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3,307,901

PROCESS FOR DYEING POLYAMIDE TEXTILE MATERIALS AND AUXILIARIES THEREFOR

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No Drawing. Continuation of application Ser. No. 306,601, Sept. 4, 1963. This application Nov. 26, 1965, Ser. No. 510,063

Claims priority, application Switzerland, May 24, 1961, 6,020/61; Apr. 18, 1962, 4,735/62; Sept. 17, 1962, 10,959/62

9 Claims. (Cl. 8—54)

This application is a continuation of our pending patent application Serial No. 306,601, filed September 4, 1963 and now abandoned, which is in turn a continuation-in-part of our application Serial No. 196,898, filed May 23, 1962, now abandoned.

The invention concerns in a first aspect a process for the dyeing of wool with sulfonated metal phthalocyanines in level, fast turquoise blue to green shades of good color strength.

In another aspect, the present invention concerns quaternary ammonium compounds which are suitable as dyeing auxiliaries, and processes for the production thereof.

Certain sulfonated or sulfated copper phthalocyanines have attained importance for the dyeing of cellulose in pure, lightfast turquoise shades. Sulfonated phthalocyanines have also been suggested for the dyeing of wool. When used in the form of their water soluble alkali metal salts without further additives for dyeing in acid liquors, e.g., in the presence of Glaubers salt, they offered only very weak, tippy and, therefore, completely unusable dyeings. A considerable improvement of the quality of such dyeings is attained when the dyeing is performed in the presence of polyglycol ethers derived from higher molecular fatty alcohols of fatty amines and which contain at least 20 or 6-10 ethyleneoxy groups respectively in the polyglycol ether radical; condensation products derived from fatty amines can also be quaternized. However, these processes still have disadvantages in that, for example, the resulting dyeings do not meet all commercial requirements regarding evenness, fastness and color strength or in that dye liquor stains the apparatuses and dyeings which is particularly evident in the dyeing of yarn wound on cheeses.

It has now been found that excellent and full wool dyeings can be obtained while avoiding the disadvantages mentioned in the foregoing, by the process according to the invention wherein wool is dyed in diluted aqueous solution of the salts of metal phthalocyanines which contain metals of the atomic numbers 28 to 29 and at least one aromatically bound sulfonic acid group or at least one sulfated sulfonic acid - β - or - γ -hydroxy-alkyl amide group and wherein the dyeing is performed in the presence of at least one condensation product according to the invention, which is that of a primary amine, containing a higher alkyl, aralkyl or higher alkenyl radical, with 7 to 30 and preferably 10 to 30 equivalents of ethylene oxide and with 1 equivalent of styrene oxide as well as, if desired, with 1 to 2 equivalents of propylene oxide, which condensation product is quaternized by reaction with the ester from a lower alkanol and a strong acid.

It has been found that particularly valuable quaternary ammonium compounds according to the invention are obtained if condensation product of one equivalent of styrene oxide, none to two equivalents of propylene oxide and from ten to about thirty equivalents of ethylene oxide with an aliphatic amine the alkyl or alkenyl radical of which contains at least twelve to twenty-two carbon atoms, is reacted with the equivalent of a reactive ester of a lower

alkanol with a strong acid, the reaction being performed at room temperature or with heating.

The formation of the quaternary compound comprises first the addition of styrene oxide to said amine. It is generally sufficient to react these components by heating at least to 60° C. and preferably to from about 100° C. to 200° C. depending on their composition and reactivity and generally in the presence of a basic catalyst such as sodium or potassium hydroxide, carbonate or alcoholate. The styrene oxide can be incorporated in solutions of the amine and catalysts in inert organic solvents, or in the melts of amine and catalyst, if necessary under pressure. In general, raised temperatures of, for example, 80° C. up to about 200° C. are employed. The reaction product of styrene oxide and amine is then, if desired, reacted with from one to two equivalents of propylene oxide, followed by a subsequent reaction with preferably 10 to 30, and optionally with 18 to 22 equivalents of ethylene oxide. The reaction with propylene oxide is not an essential requirement. Said reactions with propylene oxide and ethylene oxide are carried out preferably at a temperature of from about 80° C. to about 200° C. in the presence of a basic catalyst such as sodium or potassium hydroxide, carbonate or alcoholate but in the absence of any solvent. The resulting polyglycol ethers are thereupon quaternized at from about 70° C. to 150° C. with an ester of lower alkanol and strong acid, to form the condensation product usable according to the invention.

Preferred intermediates are the products of addition of 1 equivalent of styrene oxide, 1 to 2 equivalents of propylene oxide and about 20 equivalents of ethylene oxide to octadecenylamine or octadecylamine or to technical mixtures thereof alone or with similar higher alkylamines such as technical oleylamine or sterylamine.

Preferably dimethyl sulfate, but also diethyl sulfate, methyl or ethyl halides such as methyl iodide, methyl bromide, ethyl iodide, ethyl bromide, ethyl chloride, as well as the esters of aromatic sulfonic acids, e.g., the methyl esters of benzene sulfonic acids, toluene sulfonic acids, such as methyl or ethyl p-tosylate, halogenobenzene sulfonic acids and nitrobenzene sulfonic acids or chloro- or bromo-propionic acid methyl or ethyl esters are used as reactive esters of lower alkanols with a strong acid. The reaction is performed by gradually mixing the components, at room temperature or with heating.

It is of advantage to use a slight excess of the alkylating agent. If desired, the alkylation can also be performed in the presence of inert organic solvents and diluents which are again removed on completion of the reaction, e.g., by distilling off, preferably under vacuum.

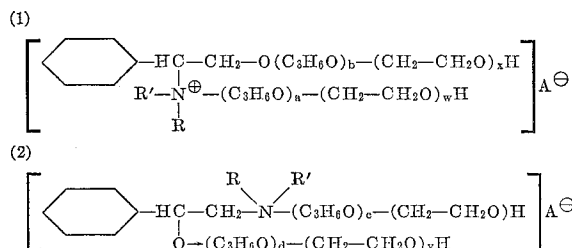
The quaternary ammonium compounds according to the invention are in the form of salts with the anions of the acids from which the alkylating agent used is derived: thus they contain as anion, e.g., one equivalent chlorine ion, bromine ion, iodine ion, benzene sulfonic acid ion, toluene sulfonic acid ion, halogenobenzene sulfonic acid ion, nitrobenzene sulfonic acid ion, ethosulfate ion and, preferably, methosulfate ion. They can also be used as salts of other inorganic or organic acids which have been produced, e.g., by double reaction with their alkali salts, e.g., as formiates, lactates, oxalates, methyl sulfonates, sulfonates, etc. The anion is of secondary importance. Quaternary ammonium compounds according to the invention form colorless, pasty, water soluble masses.

As quaternized condensation products, advantageously those are used which are derived from primary higher alkyl or aralkyl namely benzyl, or higher alkenyl amines, preferably those containing generally 8 to 19 carbon atoms and, in the case of higher alkyl and alkenylamine, preferably 10 to even as much as 22 carbon atoms, e.g., octylamine, decylamine, dodecylamine, tetradecylamine

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and mixtures thereof, hexadecylamine, octadecylamine, oleylamine and mixtures thereof, or of dodecylbenzylamine. Particularly advantageous amines are oleylamine, sterylamine, and dodecylamine, especially oleylamine and dodecylamine, but also tetradecylamine, hexadecylamine, docosylamine and preferably, octadecenylamine or octadecylamine, or technical mixtures of such higher alkylamines, particularly those having substantial contents of octadecenylamine or octadecylamine.

The condensation products resulting from the above reaction sequence and employed in the process according to this invention are preferably mixtures of quaternary compounds of the probable formulas:



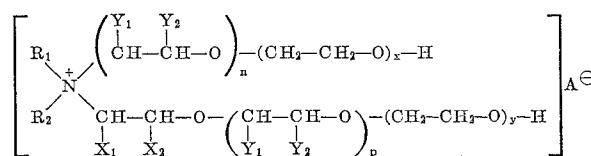
wherein R is a higher alkyl, aralkyl or higher alkenyl radical,

R' is a lower alkyl radical, preferably methyl

A⁻ is an anion of an acid (monovalent anion or the normal equivalent of a polyvalent anion),

the sum of a, b, c and d is a number from 0 to 4 inclusive (advantageously from 2 to 4 inclusive) while the sum of x, y, z and w is a number from 14 to 60 inclusive.

Allowing for the type and amount of the substances used for the starting materials and the order in which they are reacted and the reaction conditions, these compounds have the more detailed probable structural formula:



In this formula:

R₁ represents an alkyl or alkenyl radical having 12 to 22 carbon atoms, preferably the oleyl or stearyl radical;

R₂ represents a low alkyl radical, preferably the methyl group;

of X₁ and X₂, one X is hydrogen, the other X the phenyl radical;

of Y₁ and Y₂, one Y is hydrogen, the other Y is the methyl group;

m is 0 or 1;

n and p are each 0, 1 or 2 with the condition that the sum of n and p is at most 2;

x and y are whole numbers the sum of which is from 10 to 30, preferably 18 to 22;

A⁻ is the equivalent of an anion, preferably the methosulfate ion.

As is conventional, the sum of the coefficients x and y represents an average value and mixtures according to the invention contain analogous compounds having polyalkyleneoxy substitutes of various chain lengths, but of the said average value.

"Lower" used in this specification and in the appended claims in connection with an aliphatic radical means that said radical has from 1 to not more than 4 carbon atoms.

The quaternary ammonium compounds according to the invention are valuable auxiliaries for the dyeing of polyamide material with anionic dyestuffs, in particular with sulfonated dyestuffs. Their advantageous properties become particularly apparent on dyeing wool with anionic dyestuffs containing more than one sulfonic acid group,

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which dyestuffs have a relatively limited affinity to wool; when added in the usual contents of about 0.5 to 2% (calculated on the goods to be dyed) to dye liquors prepared with such dyestuffs, the quaternary ammonium compounds according to the invention act as levelling and shade-deepening agents.

For example, they make the dyeing of wool in deep, level, light fast shades possible from an acid bath with sulfonated metal phthalocyanines described more in detail below or in the sulfonated dioxazine dyestuffs which, up to now, have preferably been used for the dyeing of cellulose.

Compared with analogous quaternary ammonium compounds which, with otherwise the same structure, do not contain the characteristic phenethyleneoxy radical introduced by means of styrene oxide, the dyeing auxiliaries according to the invention are distinguished by their marked shade-strengthening action; compared with analogous compounds not containing the phenethyleneoxy radical and having the same color-strengthening action but which, then, must contain shortened polyethyleneoxy groups having less than 10 ether oxygen atoms, the dyeing auxiliaries according to the invention are distinguished in that they produce dyeings which are faster to rubbing, and they completely eliminate the troublesome staining of the dyeing apparatus.

The sulfonated or sulfated metal phthalocyanines usable according to the invention are nickel or preferably copper phthalocyanines. They must be water soluble. They can be mixtures of different degrees of sulfonation or sulfation respectively. They can contain either sulfonic acid groups or sulfuric acid monoester groups or they can contain both types of these water solubilizing substituents together. The number of the sulfonic acid groups or of the sulfated sulfonic acid -β- or -γ-hydroxyalkylamide groups is preferably 2 to 4. The sulfonic acid groups are bound to the phthalocyanine structure and/or to external aromatic radicals, in which case principally to sulfonic acid arylamide or arylester groups.

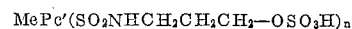
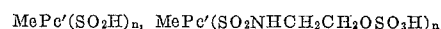
The metal phthalocyanines can contain the usual substituents in phthalocyanine dyestuffs, for example, single halogens and/or single, possibly N-substituted sulfonic acid amide groups in the phthalocyanine structure and, in the external aromatic radicals, for example, possibly substituted alkyl, cycloalkyl, aralkyl, aryl, ether groups, halogens, nitro groups, if desired N-substituted carboxylic acid and sulfonic acid amide groups, acylamino, acyl, arylazo groups of the homocyclic and heterocyclic series.

If one or more sulfonic acid amide groups are present which increase the water solubility, then a single sulfonic acid group is sufficient as salt-forming acid substituent.

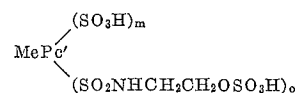
As substituent of the said N-substituted sulfonic acid amide groups can be employed: lower alkyl groups such as methyl, ethyl, propyl, butyl groups; low substituted alkyl groups such as acylaminoethyl, acylaminopropyl, acylaminoethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl groups: in particular sulphated low hydroxyalkyl groups and possibly further substituted aryl groups such as phenyl, sulphophenyl and acylaminophenyl groups.

All these dyestuffs are used in the form of their water soluble salts, particularly as alkali metal or ammonium salts.

A preferred class of metal phthalocyanines employed according to this invention are those of the formulae:



or



wherein

Me is a metal of an atomic number of 28 or preferably 29, n is 2 to 4 inclusive and the sum of m and n is a num-

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ber from 2 to 4 inclusive. However, n can be one if the phthalocyanine radical contains a further water solubilizing group as the monosulphonic acid ethanolamide group, and Pc' is a phthalocyanine radical, i.e., a unsubstituted phthalocyanine radical or a substituted phthalocyanine radical, e.g., dyestuff produced by condensation of copper phthalocyanine tetrasulphonic acid chloride with 1 mol of 2,4-diaminobenzene-1-sulphonic acid, the dyestuff produced by the condensation of a mixture of copper phthalocyanine sulphonic acid chloride which contains on the average of 2 to 3 sulphonic acid chloride groups with 1 mol of 2,5-diaminobenzene-1-sulphonic acid, saponification of the remaining sulphonic acid chloride groups with subsequent diazotisation and coupling with 1-phenyl-3-methylpyrozal-5-one, copper phthalocyanine monosulphonic acid-monosulphonic acid ethanolamide, etc.

The quaternised condensation products are used in amounts of about 0.5 gramme (g.) per litre dye liquor. The range of action, however, is to some extent dependent on the amount and type of the dyestuff used on the composition of the auxiliaries, so that the content varies from about 0.1 to 2 g. per litre of dye liquor.

In addition to the condensation product mentioned, the dye liquor can contain the auxiliaries usual in wool dyeing, e.g., salts such as sodium sulphate, ammonium sulphate, ammonium acetate, acid alkali or ammonium phosphates, esters such as methyl or ethyl lactate or tartrate, or acids such as formic acid, acetic acid, hydrochloric acid, sulphuric acid etc. Advantageously dyeing is performed in possibly buffered, weakly acid baths or in dye liquors which contain ammonium salts of difficulty volatile acids, e.g., ammonium sulphate in contents of 3% to 6% of the goods to be dyed, depending on the amount and composition of the dyestuff used. While known alkylamine ethylene oxide condensates used as dyeing auxiliaries in dyeing wool with phthalocyanine dyes of the type described impart a tacky nature to the dyeing liquors which stick to the bath vessels and moreover, lead to dyeings with a smeary aspect, use of the mixtures according to the invention as dyeing assistants in the aforesaid dyeing processes affords clear dyeing liquors, which leave the dyeing vessels clean upon removal therefrom, and which yield pure, clear dyeings.

Particularly beautiful and pure wool dyeings are obtained with dye liquors which contain, as additional auxiliary, condensation products described in U.S. Patent No. 2,089,212. These condensation products are obtained by heating a reaction mixture containing a monocarboxylic fatty acid of at least eight carbon atoms and one to three mols of a lower alkanol amine per mol of fatty acid with the simultaneous splitting off of about one mol of water per mol of alkanol amine, the ratio of fatty acid to alkanol amine in the reaction mixture being such that for each mol of fatty acid in the reaction mixture there is at least three mols of monoalkanol radicals. In the preferred form they are condensation products of fatty acids having 8 to 14 carbon atoms or mixtures of such acids and 2 mols of dialkanolamine per mol of fatty acid present.

The quaternised condensation products simultaneously deepen the shade, and improve the levelling and fastness to perspiration, wet and rubbing. Also, even when highly concentrated dyestuff solutions are used, they prevent staining of both the dyeings as well as the apparatus. Sometimes the wet fastness properties of the wool dyeings produced according to the invention by after-treatment of the wool dyeings in the known way with agents which raise the pH such as ammonia or hexamethylenetetramine, at 80–100° C., as well as with wetting agents.

The wool dyeings so obtained are distinguished by a full shade, great evenness, excellent wet fastness properties and perfect fastness to rubbing.

Further details can be seen from the following examples. Where not otherwise expressly stated, parts are given as parts by weight. The temperatures are given in

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degrees centigrade. The relationship of parts by weight to parts by volume is as that of grams to cubic centimeters.

Example 1

250 parts of woollen worsted yarn wound onto cheeses are treated in a dyeing apparatus for 10 minutes at 50° with a solution of 10 parts of ammonium sulphate and 5 parts of the quaternised nitrogen compound described below in 2800 parts of soft water. After adding a solution of 7 parts of sodium salt of copper phthalocyanine disulphonic acid in 200 parts of soft water, the temperature is raised within 40 minutes to 100° and dyeing is performed for 1 hour at 100°. The wool is then rinsed in the apparatus with hot and then with cold water. After drying a pure, level, strongly coloured blue dyeing is obtained which has good perspiration, rubbing and wet fastness properties. No coloured greasy coating has formed in the dyeing apparatus.

If, in this example, instead of the sodium salt of copper phthalocyanine disulphonic acid, 7 parts of the sodium salt of nickel phthalocyanine trisulphonic acid or 7 parts of the sodium salt of copper phthalocyanine trisulphonic acid are used and otherwise the procedure described above is followed, then with the former greener and with the latter similar dyeings are obtained, all of which have similarly good fastness properties.

The quaternised nitrogen compound used in this example is produced as follows:

100 parts of oleylamine are dissolved in 300 parts of chlorobenzene. 45 parts of styrene oxide are added dropwise to the solution while stirring. The mixture is then slowly brought to the boil and the solution is kept at the boil for 4 hours. The chlorobenzene is then distilled off under vacuum. The residue, oleylamino-phenyl ethanol, forms a pale yellow oil which gradually solidifies in the cold.

1 part of sodium is dissolved in 50 parts of ethanol and 135 parts of the above substance is mixed therewith whereupon the ethanol is distilled off while stirring well. The residue is heated to 120–130° and ethylene oxide is introduced into the melt until the increase in weight amounts to 230 parts. On cooling, the reacting product obtained solidifies into a pale, wax-like mass which completely dissolves in water.

9 parts of dimethyl sulphate are added at 70° in about 10 minutes while cooling and stirring to 75 parts of the oleylamino-phenylethanol polyglycol ether obtained. The whole is stirred for another 30 minutes at this temperature whereupon a homogeneous solution is formed. On cooling, the quaternary ammonium compound is obtained as a pale, wax-like mass which is completely soluble in water. (The amino-phenylethanol polyglycol ether as herein employed and in the subsequent examples refers to a mixture of polyglycol ethers of the formulae I and II).

Example 2

0.5 part of the sodium salt of 4, 4', 4'', 4'''-copper phthalocyanine tetrasulphonic acid are dissolved in 250 parts of hot water with the addition of 0.4 part of ammonium sulphate and 0.2 part of the quaternary nitrogen compound described below. 10 parts of woollen worsted yarn are entered into this liquor at 40°, the liquor is brought to the boil within 45 minutes and dyeing is performed for 1 hour at the boil. The woollen worsted yarn is then rinsed first with warm and then with cold water. The pure, deep, level, reddish-blue dyeing has very good wet, light and rubbing fastness properties.

The quaternary nitrogen compound used in this example is produced as follows:

1 part of sodium methylate and then 20 parts of propylene oxide are added to 133 parts of the oleylamino-phenyl ethanol described in Example 1 and the whole is stirred for 6 hours at 50–60°. The mixture is then slowly heated to 70–80° until no more propylene oxide condenses

into the reflux condenser. The temperature is then raised for a short time to 140–150°, allowed to drop and 302 parts of ethylene oxide are introduced into the mixture at 100–120°. The corresponding polyglycol ether is obtained as a pale, wax-like mass.

5 parts of dimethyl sulphate are added to 52 parts of the condensation product so obtained and the whole is stirred for half an hour at 70–80°. The wax-like quaternised product is completely soluble in water.

Example 3

0.3 part of the sodium salt of copper phthalocyanine-monosulphonic acid-monosulphonic acid ethanolamide, produced from copper phthalocyanine-monosulphonic acid-monosulphonic acid chloride and ethanolamine in water, 0.4 part of ammonium sulphate and 0.2 part of the quaternised nitrogen compound described below are dissolved in 250 parts of hot water. 10 parts of woollen worsted yarn are entered into this liquor at 40°. The liquor is brought to the boil within 40 minutes and dyeing is performed for 1 hour at the boil. The dyed woollen worsted yarn is then rinsed, first with warm and afterwards with cold water. The pure, level blue dyeing obtained has very good wet, light, perspiration and rubbing fastness properties.

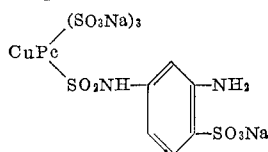
The quaternised nitrogen compound used in this example is produced as follows:

45 parts of styrene oxide are gradually added at 70° while stirring to 68 parts of dodecylamine. The mixture is heated to 140° whereupon an exothermic reaction occurs; the temperature rises to 175°. The reaction mixture is then stirred for another 4 hours at a temperature of about 140°. 2 parts of sodium ethylate are added to the melt and ethylene oxide is introduced at 110–120° until the increase in weight is 329 parts (20 mol).

10 parts of dimethyl sulphate are added within about 10 minutes at 70° while stirring and cooling to 94 parts of the dodecylamino-phenyl ethanol polyglycol ether produced according to this process. The mixture is then stirred for 1 hour at this temperature. On cooling, the quaternary nitrogen compound obtained is a wax-like mass which completely dissolves in water.

Example 4

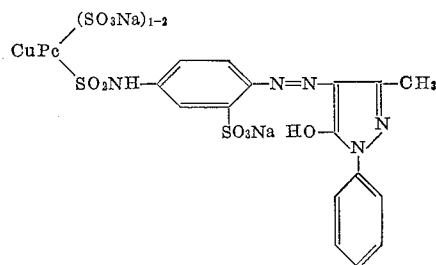
Dyeing is performed in the same way as described in Example 2 but instead of the copper phthalocyanine tetrasulphonic acid, 0.5 part of the dyestuff



are used. This dyestuff is produced by condensation of the copper phthalocyanine tetrasulphonic acid chloride with 1 mol of 2,4-diaminobenzene-1-sulphonic acid and subsequent saponification of the non-condensed sulphonic acid chloride groups. A level, blue dyeing which is fast to wet, perspiration and rubbing is obtained.

Example 5

Dyeing is performed as described in Example 2 but instead of the copper phthalocyanine tetrasulphonic acid, 0.5 part of the dyestuff of the formula



are used. This dyestuff is produced by condensation of a mixture of copper phthalocyanine sulphonic acid chloride which contains on the average 2 to 3 sulphonic acid chloride groups, with 1 mol of 2,5-diaminobenzene-1-sulphonic acid, saponification of the remaining sulphonic acid chloride groups, diazotisation and coupling with 1-phenyl-3-methylpyrazol-5-one.

A level green dyeing is obtained which is fast to perspiration, wet and rubbing.

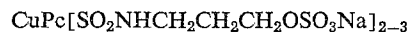
Example 6

0.4 part of the sodium salt of copper phthalocyanine trisulphonic acid are dissolved hot in 400 parts of water with the addition of 0.4 part of ammonium sulphate, 0.1 part of the quaternary nitrogen compound described in Example 2 and 0.4 part of the condensation product obtained according to U.S. Patent No. 2,089,212 from 1 mol of coconut oil fatty acids and 2 mols of diethanolamine. 10 parts of wool flannel are introduced into this liquor at 40°.

The temperature is raised within 40 minutes to the boil and dyeing is performed for 1 hour at the boil. The dyed wool flannel is then rinsed with warm and then with cold water. The full, pure, level, blue dyeing obtained has very good wet, light and rubbing fastness properties.

Example 7

0.5 part of the sodium salt of the sulphated copper phthalocyanine sulphonic acid-γ-hydroxypropylamide of the schematic formula

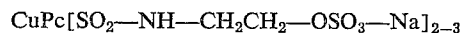


wherein Pc is the phthalocyanine moiety, are dissolved hot in 250 parts of soft water with the addition of 0.6 part of 40% acetic acid and 0.2 part of the quaternised nitrogen compound described below. 10 parts of woollen worsted yarn are introduced into this liquor at 40°.

The bath is raised to the boil within 45 minutes and dyeing is performed for 1 hour at the boil. 0.4 part of hexamethylenetetramine are then added and boiling is continued for another 30 minutes. The dyed yarn is then rinsed, first with warm and then with cold water. The pure, deep, level, blue dyeing obtained has very good fastness to wet, light and rubbing.

If in this example the corresponding nickel dyestuff is used instead of the copper-containing dyestuff, then a somewhat more greenish dyeing having similar good fastness properties is obtained.

A blue dyeing having similar properties is obtained if, instead of the above sulphated copper phthalocyanine sulphonic acid-γ-hydroxypropylamide, a corresponding number of parts of sulphated copper phthalocyanine sulphonic acid hydroxyethylamide of the schematic formula



are used.

The dyestuffs are produced as follows:

100 parts of copper or nickel phthalocyanine in 1200 parts of chlorosulphonic acid are heated for half an hour at 115° and then for 3 hours at 120°. The mixture is then cooled to 80° and 160 parts of thionyl chloride are added dropwise while stirring whereupon stirring is continued for 1 hour at 80° and then the solution is cooled. It is poured, while stirring, onto ice and the dyestuff sulphonic acid chloride which precipitates is filtered off under suction and washed with ice water until the washing water no longer colours congo red paper blue. The sulphonic acid chloride is stirred with water and then the pH of the suspension is adjusted to 7 with caustic soda lye. The dyestuff sulphonic acid chloride is then reacted with 105 parts of 1,3-propanolamine, first cold and then at 80°, and the dyestuff sulphonic acid γ-hydroxypropylamide is isolated, dried and esterified with sulphuric acid monohydrate or with chlorosulphonic acid.

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The quaternary nitrogen compound used in this example is produced as follows:

100 parts of oleylamine are dissolved in 300 parts of chlorobenzene. 45 parts of styrene oxide are added to the solution while stirring. The mixture is then slowly brought to the boil and the solution is boiled for another 4 hours. The chlorobenzene is distilled off in vacuo. The residue, oleyl amino-phenylethanol, forms a pale yellow oil which gradually solidifies in the cold.

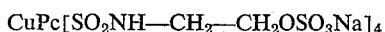
135 parts of this substance are mixed with 50 parts of ethanol in which 1 part of sodium has been dissolved and the ethanol is distilled off while stirring well. The residue is heated to 120–130° and ethylene oxide is introduced into the melt until the increase in weight amounts to 230 parts. On cooling, the reaction product obtained solidifies into a pale wax-like mass which dissolves completely in water.

9 parts of dimethyl sulphate are added at 70° within about 10 minutes while cooling and stirring to 75 parts of the oleylamino-phenylethanol polyglycol ether obtained. The whole is stirred for another 30 minutes at this temperature whereupon complete solution is obtained. On cooling, the quaternary ammonium compound is obtained as a pale wax-like mass which completely dissolves in water.

If, instead of the condensation product of oleylamino and styrene oxide, that from stearylamine and styrene oxide is used and otherwise the same procedure is followed, then a surface active quaternary nitrogen compound is obtained, which, with the dyestuffs described in this example, produces similar fast and level dyeings.

Example 8

0.5 part of the sodium salt of the sulphated copper phthalocyanine tetrasulphonic acid- β -hydroxyethylamide of the schematic formula



are dissolved in 250 parts of soft water with the addition of 0.6 part of 40% acetic acid and 0.2 part of a surface active quaternary nitrogen compound of the type described below. 10 parts of woollen worsted yarn are introduced into this solution at 40°. The bath is raised to the boil within 45 minutes and the goods are dyed for 1 hour at the boil. The 0.4 part of hexamethylenetetramine are added and the bath is boiled for another 30 minutes. The dyed yarn is then rinsed, first with warm and then with cold water. The pure, full, level, blue dyeing obtained has very good wet, light and rubbing fastness.

The dyestuff is produced as follows:

100 parts of copper phthalocyanine in 1200 parts of chlorosulphonic acid are heated for 4 hours at 142°. 160 parts of thionyl chloride are added dropwise at 80° to the solution while stirring and the whole is stirred for another hour at 80°. The solution obtained is then poured onto ice and the precipitated sulphonic acid chloride is filtered off under suction and washed with water until the washing water is neutral to congo paper. The sulphonic acid chloride is stirred with ice water and the pH of the suspension is adjusted to 7 with caustic soda lye. 106 parts of monoethanolamine are then added and the whole is stirred for some time at 80° to complete the reaction. The copper phthalocyanine tetrasulphonic acid ethanolamide is filtered off under suction, dried and sulphated by dissolving in sulphur monohydrate. The sulphated dyestuff is produced by pouring onto ice, salting out, filtering off, suspending the precipitate and carefully neutralising the suspension. It is in the form of the sodium salt and is precipitated with sodium chloride, filtered off under suction and dried.

The quaternary nitrogen compound used in this example is produced as follows:

45 parts of styrene oxide are gradually added at 70° while stirring to 68 parts of dodecylamine. The mixture is then heated to 140° whereupon an exothermic reaction

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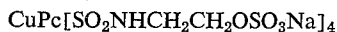
occurs; the temperature rises to 175°. The reaction mixture is then stirred for another 4 hours at a temperature of about 140°. 2 parts of sodium ethylate are added to the melt and ethylene oxide is introduced at 110–120° until the increase in weight amounts to 329 parts (20 mols).

10 parts of dimethyl sulphate are added within about 10 minutes at 70° while both stirring and cooling, to 94 parts of dodecylamino-phenylethanol polyglycol ether produced according to this process. The mixture is then stirred for 1 hour at this temperature. The quaternary nitrogen compound obtained on cooling as a wax-like mass dissolves completely in water.

If, instead of the condensation product from dodecylamine and styrene oxide, that from octylamine, decylamine, tetradecylamine or dodecylbenzylamine is used and otherwise the same procedure is followed, then a capillary active quaternary nitrogen compound is obtained which, with the dyestuff described in this example, produces similar fast and level dyeings.

Example 9

0.8 part of the sodium salt of the sulphated copper phthalocyanine tetrasulphonic acid hydroxyethylamide of the schematic formula



(produced as described in Example 8) are dissolved in 250 parts of soft water with the addition of 0.6 part of 40% acetic acid and 0.2 part of the surface active quaternary condensation product described below. Dyeing is performed as described in Example 7 and a full, pure, blue wool dyeing is obtained which is fast to light, wet and rubbing.

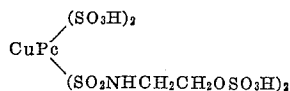
The surface active quaternary nitrogen compound used in this example is produced as follows:

1 part of sodium methylate is added to 133 parts of the oleylamino-phenylethanol described in Example 7 and then 20 parts of propylene oxide are added and the whole is stirred for 6 hours at 50–60°. The mixture is slowly heated to 70–80° until no more propylene oxide is condensed through the reflux condenser. The mixture is then heated for a short time to 140–150°, then the temperature is lowered and 302 parts of ethylene oxide are introduced at 100–120°. The corresponding polyglycol ether is obtained as a pale wax-like mass.

5 parts of dimethyl sulphate are added to 52 parts of the condensation product so obtained and the whole is stirred for half an hour at 70–80°. The wax-like quaternised product dissolves completely in water.

Example 10

Dyeing is performed in the same way as in Example 2 except that instead of copper phthalocyanine tetrasulphonic acid, 0.5 part of the dyestuff



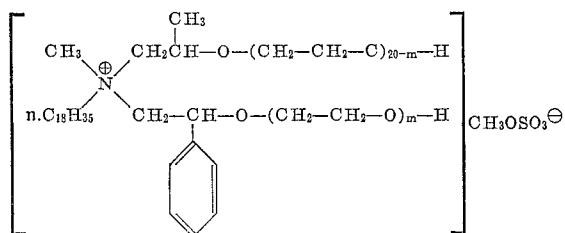
are used. This is produced by condensation of the copper phthalocyanine tetrasulphonic acid chloride with 2 mols of aminoethanol, subsequent saponification of the non-condensed sulphonic acid chloride groups and sulphation of the alcohol groups with sulphuric acid monohydrate. A level, blue dyeing is obtained which is fast to rubbing.

Example 11

1069 parts of the product of addition of 1 equivalent of styrene oxide, 1 equivalent of propylene oxide and 20 equivalents of ethylene oxide to 1 equivalent of technical oleylamine are melted at 75–80° and 102 parts of dimethyl sulfate are added dropwise to this melt within 45 minutes while stirring well. The reaction is slightly exothermic; as soon as the temperature drops, the reaction mixture is stirred for another 30 minutes at 80–85°

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and is then allowed to cool. 1171 parts of the quaternary salt of the probable formula



wherein m is a whole number from 0 to 22, are obtained as a pasty, water soluble mass. The position of the substituents in the polyethyleneoxy chains is probably correct; but isomeric compounds are also possible. The chain length of the individual polyglycol ether radicals is unknown and the sum of the chain members is, as is usual, an average value.

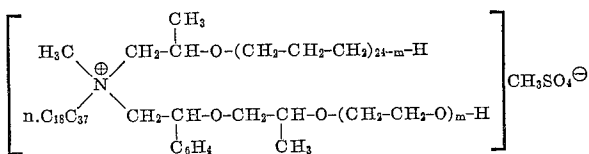
The addition product was produced by heating 240 parts of technical oleylamine with 108 parts of styrene oxide and 1.6 parts of sodium ethylate for 5 hours at 110–150°, cooling to 60°, adding 52 parts of propylene oxide within 1 hour, refluxing until the temperature attained 130° and introducing ethylene oxide at this temperature into the melt until the weight increases to 790 parts.

The new quaternary, water soluble condensation product makes it possible to attain level, light fast, deep blue dyeings on wool with dioxazine dyestuffs by, for example, the following process:

1 part of the sodium salt of 2,6-bis-phenylamino-9,10-dichlorotriphenodioxazine - di - bis - trisulphonic acid (commercial product: Sirius Light Blue FF2GL of the former I. G. Farbenindustrie in Frankfurt au Main, Germany) is dissolved in 3000 parts of hot water, 1 part of the quaternary ammonium salt described in the first paragraph and 2 parts of acetic acid are added, 100 parts of previously well wetted wool are introduced at 60° and the bath is brought to the boil within 30 minutes while circulating the liquor well. Dyeing is performed at this temperature for another 60 minutes. A deep blue, level, light fast wool dyeing is obtained and the bath is completely exhausted. The dyeing apparatus is not stained.

Example 12

632 parts of the production of addition of 1 equivalent of styrene oxide, 2 equivalents of propylene oxide, 24 equivalents of ethylene oxide to 1 equivalent of stearylamine are melted at 75–80°. 51 parts of dimethyl sulphate are added dropwise to the melt within 40 minutes while stirring well. The whole is stirred at 80–90° for another 30 minutes and then allowed to cool. The quaternary ammonium salt of the probable formula



is obtained as solid, soap-like paste which dissolves completely in the usual practical concentration in hot water.

The addition product is produced by the method described in the second paragraph of Example 1 from 121 parts of technical stearylamine, 54 parts of styrene oxide and 52 parts of propylene oxide and 475 parts of ethylene oxide.

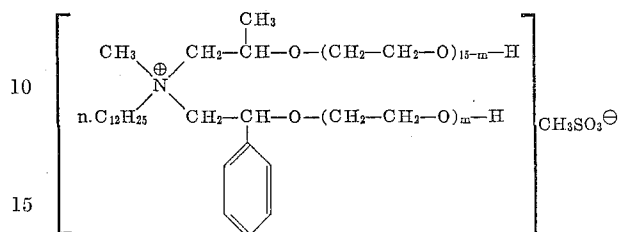
Under the dyeing conditions described in the last paragraph of Example 11, this product also produces level, strongly coloured blue dyeings on wool with the dioxazine dyestuff, Remastral Blue FF2GL, sold by Farbwerke Hoechst, in Frankfurt au Main, Germany.

Example 13

42 parts of dimethyl sulphate are added dropwise within 45 minutes at 80° while stirring well to 310 parts of the

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product of addition of 1 equivalent of styrene oxide, 1 equivalent of propylene oxide and 15 equivalents of ethylene oxide to dodecylamine. On completion of the exothermic reaction, the whole is stirred for half an hour while heating at 80–90°. It is then cooled and the quaternary ammonium salt of the probable formula



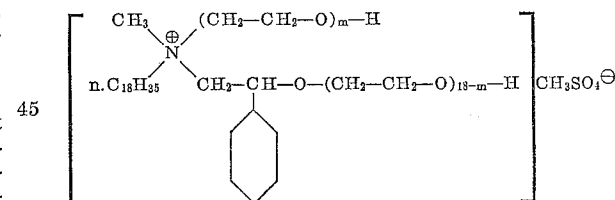
is obtained as a soap-like semi-solid paste which completely dissolves in hot water.

The addition product used is produced from 92.5 parts of technical dodecylamine, 60 parts of styrene oxide, 29 parts of propylene oxide and 330 parts of ethylene oxide by the method described in paragraph 2 of Example 11.

If 100 parts of wool are dyed for 1 hour at 98° in a liquor which contains 2 parts of the dioxazine dyestuff mentioned in Example 1, 1 part of the quaternary ammonium salt described above and 2 parts of acetic acid in 3000 parts of water, then a level, blue dyeing is obtained of good colour strength.

Example 14

65 parts of dimethyl sulphate are added dropwise within 40 minutes at 80° while stirring well to 590 parts of the product of addition of 1 equivalent of styrene oxide and 18 equivalents of ethylene oxide to 1 equivalent of oleylamine. As soon as the exothermic reaction has been completed, the whole is heated to 85–90° and stirred for another 30 minutes at this temperature. It is then cooled. The soap-like, past, water soluble quaternary salt corresponds to the probable formula



wherein m is a whole number from 0 to 18, or it is an isomeric mixture of this composition.

The addition product used above is produced by the method described in Example 11 by adding 120 parts of styrene oxide to 267 parts of oleylamine and then adding 792 parts of ethylene oxide.

This quaternary salt also produces level, light fast wool dyeings of good colour strength with polysulphonated dioxazine dyestuffs under the dyeing conditions described in the last paragraph of Example 11.

Dyeing auxiliaries having a similar action are obtained if, with otherwise the same procedure,

(a) In Example 11, the product of addition of 1 equivalent of styrene oxide, 2 equivalents of propylene oxide and 16 or 18 or 20 or 22 or 24 equivalents of ethylene oxide to oleylamine is used;

(b) In Example 12, the product of addition of 1 equivalent of styrene oxide and 16, 18, 20, 22 or 24 equivalents of ethylene oxide to hexadecylamine, octadecylamine, docosylamine is used.

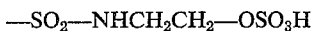
(c) In Example 13, the product of addition of 1 equivalent of styrene oxide, 2 equivalents of propylene oxide and 12, 14, 16, 18 or 20 equivalents of ethylene oxide to dodecylamine, tetradecylamine or hexadecylamine is used;

(d) In Example 14, the product of addition of 1

equivalent of styrene oxide and 18, 20 or 22 equivalents of ethylene oxide to stearylamine is used.

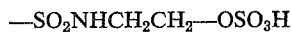
We claim:

1. In a process for the dyeing of wool with an aqueous dye bath containing a water soluble salt of a metal phthalocyanine containing chemically bound at least one member selected from the group consisting of $-\text{SO}_3\text{H}$,



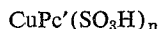
and $-\text{SO}_2-\text{NHCH}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ and mixtures thereof wherein the metal is of atomic number of 28 to 29, the improvement comprising mixing with the aqueous dyebath containing the aforesaid salt a quaternary condensation product of a primary amine selected from the group consisting of a higher alkylamine, a higher alkenylamine and higher alkyl-benzylamine, with, per equivalent of said primary amine from 7-30 equivalents of ethylene oxide, one equivalent of styrene oxide and from 0 to 2 equivalents of propylene oxide quaternized with the ester of a lower alkanol and a strong acid.

2. In a process for the dyeing of wool with an aqueous dyebath containing a water soluble salt of a metal phthalocyanine containing chemically bound at least one member selected from the group consisting of $-\text{SO}_3\text{H}$,



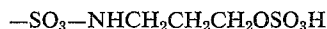
and $-\text{SO}_2-\text{NHCH}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ wherein the metal is of atomic number from 28 to 29 and said dyebath containing a condensation product obtained by heating a reaction mixture containing a monocarboxylic fatty acid of at least eight carbon atoms and one to three mols of a lower alkanol amine per mol of said fatty acid with the simultaneous splitting off of about one mol of water per mol of alkanolamine, the ratio of fatty acid to alkanolamine in said reaction mixture being such that for each mol of fatty acid in the reaction mixture there are at least three mols of monoalkanol radicals, the improvement which comprises mixing with the aqueous dyebath containing the aforesaid salt a quaternary condensation product of a primary amine selected from the group consisting of a higher alkylamine, a higher alkenylamine and higher alkyl-benzylamine, with, per equivalent of said primary amine, from 7 to 30 equivalents of ethylene oxide one equivalent of styrene oxide and from 0 to 2 equivalents of propylene oxide quaternized with the ester of a lower alkanol and a strong acid.

3. In a process for the dyeing of wool with an aqueous dyebath containing a water soluble salt of the formula



wherein Pc' is a phthalocyanine radical and n is a number from 2 to 4, the improvement which comprises mixing with the dyebath containing the aforesaid salt a quaternary condensation product of a primary amine selected from the group consisting of a higher alkylamine, a higher alkenylamine and higher alkyl-benzylamine, with, per equivalent of said primary amine, from 7 to 30 equivalents of ethylene oxide, one equivalent of styrene oxide and from 0 to 2 equivalents of propylene oxide quaternized with the ester of a lower alkanol and a strong acid.

4. In a process for the dyeing of wool with an aqueous dyebath containing a water soluble salt of a metal phthalocyanine containing chemically bound at least one member selected from the group consisting of



and mixtures thereof wherein the metal is of atomic number of 28 to 29, the improvement comprising mixing with the aqueous dyebath containing the aforesaid salt a quaternary condensation product of a primary amine selected from the group consisting of a higher alkylamine, a higher alkenylamine and higher alkyl-benzylamine, with, per equivalent of said primary amine, from 7 to 30 equivalents of ethylene oxide, one equivalent of styrene oxide and from 0 to 2 equivalents of propylene oxide quaternized with the ester of a lower alkanol and a strong acid.

5. As a levelling and shade-deepening agent in the dyeing of textile materials, a quaternary condensation product of a primary amine selected from the group consisting of a higher alkylamine, a higher alkenylamine and higher alkyl-benzylamine, with, per equivalent of said primary amine, from 7 to 30 equivalents of ethylene oxide, one equivalent of styrene oxide and from 0 to 2 equivalents of propylene oxide quaternized with the ester of a lower alkanol and a strong acid.

6. As a levelling and shade-deepening agent in the dyeing of textile materials, a quaternary condensation product of oleylamine, with, per equivalent thereof, about one equivalent of styrene oxide and with about 10 to 30 equivalents of ethylene oxide, quaternized with dimethyl sulfate.

7. As a levelling and shade-deepening agent in the dyeing of textile materials, a quaternary condensation product of oleylamine with, per equivalent thereof about one equivalent of styrene oxide, about two equivalents of propylene oxide and from about 16 to 24 equivalents of ethylene oxide, quaternized with dimethyl sulfate.

8. As a levelling and shade-deepening agent in the dyeing of textile materials, a quaternary condensation product of dodecylamine with per equivalent thereof, about one equivalent of styrene oxide, and about 20 equivalents of ethylene oxide quaternized with dimethyl sulfate.

9. As a levelling and shade-deepening agent in the dyeing of textile materials, a quaternary condensation product of stearylamine with, per equivalent thereof about one equivalent of styrene-oxide, about two equivalents of propylene oxide and about 24 equivalents of ethylene oxide, quaternized with dimethyl sulfate.

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