

UNITED STATES PATENT OFFICE

2,133,238

DYEING

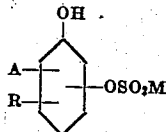
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No Drawing. Application September 25, 1935,
Serial No. 42,163

8 Claims. (Cl. 8-5)

This invention relates to improvements in the dyeing of animal and vegetable fibers including wool, silk, cotton, regenerated cellulose (rayon), linen, hair, straw, leather, hides, skins, feathers, paper, etc. It relates more particularly to improved dyeing compositions and the use thereof in the dyeing of said animal and vegetable fibers, and especially to new dyeing and levelling assistants.

10 According to the present invention, animal and vegetable fibers in the form of the unspun fiber, thread, skeins, yarn, knitted and woven cloth, and other textiles, alone or in admixture with other textile fibrous material of animal, vegetable or other origin, is dyed with the aid of a
15 composition comprising an alkyl phenol sulfonic acid compound which corresponds with the general formula



25 in which A represents hydrogen or a methyl group, R represents a nuclear alkyl hydrocarbon radical (saturated or unsaturated) containing 12 or more (preferably 12 to 23, and especially 14 to 19) carbon atoms, and M represents hydrogen or a metal, particularly an alkali metal, or an ammonium or organic ammonium radical.

30 The said alkyl phenol sulfonic acid compounds employed in accordance with the present invention are derivatives of phenol (hydroxybenzene) and of the cresols (1,2-, 1,3-, and 1,4-methyl-
35 hydroxybenzene) in which the alkyl hydrocarbon radical represented by R in the foregoing formula is directly linked to a nuclear carbon atom and in which the sulfonate group (represented in the foregoing formula by $-SO_2OM$) is
40 also directly linked to a nuclear carbon atom. For convenience they will be hereinafter referred to as "alkyl phenol sulfonates", which term generically includes the phenol and cresol derivatives, in the form of the free acids or their salts.
45 The alkyl phenol sulfonates preferably employed in accordance with the present invention are those in which the alkyl group contains a branched carbon chain, whether linked to the
50 benzene nucleus by an end carbon atom (an alpha carbon atom) or an intermediate carbon atom (that is, whether a primary, secondary or tertiary alkyl group).

It has been found according to the present invention that the said alkyl phenol sulfonates

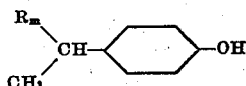
have the valuable property of serving as dyeing and levelling agents. Thus it has been found that the said alkyl phenol sulfonates impart great penetrating power to the dyeing composition whereby the levelling, brilliancy and fastness
5 characteristics of the dye as well as penetration of the dye into the fiber are enhanced. The improved penetration is secured regardless of the acid, alkaline, or neutral nature of the solution and is effective in all manner of dyeing processes.
10 In acid treating baths, as for example in acid dyeing baths, the said alkyl phenol sulfonates serve as anti-acid and acid protective agents; further, they appear to react with silk and protect it, as for example, against staining by cotton
15 direct dyes. They inhibit the deposition of insoluble soaps in baths which contain hard water and soaps. They do not form insoluble precipitates with hard water, and hence permit the employment of hard water, as well as permitting the
20 use of salt water in dyeing processes. By virtue of their excellent wetting action they produce rapid wetting out of the material to be dyed and aid in the wetting out of the dyes and in many cases improve their solubility.

25 The said alkyl phenol sulfonates may be incorporated in compositions prepared and applied with various kinds of dyes or mixtures of dyes; as for example, acid, chrome, developing, direct, the so-called "ice colors", vat dyes, sulfur dyes, etc. They may be used in baths or other preparations for dyeing, printing, stencilling, stamping, developing or coloring fibrous material in any manner.

35 The following examples illustrate several methods of preparing alkyl phenol sulfonates useful in connection with the present invention. It will be evident from a consideration of the disclosure herein that the invention is not limited to the use of products prepared in this manner, but includes
40 products of the type referred to herein prepared in other ways. The parts are by weight and temperatures are in degrees centigrade.

45 *Example 1.*—100 parts of commercial cetyl alcohol (containing 30 to 40 per cent of normal cetyl alcohol, 30 to 40 per cent of higher alcohols than cetyl, such as stearyl, etc., about 10 per cent of normal lauryl alcohol and about 20 per cent of normal myristyl alcohol), 100 parts of phenol, and 100 parts of anhydrous zinc chloride are
50 heated at 160° to 180° under a reflux condenser, with agitation for 16 hours. The condensation product is washed with water until practically free from water soluble products. The resulting oil is fractionally distilled in vacuo. The 55

fraction of the distillate which is collected between 195° and 240° at 15 mm. pressure of mercury is a faint yellow to water-white oil consisting chiefly of a mixture of alkyl phenols having the probable general formula:



in which R_m is a straight chain hydrocarbon radical having the formula:



the compound in which R_m is $C_{14}H_{29}$ being a predominating compound with a small amount of normal alkyl phenols and probably some ortho isomers present.

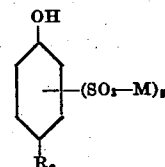
100 parts of the resulting purified alkyl phenol mixture, 40 parts of acetic anhydride and 160 parts of sulfuric acid monohydrate are mixed together and warmed gently to 70° to 75° until the product is completely soluble in water and a 0.2 per cent solution of which, after neutralization does not precipitate calcium salts from a calcium chloride or other soluble calcium salt solution containing the equivalent of 0.224 gram calcium oxide per liter. The mass is diluted with water to a final volume of 450 to 600 parts and neutralized with alkali, as for example, caustic soda or caustic potash or their equivalents. The neutral solution is clarified, if desired by filtration, and evaporated to dryness. The product is a brown to white solid soluble in water to give brown to white solid solutions. It comprises a mixture of inorganic salts (e. g., sodium sulfate) with sulfonates of the said alkyl phenols (e. g., in the form of the sodium salts), of which mixture the inorganic salts constitute in the neighborhood of 60 per cent. The alkyl phenol sulfonates present are soluble in alcohol, benzene and other organic solvents.

Example 2.—700 parts of an olefine with a boiling point ranging from 237° to 262° and having an average carbon content of 14 to 15 carbon atoms (and obtained by dechlorination of the monochlor hydrocarbons separated by fractionation from the products resulting from chlorination of petroleum distillates which boil at approximately 250° at atmospheric pressure), 700 parts of phenol, and 350 parts of anhydrous zinc chloride are mixed and heated together while agitated under reflux condenser at a temperature around 180° to 190° for from 5 to 16 hours. The condensed mass is diluted and washed with water until reasonably free of water-soluble impurities, and the crude brownish oil is distilled in vacuo. The fraction of the distillate boiling between 195° and 240° at 15 mm. pressure is collected separately. It is a faintly colored to water-white oil, insoluble in water and dilute caustic soda.

100 parts by weight of the resulting oil are mixed with 148 parts by weight of sulfuric acid monohydrate at 30°, then heated to 70°-75° and held there until a sample is completely soluble in water and in neutral, acid or alkaline aqueous solutions, and a 0.2 per cent solution of which, after neutralization, does not precipitate calcium salts from a soluble calcium salt solution containing the equivalent of 0.224 gram calcium oxide per liter. The sulfonation mix is poured into water, diluted to a final volume at 450 to 600 parts, and made neutral (for example, to delta paper, Congo Red paper, brilliant yellow, or brom-cresol-blue) with alkali, for example

caustic soda, or potash or their equivalents. The neutral solution is evaporated to dryness. If desired, the neutral solution can be clarified by filtration before being evaporated to dryness.

The product thus obtained is a mixture of which the chief components are alkyl phenol sulfonates having the probable formula



where R_c represents an aliphatic hydrocarbon group, M represents an alkali metal or equivalent derived from the base used for neutralization, and p is 1 or 2 but mainly 1. For the most part, the alkyl phenol sulfonates contain branched carbon chains in the groups represented by R_c and these groups are connected to the phenol nucleus by primary, secondary or tertiary carbon atoms. The chief components of the mixture contain 14 or 15 carbon atoms in the alkyl group represented by R_c .

In the form of the alkali metal and alkaline earth metal salts it is a faintly colored light brown to white, friable solid, readily reduced to a comminuted or powdery form (resembling powdered soap) and readily soluble in water.

The products of the above examples contain inorganic salts (alkali metal sulfates) in admixture with the alkyl phenol sulfonates. When it is desired to employ the alkyl phenol sulfonates in a form free from inorganic salts, they may be obtained from the mixed products produced by such processes as are given in the above specific examples by taking advantage of the solubility of the alkyl phenol sulfonate salts in alcohol and other organic solvents. Thus a mixture of a salt of the sulfonated product and an inorganic sulfate may be extracted with alcohol, and the resulting extract may be evaporated to leave a residue of the purified salt of the sulfonated product, as illustrated by the following specific example.

Example 3.—The neutralized solutions containing alkyl phenol sulfonates prepared in Examples 1 and 2, or equivalent aqueous solutions prepared from the final dry sulfonates, are diluted with an equal volume of commercial denatured alcohol, thoroughly mixed for several hours, filtered, and evaporated to dryness; or the dry sulfonates are extracted with successive portions of denatured alcohol, the total amount of alcohol used for this extraction preferably being not more than approximately four times the weight of the dry unextracted sulfonate, the combined extracts are mixed and digested with a small amount of animal charcoal, filtered, and evaporated to dryness. The residue obtained in either case is an alkyl phenol sulfonate in the salt (e. g., sodium salt) form, practically free from salts of mineral acids. By adding a small amount of alkali before evaporation, a white friable solid having a soap-like appearance and which is readily soluble in water is obtained.

The following examples illustrate the use of the products hereinbefore described. These examples are directed to the use of the mixed products resulting from the processes of Examples 1 and 2 in the form of the sodium salts and containing sodium sulfate and other impurities resulting from the said processes unless otherwise speci-

fied. For convenience, the said mixed products are hereinafter identified as "sodium secondary hexadecyl phenol sulfonate" and "sodium tetradecyl phenol sulfonate", respectively. It will be understood, however, that these examples are merely illustrative and that any of the other sulfonated products herein described may be similarly employed.

Example 4.—Dyeing wool.

A 10 gram skein of scoured woolen yarn is dyed at the boil for one hour in the following dye bath:

0.15 gram of National Cyanone R (Color Index No. 289)

2.5 cc. of 1% sodium bichromate solution

5.0 cc. of 10% acetic acid solution

0.5 gram of secondary hexadecyl phenol sodium sulfonate or 1 gram of tetradecyl phenol sodium sulfonate, and

500 cc. of water.

The alkyl phenol sulfonate imparts great penetrating power to the dye solution, which results in improved leveling (uniformity of shade).

Example 5.—Dyeing wool felt.

A 10 gram piece of wool felt is dyed in a bath containing the following substances:

0.15 gram of National Alzarine Sapphire BLN

0.3 gram of sulfuric acid or 0.15 gram of acetic acid

2 grams of Glauber's salt

0.3 gram of sodium secondary hexadecyl phenol sulfonate, and

400 grams of water.

The wool felt is introduced into the dye bath at a temperature of 50° C., and the bath is brought to a boil during one-half hour and is then boiled for 2 hours. The felt is then removed from the dye bath, rinsed and dried.

The action of the dyeing assistant is to retard the dyeing effect whereby the dye is carried into and combined with the fiber throughout the felt.

Example 6.—Vat dyeing.

A vat dye bath is made up by mixing:

1 gram of a vat dye—e. g., Vat Pink FF (U. S. P. -892,897)

0.2 gram of sodium secondary hexadecyl phenol sulfonate or of a sodium tetradecyl phenol sulfonate,

3 cc. of 30° Bé. caustic soda solution, and

1.5 gram of sodium hydrosulfite, in

300 cc. of water at 85° to 90° C.

When the dye bath is in a reduced state (i. e., about 15 to 20 minutes after the above bath mixture reaches 85° to 90° C.) it is diluted to 400 cc. A 20 gram skein of cotton yarn is immersed therein, dyed for 40 minutes in a cooling bath, and finished in the usual manner.

The presence of the alkyl phenol sulfonate in the dye bath not only improves the solubility of the leuco dye in the bath but produces on the fiber improved level shades of greater strength and brilliancy.

Example 7.—Dyeing composition of the Naphthol-AS type.

An impregnating solution is made up to contain 100 cc. water, 6 grams Naphthol-AS (beta-hydroxynaphthoic acid anilide), 12 cc. Turkey Red Oil, 12 cc. caustic soda solution (30° Bé.) and 1 gram of secondary hexadecyl phenol sodium sulfonate or 2 grams of tetradecyl phenol sodium sulfonate. This mixture is warmed to 170° to 180° F. until solution is complete and then diluted to a volume of 1 liter. 16 grams of salt, and 3 cc.

of 37% formaldehyde are then added and the whole is allowed to cool to about 100° F. The cloth to be impregnated is treated with this solution at about 100° F. by the usual methods, e. g., padding. The presence of the alkyl phenol sulfonate in the impregnating solution imparts greatly increased penetrating power to this solution and results in improved quality, strength and brilliancy of shades obtained upon development of dye on the fabric by means of an aromatic diazo body.

Example 8.—Direct dyeing of cotton.

A dye bath is prepared containing 100 cc. of an aqueous solution of Diazine Black AH Extra (Color Index No. 401) containing 0.4 gram of dyestuff, 20 cc. of a 20 per cent. common salt solution, and 1 gram sodium secondary hexadecyl phenol sulfonate. A 20 gram skein of boiled-out cotton yarn having attached thereto ties of real silk, is dyed for 45 minutes in this dye bath. As compared with dyeings obtained with a similar bath from which the alkyl phenol sulfonate is absent, the resulting dyeings show a marked increase in brilliancy of shade, more complete exhaustion of the dye bath, and a marked reduction in the staining of the real silk ties.

It will be realized by those skilled in the art that changes may be made in the compositions, and in the processes of preparing and using them, hereinbefore described, without departing from the scope of the invention.

The alkyl phenol sulfonates employed in accordance with the present invention may be prepared in various ways, as disclosed more fully in applications Serial Nos. 691,081 and 691,082, filed September 26, 1933, of which this application is a continuation-in-part. According to one method of preparation, an alkyl phenol or cresol of the



in which the symbols A and R have the meaning defined above, may be treated with a sulfonating agent, in the presence or absence of a solvent or diluent and/or a sulfonation assistant. As sulfonating agents there may be employed sulfuric acids of various strengths (e. g., 66° Bé. sulfuric acid, sulfuric acid monohydrate, oleum), chlor-sulfonic acid, etc. As solvents or diluent there may be employed any inert organic liquid which is not readily sulfonated such as halogenated hydrocarbons of the aliphatic and aromatic series, as for example, carbon tetrachloride, dichloroethane, tetrachlorethane, dichlorobenzene, etc. As sulfonation assistants there may be employed the lower organic acids and/or their anhydrides, as for example, acetic acid, acetic anhydride, etc.

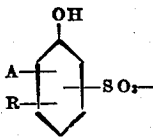
The sulfonation may be carried out with the aid of heating or cooling, as required, depending upon the ease of sulfonation of the alkyl phenol or cresol and the sulfonating power of the sulfonating agents. The sulfonation of the alkyl phenol or cresol may be carried out to an extent such that mainly one, or more or less than one, sulfonic acid group is present in the final product (based on the alkyl phenol or cresol). In general the extent of sulfonation of the alkyl phenol or cresol treated is such as to form chiefly the mono-sulfonic acid of the alkyl phenol, and to sulfonate impurities as well, if present.

The alkyl phenol sulfonates may be employed in accordance with the present invention in the form of their free sulfonic acids or in the form of salts of metals (as for example, of the alkali metals) or of organic bases, or of ammonia, etc. The salts may be obtained in any suitable manner; for example by reacting the sulfonated product, either in the crude form resulting from the sulfonation or in a purified form, with a metal oxide or hydroxide, ammonia or an organic base, or a suitable salt of one of these, in an amount adapted to form a neutral product. Among the bases, oxides and salts which may be combined with the sulfonated products to produce salts useful in accordance with the present invention are, for example, sodium, potassium and ammonium hydroxides; sodium, potassium and ammonium carbonates and bicarbonates; ammonia, magnesium oxide; ethylamine; pyridine; triethanolamine; propanolamines; butanolamines; diamino propanol; ethylenediamine; triethylene tetramine; etc.

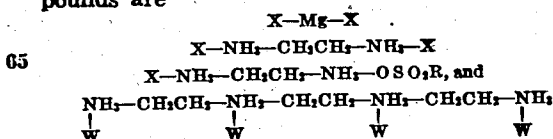
The sulfonated products in the form of metallic salts or salts of inorganic bases are usually yellowish to white, friable solids; and in the form of salts of organic bases vary from viscous oils to semi-solids to solids. In general, the salts are readily soluble in water and in aqueous (neutral, acid or alkaline) solutions to form solutions which are faintly colored brown or yellow, which are of a soapy nature and which foam readily. Certain of the salts, such as the salts of the aromatic monoamines and the aliphatic and aromatic polyamines, are oils which generally are insoluble in water but soluble in organic solvents (as for example, benzene, gasoline, etc.) and in aqueous solutions of alkalis (presumably by conversion to the salts of the alkalis).

It is to be understood that the invention includes the use of products containing a plurality of alkyl phenol sulfonic acid nuclei linked together through the sulfonic acid groups by a polyvalent metal or organic basic radical, as well as products in which an alkyl phenol sulfonic acid is linked through the sulfonic acid group to a different acid compound by a polyvalent metal or organic basic radical.

Thus the invention comprehends compounds of the type $(X)_n-Z-(X')_n$ and $(X)_n-Z-(Y)_n$, wherein X and X' each represent the radical



which may be the same or different, Z represents a polyvalent metal or organic base, Y represents a radical containing an acid group, n represents a whole member and A and R have the meaning defined above. Examples of such types of compounds are



wherein X and R have the meaning defined above, and W represents a radical containing an acid group at least one of which is a radical of the type represented by X.

The alkyl phenols may be prepared in various ways from various intermediates; for example,

phenol-ortho-, meta-, or para-cresol, or their mixtures may be condensed with an alkylating agent adapted to substitute an alkyl group containing at least 12 carbon atoms in the aromatic nucleus; or an alkyl ether of phenol or cresol in which an alkyl group containing at least 12 carbon atoms is linked by an oxygen atom to the aromatic nucleus, may be rearranged to the alkyl phenol; or the alkyl group may be substituted in the aromatic nucleus in the form of a ketone by condensing phenol or a cresol with a fatty acid or acid chloride corresponding with the desired alkyl group, in place of an alkylating agent in the process just enumerated, and subsequently reducing the resulting ketone.

In the condensation of phenol or a cresol with an alkylating agent there may be employed as alkylating agents non-aromatic alcohols (a. for example, straight-chain, primary mono-hydric alcohols; straight-chain, secondary monohydric alcohols; branched-chain primary alcohols; branched-chain secondary alcohols; tertiary alcohols of all types; etc.), olefine hydrocarbons containing straight or branched-chains, and preferably containing a double bond between the ultimate and penultimate carbon atoms; and halogen derivatives of hydrocarbons; all containing at least 12 carbon atoms, and preferably 12 to 23 carbon atoms, in an alkyl hydrocarbon chain. A preferred alkylating agent is commercial cetyl alcohol containing a mixture of normal alcohols, including a major proportion of cetyl alcohol together with lauryl alcohol, myristyl alcohol and alcohols higher than cetyl. As suitable condensing agents, there may be employed anhydrous zinc chloride, anhydrous aluminum chloride, anhydrous antimonium chloride, anhydrous ferric chloride, zinc, copper, etc.

It is to be noted that mixtures of two or more of the sulfonated products hereinbefore referred to may be employed. Furthermore, any of the said sulfonated products or their mixtures may be employed in connection with other hydro-tropic substances; dispersing, emulsifying and/or penetrating agents; aliphatic or aromatic sulfonic acids; acid alkyl esters of sulfuric acid; sulfonation products of petroleum oil; alkyl aryl sulfonates free from a nuclear hydroxyl group; and/or their derivatives.

For the purpose of illustration, the following additional products, in the form of the free sulfonic acids and in the salt (e. g., sodium salt) form, are mentioned as suitable for use in accordance with the present invention; but the invention is not limited thereto, as will be evident from the disclosure herein:

Cetyl phenol sulfonate (resulting from the condensation of cetyl alcohol with phenol and sulfonation of the resulting cetyl phenol);

Alkyl ortho-, meta- or para-cresol sulfonates, or mixtures thereof, in which the alkyl groups correspond with the alcohols contained in commercial cetyl alcohol (and obtainable by condensing commercial cetyl alcohol with ortho-, meta- or para-cresol and sulfonating the resulting mixture of alkyl ortho-, meta- or para-cresols);

Lauryl phenol or cresol sulfonates, or mixtures thereof with homologous alkyl phenol or cresol sulfonates (obtained by condensing phenol or cresol with a commercial mixture of lauryl alcohol and homologous fatty alcohols corresponding with the fatty acids of cocconut oil, and sulfonating the resulting alkyl phenol or alkyl cresol mixture);

Octadecyl (stearyl) phenol sulfonate (1-methyl-heptadecyl phenol sulfonate);

Normal primary hexadecyl phenol sulfonates (obtainable by reducing palmito- hydroxy benzophenone and sulfonating the resulting alkyl phenol);

Pentadecyl phenol sulfonate (obtainable by condensing phenol with the pentadecyl alcohol resulting from the polymerization of amyl alcohol, and sulfonating the resulting alkyl phenol);

Tricosanol phenol sulfonate (obtainable by condensing tricosanol-7 with phenol, followed by sulfonation); Alpha-alpha-dimethyl-hexadecyl-phenol sulfonate (obtainable by condensing dimethyl pentadecyl carbinol with phenol and sulfonating the resulting alkyl phenol).

I claim:

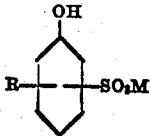
1. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid bath containing an alkyl phenol sulfonate having a single higher alkyl radical, said higher alkyl radical consisting of an alkyl hydrocarbon radical containing at least 12 carbon atoms.

2. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid bath containing an alkyl phenol sulfonate having a single higher alkyl radical, said higher alkyl radical consisting of an open chain hydrocarbon radical containing 12 to 23 carbon atoms.

3. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid bath containing an alkyl phenol sulfonate having a single higher alkyl radical, said higher alkyl radical consisting of an open chain hydrocarbon radical containing 12 to 23 carbon atoms in a branched carbon chain.

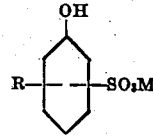
4. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid bath containing an alkyl phenol sulfonate having a single higher alkyl radical, said higher alkyl radical consisting of an open chain hydrocarbon radical containing 14 to 19 carbon atoms.

5. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid dye bath containing an alkyl phenol sulfonate having the general formula



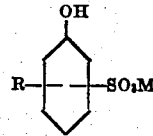
in which R represents an open-chain hydrocarbon radical containing at least 12 carbon atoms, and M represents hydrogen or a metal or an ammonium or organic ammonium radical.

6. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid dye bath containing an alkyl phenol sulfonate having the general formula



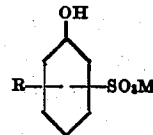
in which R represents an open-chain hydrocarbon radical containing 12 to 23 carbon atoms, and M represents hydrogen or a metal or an ammonium or organic ammonium radical.

7. A method of improving the leveling action of acid dyes on animal fibers, which comprises dyeing the fiber in an acid dye bath containing an alkyl phenol sulfonate having the general formula



in which R represents an open-chain hydrocarbon radical containing 14 to 19 carbon atoms, and M represents hydrogen or a metal or an ammonium or organic ammonium radical.

8. A method of improving the leveling action of acid dyes on wool, which comprises dyeing the wool in an acid dye bath containing an acid wool dye and an alkyl phenol sulfonate having the general formula



in which R represents an open-chain hydrocarbon radical containing 12 to 23 carbon atoms, and M represents hydrogen or a metal or an ammonium or organic ammonium radical.

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