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DYEING VEGETABLE FIBER

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8 Claims. (Cl. 8—5)

This invention consists in the production of fast tints on vegetable fibers by dyeing the vegetable fiber, for instance, cotton or artificial silk made from regenerated cellulose, with a sparingly soluble or insoluble complex metallic compound of a direct cotton dyestuff.

As direct cotton dyestuffs which in this invention are used in the form of their sparingly soluble or insoluble complex metallic compounds, are to be understood, for example, such dis- and polyazo-dyestuffs as have affinity for the vegetable fiber; such dyestuffs may be constructed from diazotized aromatic amines which impart an affinity for vegetable fiber to dyestuffs and any coupling components, for example phenols, naphthols or amines of the benzene or naphthalene series; or the dyestuffs may be made by coupling any diazotized aromatic amine with a coupling component which imparts to the dyestuff affinity for vegetable fibers. Furthermore, such direct cotton dyestuffs may be obtained by using diazo-components which give the dyestuff affinity for vegetable fiber and coupling components having a like property. The selected diazo-component for making the direct cotton dyestuff must be one which will ensure at least one lake-forming group in the direct cotton dyestuff; such diazo-components are, for example, those containing in ortho-position to the diazo-group a hydroxyl-, carboxyl- or alkoxy-group or the salicylic acid grouping. In order to obtain from the direct cotton dyestuff the sparingly soluble or insoluble complex metal compound by treatment with an agent yielding metal there may be used either an insoluble direct cotton dyestuff or a soluble dyestuff of which the complex metal compounds are sparingly soluble or insoluble.

From the preceding it will be seen that for the construction of the direct cotton dyestuffs there are available, besides the usual aromatic amines of the benzene and naphthalene series, which may contain lake-forming groups, as diazo-components, and besides the usual phenols, naphthols and amines as coupling components, in particular direct dyeing components, for example stilbene, derivatives or ureas from arylene diamines; also acetoacetic acid arylides, aminonaphthols and their sulfonic acids and the like.

In producing the complex metallic compounds serving as parent material for the invention and which may contain two or more metals, such as components of chromium, iron, cobalt, nickel, aluminium, manganese, zinc, vanadium, titanium and especially copper, the direct cotton dyestuffs or mixtures of such dyestuffs may be treated with the agent yielding metal in acid, neutral or alkaline medium in a finely divided state, either under pressure or not, and in presence or absence of additions, for instance salts of organic or inorganic acids, or free acids, for example sodium formate, benzenesulfonic acid, naphthalenesulfonic acids, sodium acetate, common salt, Glauber's salt, formic acid, acetic acid or tartaric acid.

Vegetable fibers may be dyed with the sparingly soluble or insoluble complex metallic compounds of direct cotton dyestuffs in the manner usual for dyeing with direct cotton dyestuffs, for example by means of baths containing the dyestuff and Glauber's salt and, advantageously, alkali carbonate, such as sodium carbonate. It is advantageous to use the dyestuff in the most finely subdivided or highly dispersed form; for instance the form obtained by grinding the dyestuff as powder or as a paste containing fluid material, for example an aqueous paste, in the usual apparatus, such as a ball mill or a roller mill, or by wind sifting. In many cases it has been found advisable to dye with the dyestuff in presence of a dispersing agent, a wetting agent or emulsifying agent, that is to say in presence of capillary active anions or cathions or capillary active substances which are not ionized. Such materials are, for example, organic derivatives of ammonia, for example amines of the aliphatic, hydroaromatic or aromatic series, which may also contain hydroxyl-groups or other substituents (for example pyridine, amines, alkylamines, methanolamines, ethanolamines, cyclohexylethanolamines, butylethanolamines), sulfonic acids of the benzene or naphthalene series, which contain alkyl-

groups; alcohol, such as glycerine, alcohol sulfonates, soluble condensation products of higher fatty acids or of ethylene oxide and amines, oxyoleic acids, sulforicinates, glue, sulfite cellulose liquor, dextrin, albumen degradation products, such as protalbinic acid or lysalbinic acid, organic compounds of high molecular weight, for example polymerization products from aldehydes and soluble degradation products of cellulose.

In many cases good dyeing results are particularly obtained when the finely dispersed dyestuff is boiled with water for some time in the so-called dissolving vat or when the finely dispersed dyestuff is added directly to the boiling dye-bath, which may contain the usual additions, such as Glauber's salt and sodium carbonate at the beginning of the dyeing; the duration of dyeing can be somewhat longer than that usual, that is to say about 1–2 hours.

That form of the invention has proved very satisfactory in which dyeing is conducted in the presence of ammonia or an organic derivative of ammonia; of these the aliphatic amines and particularly those which contain hydroxyl-groups, such as the alkylolamines (for instance mono-, di- or triethanolamine or mixtures of these bodies) give good results. Instead of adding these amines and these dyestuffs or the mixture of these amines with these dyestuffs, obtainable by grinding the amine with the dyestuff, to the dye-bath, the procedure may be such that the product formed from the agent yielding metal, the amine and the dyestuff may be so added. Such products may be made, for instance, by treating the dyestuff with the agent yielding metal in presence of the amine or by the action of the amine on the metalliferous dyestuff, water present in the reaction mixture being distilled, if desired. These products are of the consistency of thick liquids; they are soluble in water and in consequence of this property are well suited for the present invention, in which the amine is at least partially decomposed by hydrolysis in the dyeing process.

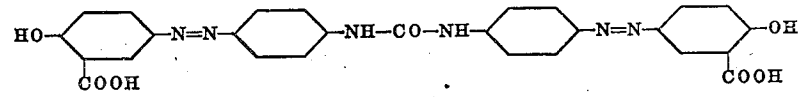
In many cases it is also of advantage to develop the dyeings obtained by treating the goods, for example for some time, in a soap bath or a bath containing soap and sodium carbonate, at about 50–75° C.

The dyeings obtained by the invention are distinguished by very good properties of fastness. It is particularly valuable that these dyeings in many cases do not bleed on to undyed cotton, not merely when the goods are washed at 50° C. in a bath containing 5 parts of soap and 2 parts of sodium carbonate per litre of liquor but also when they are washed at 75° C., or, indeed, at 90–100° C.

The following examples illustrate the invention, the parts being by weight:—

Example 1

10 parts of the copper compound of the dyestuff of the formula:



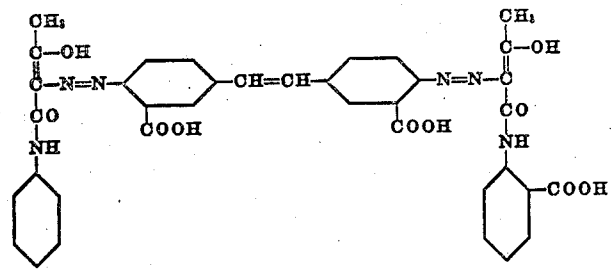
are heated in the form of an aqueous paste with 20 parts of commercial triethanolamine while stirring on the boiling waterbath until the dyestuff has dissolved. A part of the water is then evaporated and there is obtained a yellow viscid mass which dissolves clearly in water.

The dye-bath is prepared, consisting of 2000 parts of water at 30–40° C., 2 parts of calcined sodium carbonate and 2.5 parts of the solution of the dyestuff obtained as described above; 100 parts of cotton are entered and the bath is heated in the course of half-an-hour to 90–100° C. 30 parts of crystallized sodium sulfate are added and dyeing is continued at the same temperature for 30–40 minutes. The goods are then rinsed and soaped in another bath containing per litre 5 parts of Marseilles soap for half-an-hour at 50° C. Rinsing and drying follow.

The cotton is dyed yellow tints of very good fastness, particularly to washing. When the dyed goods are washed for half-an-hour in a bath at 75–90° C. containing, per litre, 2 parts of calcined sodium carbonate and 5 parts of Marseilles soap, together with white cotton, the latter remains uncoloured.

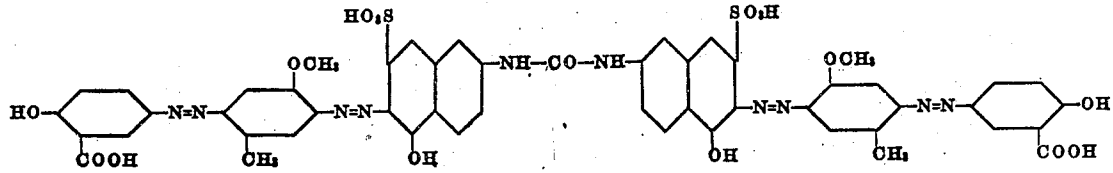
Instead of triethanolamine there may also be used ethylene-diamine or polyalkylenediamines.

When there is used for the dyeing a dyestuff solution obtained by treating the copper compound of the azo-dyestuff of the formula

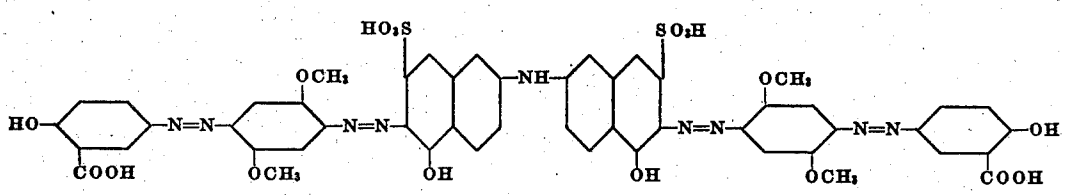


with triethanolamine there is obtained a brown orange tint which also has good fastness to washing.

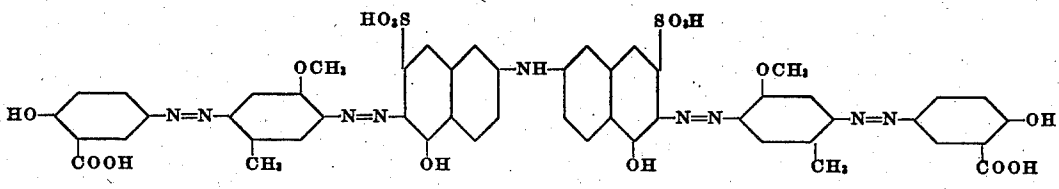
Blue-violet tints fast to washing are obtained when the dyestuff used is obtained by the action of triethanolamine on the copper compound of the dyestuff of the formula



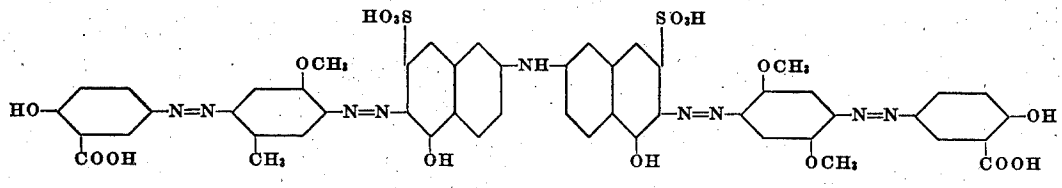
By operating in analogous manner with the product of the action of triethanolamine on the copper compound of the dyestuff of the formula



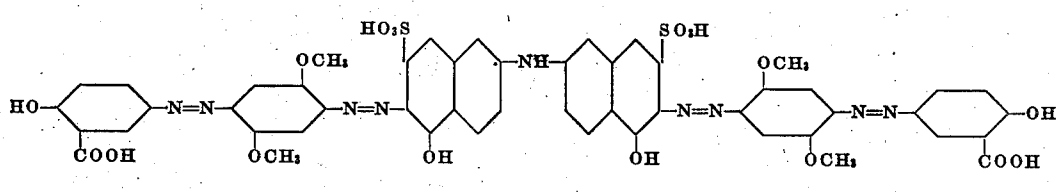
a blue dyeing fast to washing is obtained, and from the product of the action of triethanolamine on the copper compound of the dyestuff of the formula



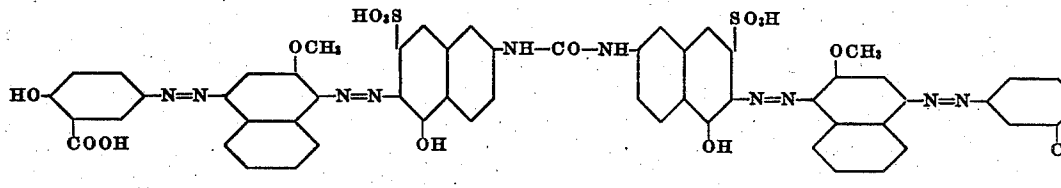
there is also obtained a blue dyeing fast to washing; from the product of the action of triethanolamine on the copper compound of the dyestuff of the formula



a blue dyeing fast to washing is obtained; from the product of the action of triethanolamine on the copper compound of the dyestuff of the formula



a greenish-grey dyeing is obtained, and from the product of the action of triethanolamine on the copper compound of the dyestuff of the formula



a blue grey fast dyeing is obtained.

In a similar manner to that described in the second paragraph of this example artificial silk made from regenerated cellulose can be dyed but the temperature of the dyeing operation should be about 75–80° C.

Example 2

A boiling dye-bath is prepared consisting of 2000 parts of water, 2 parts of calcined sodium carbonate and 0.25 part of the finely ground paste of the copper compound of the dyestuff of the formula

100 parts of cotton are entered and boiling is continued for about 1½ hours. The goods are then rinsed and soaped in another bath containing per litre 5 parts of Marseilles soap for half-an-hour at 50° C. Rinsing and dyeing follow.

The cotton is dyed blue tints fast to washing.

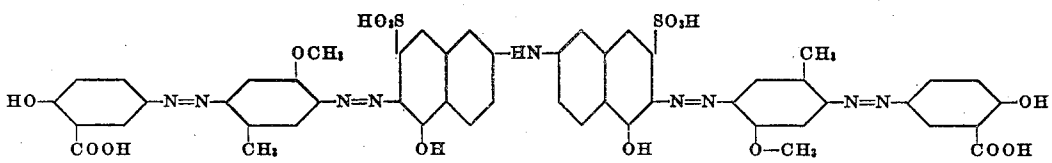
In like manner the copper compounds of the dyestuffs named in Example 1 may be used.

A similar result is obtained if 30 parts of crystallized Glauber's salt are added to the dye-bath after it has been boiling for 1 hour.

The result in respect of the uniformity of the tints obtained is favourably influenced when the dye-bath receives an addition of 2–5 parts of sulfite cellulose waste liquor.

Example 3

A dye-bath is prepared from 2000 parts of boiling water, 2 parts of calcined sodium carbonate, 1½ parts of Marseilles soap and 2 parts of the very finely subdivided copper compound of the dyestuff of the formula



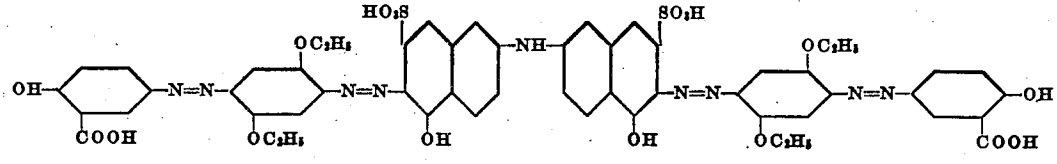
100 parts of cotton are entered and are handled for 1–1½ hours, whereupon 30 parts of crystallized Glauber's salt are added and dyeing is continued for half-an-hour at boiling temperature. The goods are then rinsed and soaped in a bath containing per litre 5 grams of soap at 50° C. Rinsing and drying follow. The dyeings obtained are excellently fast to washing.

Similar results are produced when the dyestuff is boiled in the dissolving vat together with the sodium carbonate and the soap and then added to the boiling dye-bath. Good results are also obtained by treating the finely subdivided dyestuff in the form of paste or powder in a dispersing mill before it is used for dyeing.

If, in the dye-bath prescribed above, there is substituted for the Marseilles soap 1 part of Turkey red oil or 2 parts of sulfite cellulose waste liquor or 1 part of sodium 1-iso-propyl-naphthalene-3-sulfonate or 1–1½ parts of fatty alcohol sulfonate (laurylalcohol-sulfonate), there are obtained similar dyeing results with like fastness to washing of the dyeings.

Example 4

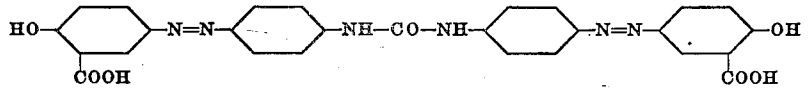
A dye-bath is prepared consisting of 2500–3000 parts of water, a solution of the copper compound of the dyestuff of the formula



obtained by dissolving 1 part of this dyestuff by means of 0.75 part of glycocoll and 1 part of calcined sodium carbonate in 100 parts of boiling water, and 20–25 parts of Glauber's salt. 100 parts of cotton are entered at 40° C., the temperature of the bath is raised to 95° C. in the course of ½ hour, and the bath is kept at this temperature for about 1 hour. The material is then rinsed, soaped in another bath containing per liter 5 grams of Marseilles soap for ½ hour at 50° C., rinsed again and dried. The cotton is dyed greenish-blue tints of very good fastness to washing.

Example 5

2.5 parts of the azo-dyestuff of the formula



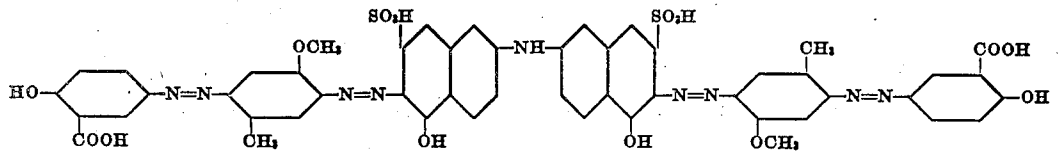
are converted into the copper compound by treatment with copper sulfate. The insoluble precipitate is filtered, pressed and treated in the form of a moist paste with 7.5 parts of triethanolamine on the water-bath until a syrupy mass clearly soluble in water has been formed, whereupon the water is distilled off. There are obtained 10 parts of the complex copper compound of the azo-dyestuff which has been rendered soluble and which is dissolved in 3000 parts of water. 100 parts of boiled jute yarn are entered into this solution, mixed with 40 parts of Glauber's salt and dyed for 1 hour while boiling.

The jute yarn is dyed yellow tints which are fast to light and water.

Instead of jute yarn, wood bast and straw-plaiting may be dyed in analogous manner.

Example 6

10 parts of the copper compound of the azo-dyestuff of the formula

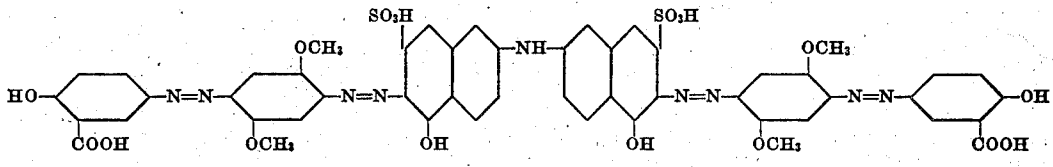


are dissolved with 40 parts of triethanolamine in 500 parts of hot water. The clear solution is added to a paper mass containing 1000 parts of cellulose. The whole is mixed for sometime whereby the cellulose is strongly dyed by the dyestuff. 60 parts of aluminium sulfate and 40 parts of resin glue are then added to the mixture and worked up in the manner usual for

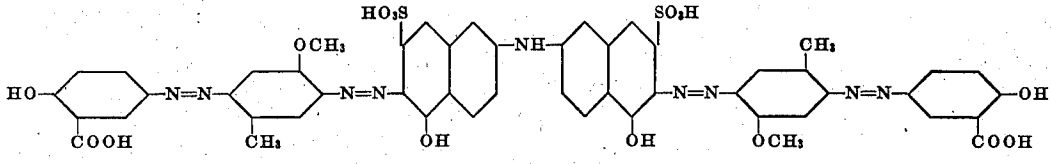
paper. There is obtained a grey-blue colored paper of excellent fastness to water and light.

Example 7

10 parts of the azo-dyestuff of the formula

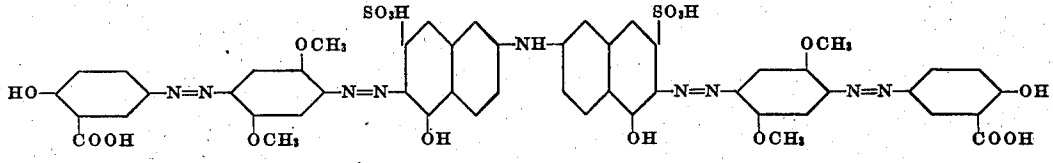


are dissolved in 500 parts of water and mixed at 70–80° C. with a solution of 6 parts of the copper salt of glycollic acid in warm water. The whole is stirred for sometime at 70–80° C. For dyeing there may be used either the solution of the azo-dyestuff containing copper and glycocollic acid complexly bound which has formed, or the new



complex compound can be separated by means of common salt and dried. The complex copper compound which has separated remains water-soluble also after drying, whereas by treating with the usual coppering agents, such as copper sulfate, copper acetate, ammoniacal copper oxide, sparingly soluble to insoluble complex copper compounds are obtained.

A paper mass containing 1000 parts of solid cellulose mass is dyed with the solution of the copper complex of the dyestuff obtained in the preceding paragraph, by treating the paper mass with the dyestuff solution for some time in the shaking machine or the rolling mill. The complex copper compound of the dyestuff is thereby completely absorbed by the paper mass. After addition of 60 parts of aluminium sulfate and 40 parts of resin glue the whole is worked up in the manner usual for paper. There is obtained a gray-blue colored paper of good fastness to light and very good fastness to water.



Example 8

3 parts of the dyestuff obtainable by condensing 1 mole of dinitrostilbene-disulfonic acid with 2 moles of the azo-dyestuff from diazotized 1-amino-4-hydroxybenzene-3-carboxylic acid and 1:3-phenylenediamine in the presence of caustic soda solution according to the process of U. S. Patent 1,861,323, are boiled with 1.5-part of the copper salt of glycocollic acid in 100 parts of water, and the solution thus obtained is diluted with water to 3000 parts by volume. 100 parts of jute yarn are introduced into the dyeing liquor and after addition of 40 parts of Glauber's salt the material is dyed for 1 hour at 95° C. There is obtained a brown dyeing of very good fastness to water.

Coconut fiber can be dyed in analogous manner.

Example 9

2 parts of the copper compound of the azo-dyestuff of the formula

are ground in a ball mill with 2 parts of the sodium salt of the sulfonated condensation product from benzylchloride and naphthalene until a fine homogeneous mixture has been formed.

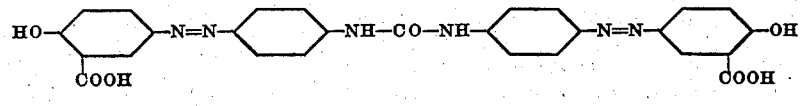
A dye-bath is prepared with 2000 parts of water, 2 parts of calcined sodium carbonate and 2 parts of the above mentioned mixture, into which 100 parts of cotton are introduced at 30–40° C. The temperature of the bath is raised to boiling in the course of ½ hour, whereupon 30 parts of Glauber's salt are added and dyeing is continued for 1 hour at 95–100° C. The cotton is then washed and dried. There are obtained blue tints of very good fastness to light and washing.

Similar results are obtained when dyeing with a mixture which has been obtained by grinding together 2 parts of the copper compound of the dyestuff of the formula

with 2 parts of the sodium salt of the sulfonated condensation product from benzylchloride and naphthalene.

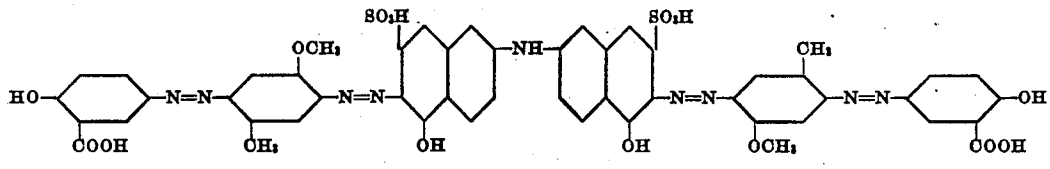
Greenish-blue dyeings of good fastness to light and washing are obtained.

A yellow dyeing of very good fastness to washing and light is obtained by a similar method of working when using the copper compound of the dyestuff



Example 10

10 parts of the copper compound of the dyestuff of the formula



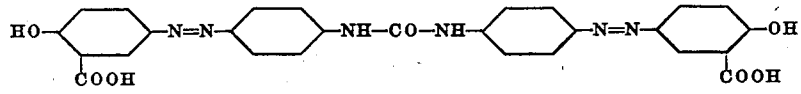
in the form of an aqueous paste containing 20 per cent. of dyestuff are suspended in 200 parts of water, mixed with 10 parts of an emulsifying agent consisting of glue and soap, heated for a long time to 40 to 60° C., and vigorously stirred. This treatment may also be carried out for a shorter or longer time at higher temperatures, for example at 90–100° C. The mixture thus obtained is used either directly for dyeing, or it may be partly or completely evaporated in a vacuum and then ground.

For dyeing there is prepared a bath having a temperature of 30–40° C. and containing per 100 parts of cotton 2 parts of calcined sodium carbonate and 2 parts of the above mentioned aqueous paste. The cotton is introduced and the bath is heated to boiling temperature within ½ hour, whereupon 30 parts of Glauber's salt are added and dyeing is continued for a further hour at 95–100° C. After washing and drying there are obtained blue tints of very good fastness to light and washing.

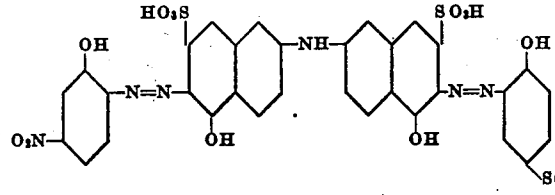
If instead of the emulsifying agent mentioned in this example there is used a pyridine solution of castor oil sulfonate similar results are obtained.

Example 11

10 parts of the dyestuff of the formula



are converted into the complex copper compound with copper sulfate in usual manner. The water-insoluble copper compound is filtered, washed and pressed. The pressed material is made up into a paste of 50 parts by weight by means of



water, mixed with 10 parts of the sulfonated condensation product from stearic acid and orthophenylenediamine, and vigorously stirred for a long time, until a homogeneous mass has been formed. A dye-bath is now prepared consisting of 2000 parts of water, 2 parts of sodium carbonate and 6 parts of the above named mixture, into which 100 parts of cotton are introduced at 30–40° C. The temperature is raised to boiling in the course of ½ hour, whereupon 30 parts of Glauber's salt are added and dyeing is continued for 1 hour at 95–100° C. The cotton is then washed and dried. There are obtained yellow tints of very good fastness to light and washing.

Similar results are obtained when using under otherwise unchanged conditions instead of the sulfonated condensation product from stearic acid and ortho-phenylenediamine an emulsifying agent consisting of glue and soap, or sodium isopropylnaphthalenesulfonate.

Example 12

The dyestuff of Example 9 of U. S. Patent 1,861,323, page 3, lines 102–106, obtained by condensation of dinitrostilbene-disulfonic acid with the azo-dyestuff from diazotized 1-acetylamino-4-aminobenzene and salicylic acid in the presence of caustic soda solution, is converted into the water-insoluble complex copper compound by treatment with an agent yielding copper. The copper compound is separated, washed and made up into an aqueous paste containing 20 per cent. of dyestuff. To this aqueous paste there are added 4 parts of dithiodiglycol for every 20 parts of paste, the whole is slowly diluted with water to 100–200 parts and stirred for 10 hours. The suspension thus obtained can be used directly for dyeing or can be evaporated in a vacuum for later use.

A dye-bath is prepared, consisting of 2000 parts of water, 2 parts of calcined sodium carbonate, and 2 parts of the dispersed dyestuff; 100 parts of cotton are entered at 30–40° C., and the bath is heated to boiling in the course of ½ hour, whereupon 30 parts of Glauber's salt are added and dyeing is continued for a further hour at 95–100° C. The cotton is then washed and dried. There are obtained orange tints of very good fastness to light and washing.

Example 13

The dyestuff of the formula

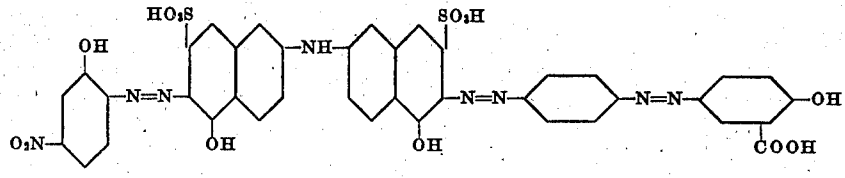
is converted in an aqueous solution into the very difficultly soluble copper compound by treating it in the usual manner with agents yielding copper. After filtering and washing the copper compound is dried and ground in a ball mill or roller mill with equal parts of the sodium salt of the diamylsulfophthalic acid ester.

2 parts of the dyestuff mixture thus obtained are boiled in about 10 litres of water and added to a dye-bath at 30–40° C. and containing 1500–2000 parts of water as well as 2 parts of calcined sodium carbonate. 100 parts of cotton are entered and the temperature of the bath is raised to boiling in the course of ¼–½ hour, whereupon 30 parts of Glauber's salt are added and the temperature is maintained between 95–100° C. for

one hour. The cotton is then rinsed and dried. There are obtained blue-violet tints of good fastness to light and washing.

Example 14

The dyestuff of the formula



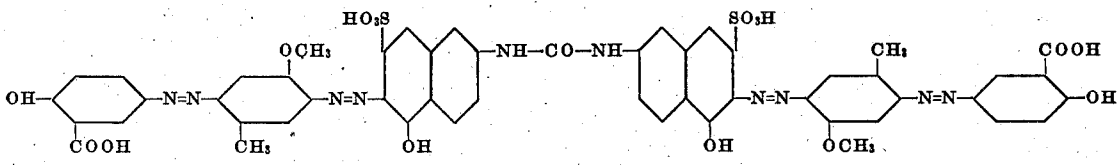
is converted into the complex nickel compound by dissolving 2 parts of the azo-dyestuff in 100 parts of water at 80–100° C. and mixing with 1.5 parts of crystallized nickel sulfate in aqueous solution. The separated water-insoluble precipitate is filtered. Into a dye-bath consisting of 1500 parts of water, 2 parts of calcined sodium carbonate, 30 parts of Glauber's salt, 2 parts of the sodium salt of the diamylsulfophthalic acid ester and the complex nickel compound produced above, are introduced 100 parts of cotton at 30–40° C.; the temperature of the bath is raised to boiling in the course of ½ hour and maintained for about ¾–1 hour, whereupon the material is rinsed and dried. The reddish blue dyeings thus obtained are of good fastness to light and washing.

Similar tinctorial results are obtained when using the cobalt compound of the above named dyestuff under otherwise unchanged conditions.

Instead of the sodium salt of the diamylsulfophthalic acid-ester there may also be used the sodium salt of the sulfonated condensation product from benzyl chloride and naphthalene, or an emulsifying agent consisting of glue and soap.

Example 15

The dyestuff of the formula



is converted into the complex cobalt compound by mixing for example 2 parts of this azo-dyestuff, dissolved in 100 parts of water, at 80–100° C. with an aqueous solution of 1.5 parts of cobalt chloride, stirring for some time and filtering the water-insoluble cobalt compound of the dyestuff which has separated. For dyeing 100 parts of cotton 2 parts of the complex cobalt compound are added to a dye-bath consisting of 1500 parts of water, 2 parts of the sodium salt of the diamylsulfophthalic acid ester, 2 parts of calcined sodium carbonate and 30 parts of Glauber's salt. The material is introduced at 30–40° C., the temperature of the bath is raised to boiling within ½ hour and maintained for about 1 hour, whereupon the cotton is washed and dried.

There are obtained brown-violet tints of very good fastness to washing and light which may still be improved by soaping in another bath containing per liter 0.5 gram of Marseilles soap at 40° C.

Instead of the sodium salt of the diamylsulfophthalic acid-ester there may also be used the same quantity of an emulsifying agent consisting of a mixture of glue and soap, or the corresponding quantity of the sodium salt of the sulfonated condensation product from benzylchloride and naphthalene.

Example 16

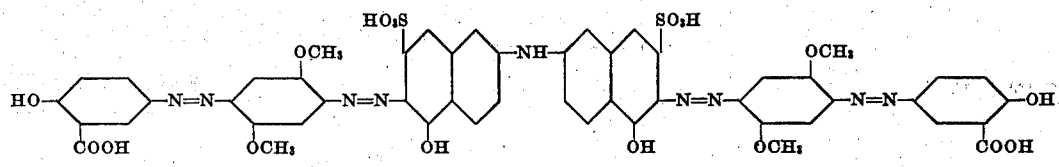
The dyestuff obtained by condensation of 1 mole of dinitrostilbene sulfonic acid with 2 moles of the azo-dyestuff from diazotized 1-amino-4-hydroxybenzene-3-carboxylic acid and 1.3-phenylenediamine, in the presence of caustic soda solution according to the process of U. S. Patent 1,861,323, is converted in an aqueous solution into the water-insoluble complex copper compound by treatment in the usual manner with agents yielding copper. The copper compound is separated, washed, dried and extremely finely ground.

2 parts of this cupriferous dyestuff are ground with 1 part of the sodium salt of glycocollic acid, whereby there is obtained a water-soluble form of the complex copper compound which is suitable for dyeing cotton from a neutral or soda-alkaline Glauber's salt bath.

2 parts of the ground material are boiled with about 100 parts of water and added to a dye-bath containing 1500–2000 parts of water and 2 parts of calcined sodium carbonate at 30–40° C. 100 parts of cotton are introduced into this bath and the temperature is raised to boiling in the course of ¼–½ hour, whereupon 30 parts of Glauber's salt are added and the temperature is maintained for 1 hour between 95–100° C. The cotton is then rinsed and dried. There are obtained brown tints of good fastness to light and washing.

Example 17

1 part of the dyestuff of the formula

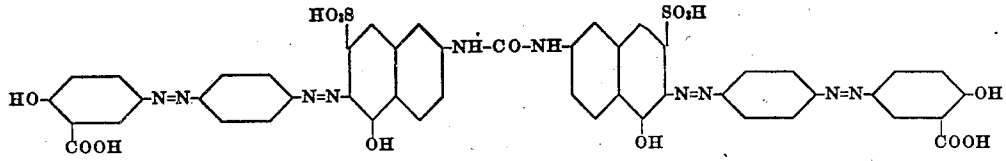


(sodium salt) is ground in a mill with 0.5 part of the copper salt of glycocollic acid and 0.5 part of the nickel salt of glycocollic acid. The ground material is used for dyeing 100 parts of cotton

by dissolving it in 1500 parts of water, 2 parts of calcined sodium carbonate, and dyeing the cotton for 1 hour at 90–100° C. Washing and drying follow. There are obtained blue tints of good fastness to washing and light. Before drying the dyeing may be soaped for about ½ hour in another bath containing ½ per cent of soap, whereby the fastness to washing is improved.

Example 18

The dyestuff of the forumla

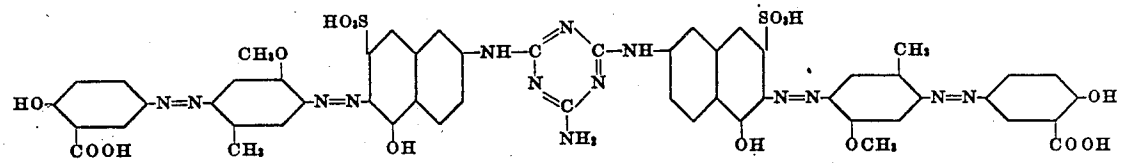


is converted into the complex nickel-cobalt compound by mixing 1 part of the dyestuff in aqueous solution with the solutions of 0.28 part of crystallized nickel sulfate and 0.28 part of cobalt sulfate, stirring the whole in the heat and filtering the precipitate. To the paste of the complex metal compound thus obtained there is added 1 part of a mixture consisting of equal parts of Marseilles soap and glue, the whole is homogeneously mixed and evaporated to dryness in a vacuum. The dried material is then finely ground.

A dye-bath is prepared consisting of 1000–1500 parts of water, 2 parts of calcined sodium carbonate and 30 parts of Glauber's salt. 100 parts of cotton are dyed by introducing the material at 30–40° C., heating the bath to boiling in the course of 20–30 minutes, maintaining this temperature for about 1 hour, washing and drying. The dyeing thus obtained has good fastness to washing and light.

Example 19

1 part of the dyestuff of the formula



is ground with 0.5 part of the nickel salt of glycocollic acid and 0.5 part of the cobalt salt of glycocollic acid.

For dyeing 100 parts of cotton the ground material is dissolved in 1500 parts of water to which are added 2 parts of calcined sodium carbonate and 30 parts of Glauber's salt, and the cotton is dyed for 1 hour at 90–100° C. Washing and drying follow. There are obtained blue-grey tints of good fastness to washing and light.

What we claim is:—

1. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with finely subdivided complex metal compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies.

2. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with finely subdivided complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies.

3. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, in presence of compounds selected from the group consisting of dispersing, wetting and emulsifying agents.

4. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, in presence of organic ammonium bases.

5. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, in presence of aliphatic amines.

6. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, in presence of aliphatic amines containing hydroxyl groups.

7. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with finely subdivided complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, and soaping the dyeing thus obtained.

8. Process for the production of fast tints on vegetable fiber, comprising dyeing the vegetable fiber with complex copper compounds of direct azo-dyestuffs for cotton, said compounds being sparingly soluble to insoluble in water and in dilute alkalies, in presence of aliphatic amines containing hydroxyl groups, and soaping the dyeings thus obtained.

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WALTER ANDERAU.