglutaric acid is used instead of saccharic acid.

Example 12

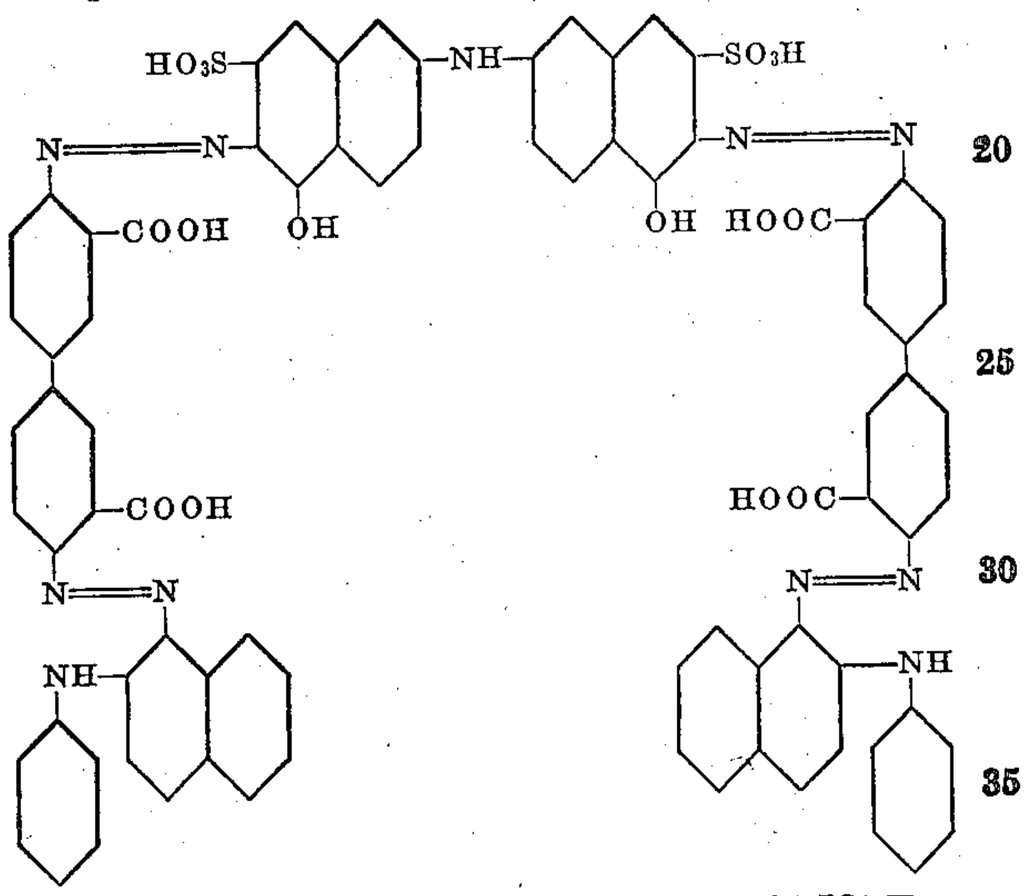
1.5 parts of the dyestuff of the formula



(compare German specification No. 410,758, Example 1) are dissolved in 2000 parts of water with addition of 2 parts of sodium carbonate. 100 parts of cotton are introduced at 30–40° C., the bath is brought to the boil, 30 parts of crystalline Glauber's salt are added and dyeing is continued for 45 minutes at 90–100° C. Then there are added 200 parts of a neutral or only weakly alkaline copper solution containing per litre 10 grams of crystalline copper sulfate, 15.2 grams of glycocollic acid and 8.64 grams of caustic soda. Dyeing is continued for 30 minutes longer at 90–100° C., the material is rinsed, then washed for about 20–30 minutes at 75° C. in a bath containing per litre 2 grams of calcined sodium carbonate, 5 grams of Marseilles soap and 1 gram of a fatty alcohol sulfonate, then again rinsed and dried. There are obtained olive shades of good fastness to washing.

Example 13

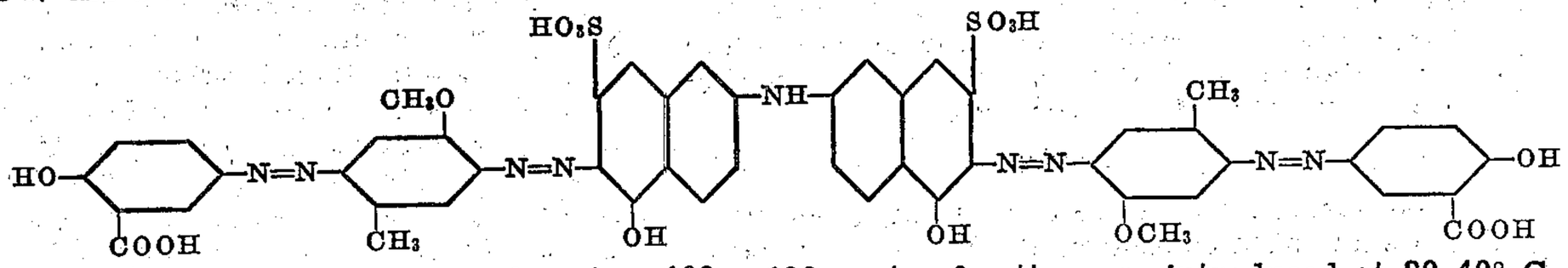
1 part of the dyestuff of the formula



(compare German specification No. 410,758, Example 3) is dissolved in 2000 parts of water with the addition of 2 parts of sodium carbonate. 100 parts of cotton are introduced at 30–40° C., the bath is brought to the boil, and with addition of 30 parts of crystalline Gauber's salt the dyeing is continued for 45 minutes at 95–100° C. Then there are added 200 parts of a neutral or only weakly alkaline copper solution containing per litre 10 grams of crystallized copper sulfate, 12 grams of tartaric acid and 8.64 grams of caustic soda, and dyeing is continued for 30 minutes longer at 90–100° C. Then cold water is run into the bath until its temperature has fallen to 75° C., whereupon there is added a quantity of Marseilles soap solution such that there are present 5 grams of soap for each litre of liquor. The material is handled in this bath for about 20–30 minutes at about 40–50° C., then rinsed and dried. There are obtained reddish-blue shades of good fastness to washing.

Example 14

Into a dye bath prepared from 1500 parts of water, 2 parts of sodium carbonate, 30 parts of Glauber's salt and 1 part of the dyestuff of the formula



100 parts of cotton are introduced at 30–40° C., and the temperature of the bath is raised in the course of ¾ hour to 90–100° C. Then there is added to the bath an alkaline solution of chro-

mium tartrate corresponding with 0.3 part of chromium oxide. The temperature of the bath is maintained at 90–100° C. for 25–30 minutes longer, and the material is then rinsed and soaped for about ½ hour in a soap bath of 0.5 per cent. strength and having a temperature of 50° C. Fast blue shades of good fastness to washing and to light are obtained.

The alkaline chromium tartrate solution used in this example is prepared by mixing an aqueous chromium sulfate solution with an equivalent proportion of tartaric acid and then rendering the mixture alkaline with caustic soda solution.

Example 15

The dye bath consists of 1500 parts of water, 2 parts of sodium carbonate, 30 parts of Glauber's salt and 1 part of the dyestuff made according to the process of U. S. specification No. 1,861,323 by condensation of 1 mol. of dinitro-stilbene-disulfonic acid with 2 mols of 4-amino-1-hydroxy-benzene-2-carboxylic acid in the presence of alkali under pressure. 100 parts of cotton are introduced at 30–40° C. and the bath is brought to the boil in the course of ½ hour. After dyeing for ¾ hour there is added to the bath an alkaline chromium tartrate solution prepared by dissolving with the aid of heat 0.3 part of chromium oxide and 0.3 part of tartaric acid in dilute caustic soda solution. Dyeing is continued at 90–100° C. for 30 minutes longer, and the material is then rinsed and dried. There are obtained orange shades of very good fastness to washing and to light.

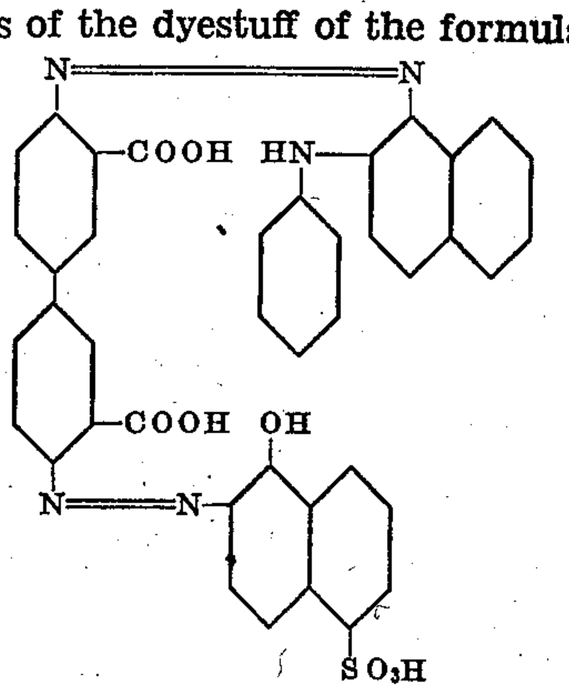
If instead of the alkaline chromium tartrate solution there is used an alkaline nickel-tartrate solution there are likewise obtained fast orange shades. The tinctorial results can be further improved by subsequently soaping at 40–50° C. in a bath containing 5 grams of soap per litre.

Example 16

The dye bath consists of 1500 parts of water, 2 parts of calcined sodium carbonate, 30 parts of Glauber's salt and 1 part of the dyestuff prepared by the process of U. S. specification No. 1,861,323 by condensation of 1 mol. of dinitro-stilbene-disulfonic acid with 2 mols of 2:4-diamino-4'-hydroxy-3'-carboxyazobenzene in presence of alkali under pressure. 100 parts of cotton are introduced and dyed for 45–60 minutes at 90–100° C. Then there is added an ammoniacal solution of cobalt oxide corresponding with 0.2–0.3 part of cobalt, and dyeing is continued for 15 minutes longer. There are obtained brown shades of good fastness to washing. Their properties can be improved by treatment for about ½ hour in a soap bath at 50° C.

Example 17

1.5 parts of the dyestuff of the formula



(compare German specification No. 410,758, Example 4) is dissolved in 1500 parts of water with addition of 2 parts of calcined sodium carbonate. 100 parts of cotton are introduced at 30–40° C., the bath is brought to the boil and 30 parts of crystalline Glauber's salt are added, whereafter dyeing is continued for 45 minutes at 90–100° C. Then there are added 200 parts of a neutral or weakly alkaline copper solution containing per litre 10 grams of crystallized copper sulfate, 19.6 grams of gluconic acid and 8.64 grams of caustic soda. After dyeing has continued for about 30 minutes longer at 90–100° C. the material is rinsed and soaped for ½ hour at 50° C. in a fresh bath containing 5 grams of Marseilles soap per litre. The material is again rinsed and then washed for ½ hour at 75° C. in a fresh bath containing per litre 2 grams of calcined sodium carbonate and 5 grams of Marseilles soap. Finally the material is rinsed and dried. There are obtained violet shades of excellent fastness to washing.

Similar results are obtained if maleic acid is used instead of gluconic acid in this example.

What we claim is:

1. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath.

2. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath, and using an agent yielding copper as an agent yielding metal.

3. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises neutralizing the dye-bath after dyeing and before the after-treatment, conducting the after-treatment with the agent yielding metal in the same bath as the dyeing, and using an agent yielding copper as an agent yielding metal.

4. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises neutralizing the dye-bath after dyeing and before the after-treatment, conducting the after-treatment with the agent yielding metal in the same bath as the dyeing, using an agent yielding copper as an agent yielding metal and finally developing the dyeings thus obtained.

5. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton

azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath and using an agent yielding copper which is stable towards dilute alkali as an agent yielding metal.

6. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath, and using as an agent yielding metal an aqueous solution having an alkaline reaction which is formed by mixing the product of the action of an ordinary agent yielding copper on an aliphatic hydroxycarboxylic acid with a base until the reaction is alkaline.

7. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath, and using as an agent yielding metal an aqueous solution having an alkaline reaction which is formed by mixing the product of the action of an ordinary agent yielding copper on tartaric acid with a base until the reaction is alkaline.

8. A process for producing fast tints on cellulosic fibers by dyeing the fibers with direct cotton azo-dyestuffs of which the complex metal compounds are sparingly soluble to insoluble in water and in dilute alkalies, and after-treating the dyeings with agents which yield metal capable of forming complex compounds with the said dyestuffs, which process comprises conducting the dyeing and the after-treatment with the agent yielding metal in one and the same bath, using as an agent yielding metal an aqueous solution having an alkaline reaction which is formed by mixing the product of the action of an ordinary agent yielding copper on tartaric acid with a base until the reaction is alkaline, and finally developing the dyeings thus obtained.

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