United States Patent Office

3,442,600
Patented May 6, 1969

3,442,600

DYEING AND PRINTING FIBERS OF NATURAL AND SYNTHETIC POLYAMIDES

Manfred Daeuble, Frankenthal, Pfalz, and Klaus Dieck, Hans Heinrich, Heinz-Guenther Witsch, and Dietmar Theilig, Ludwigshafen (Rhine), Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen am Rhine, Germany

No Drawing. Filed Mar. 10, 1966, Ser. No. 533,243
Claims priority, application Germany, Mar. 18, 1965, B 81,037
Int. Cl. D06p *5/02, 3/24, 1/68*
U.S. Cl. 8—54
8 Claims

The present invention relates to a process for dyeing and printing fibers of natural and synthetic polyamides with anionic dyes.

It is known that fibers of natural or synthetic polyamides (hereinafter called polyamide fibers), particularly those of wool, can be dyed or printed by applying to material containing these fibers an aqueous solution of an anionic dye at a temperature below that at which the dye will go onto the fibers and then finishing off the dyeing or print by steaming and/or introducing it into a hot acid liquor. This method has serious disadvantages; for example it gives uneven dyeings.

It has therefore already been proposed to add further assistants to the dye solutions. In one known method of this type, condensation products of high molecular weight fatty acids with two equivalents of an alkanolamine, anion-active dispersing agents and if desired swelling agents for the fibers to be dyed are added as assistants to the dye solution. Another prior proposal is to add a soluble salt of a saturated, aliphatic, high molecular weight monocarboxylic acid to the dye solution. These prior art methods have the disadvantage that they require alkaline dye solutions because the assistants lose their effect in the acid range. Heat treatment of wool which has been impregnated with an alkaline liquor may however result in serious damage to the fibers.

It has therefore already been recommended that, to avoid this disadvantage, polyethylene glycol derivatives which have a chain of up to five ethylene oxide units attached at one end to a hydrophobic radical and at the other end to an anionic hydrophilic atom grouping should be added as assistants to the dye solutions. It has been found that this method does not yield results which are to some extent satisfactory unless the dye solution also contains a thickener. The method is therefore not universally applicable.

It is an object of the present invention to dye polyamide fibers uniformly by impregnation or printing with anionic dyes followed by steaming and/or introduction into a hot acid liquor.

Another object of the invention is to achieve uniform dyeings and prints by such a method in continuous operation.

Yet another object of the invention is to dye or print woolen fibers without damage.

It is moreover an object of the invention to dye or print polyamide fibers without the coemployment of thickeners.

Finally it is an object of the invention to prevent the marked soiling of the apparatus used for dyeing and printing polyamide fibers.

These and other objects are achieved by the present invention.

We have found that the abovementioned disadvantages are avoided and polyamide fibers can be dyed and printed particularly advantageously by applying an aqueous solution which contains (a) at least one anionic dye and (b) at least one anion-active assistant to the fibers at a temperature which is lower than the absorption temperature of all the dyes present and finishing off the dyeing or the print by steaming and/or introduction into a hot acid liquid (i.e. fixing the dye), when the said aqueous dye solution also contains (c) at least one adduct of 2 to 8, preferably 3 to 6, moles of ethylene oxide to 1 mole of a linear or preferably branched primary, secondary or tertiary alcohol having six to eighteen, preferably six to fifteen, carbon atoms or an adduct of 2 to 6, preferably 2 to 4, moles of ethylene oxide to 1 mole of an alkylphenol having six to fifteen carbon atoms in the alkyl radical and (d) at least one adduct of 1 to 2 moles of ethylene oxide to 1 mole of a hydroxy compound of the benzene or naphthalene series which may bear further low molecular weight nonionic radicals on the aromatic nucleus.

The anionic dyes to be used according to this invention may belong to any class of dyes, such as the azo, anthraquinone, phthalocyanine or nitro dyes. They may be for example 1:1 or 1:2 metal-complex dyes free from or containing sulfonic groups, chrome dyes which may be used together with agents yielding chromium, such as potassium dichromate, chromium fluoride or chromium acetate, or reactive dyes.

Anionic dyes in the present specification are defined as dyes which are described in the Colour Index (Second edition, 1956) as Acid Dyes, Mordant Dyes and Reactive Dyes.

Anion-active assistants are commonly used as additives in dyeing with anionic dyes. Preferred agents of this type are water-soluble salts of sulfonic acids or sulfuric acid hemiesters which contain a hydrophobic grouping in the molecule, especially their salts with alkali metals, ammonium and particularly organic bases. The following may be given as examples: the water-soluble salts of sulfuric acid hemiesters of aliphatic alcohols having ten to twenty, preferably twelve to eighteen, carbon atoms, of sulfuric acid hemiesters of adducts of alkylphenols and 1 to 5 moles of ethylene oxide having six to twelve carbon atoms in the alkyl radical, of alkyl and alkylaryl sulfonic acids having ten to twenty carbon atoms and of N-acyltaurines having ten to twenty carbon atoms in the acyl radical. Further anion-active assistants are the water-soluble salts of aminobenzenesulfonic acids which bear hydrophobic radicals as substituents on the nitrogen, and of sulfosuccinic alkyl esters. It has proved to be particularly suitable to use at least 5 parts by weight of anion-active assistant (b) to each 1000 parts by weight of dye liquor or print paste. In other respects it is advantageous to adapt the amount of anion-active assistant to the amount of agent (c). If the latter is easily soluble in water or easily dispersable therein, a weight ratio of agent (b) to agent (c) of 0.25:1 to 0.5:1 is sufficient. On the other hand, if sparingly soluble and poorly dispersable agents (c) are used, the said ratio is advantageously increased, the upper limit being about 2:1. It is in fact possible to raise the amount of anionic agent even further but it is recommended, in the interests of economical operation not to use more than 60 parts by weight of agent (b) to 1000 parts by weight of liquor or paste.

Starting materials for products of the type specified under (c) may be alkylphenols, preferably p-alkylphenols, which contain a linear or branched alkyl radical having six to fifteen, preferably eight to ten, carbon atoms; they may also bear on the benzene nucleus low molecular weight alkyl radicals, such as methyl, ethyl, and propyl radicals, but monoalkyl phenols are preferred. Other starting materials are linear or branched aliphatic alcohols which contain six to eighteen, preferably six to fifteen, carbon atoms. Examples of these are: p-n-hexylphenol, p-n-octylphenol, p-i-nonylphenol, o-n-decylphenol, m-n-dodecylphenol, n-hexanol, 2-ethylhexanol, isooctanol, nonanols, decanols, dodecanols, hexadecanols and octadecanols. Mixtures of such starting materials such as are obtained by syntheses or by derivation from natural raw materials, are also suitable. Branched-chain alcohols, such as are obtainable for example from oligomers of propylene or butylene, such as trimeric propylene, tetrameric propylene, diisobutylene or triisobutylene, by oxo synthesis and hydrogenation, are particularly advantageous as starting materials.

The products defined under (c) are obtainable from these initial materials by adding on ethylene oxide in the amounts given above to the alkylphenols or alcohols by a conventional method.

It is however also possible for example to react alkylphenols with preformed polyglycols and 2,2'-dichlorodiethyl ether in the presence of sodium hydroxide to obtain products of the type defined under (c).

The agent (c) is used preferably in an amount of 5 to 30 parts by weight to each 1000 parts by weight of dye liquor or print paste. Larger amounts may be used, but the economy of the process may suffer.

The adducts specified under (d) and derived from 1 to 2 moles of ethylene oxide and 1 mole of a hydroxy compound of the benzene or naphthalene series are monophenyl ethers or mononaphthyl ethers of ethylene glycol or diethylene glycol. They may bear as further low molecular weight nonionic radicals, particularly halogen atoms, preferably chlorine atoms, hydroxyl groups, low molecular weight aryl groups, in particular phenyl groups, alkyl groups having up to five carbon atoms and/or alkoxy groups having up to five carbon atoms, on the aromatic nucleus. Examples are the reaction products of 1 to 2 moles of ethylene oxide with 1 mole of hydroxybenzene, 1-hydroxy-2-methylbenzene, 1-hydroxy-4-methylbenzene, 1-hydroxy-4-phenylbenzene, 1-hydroxy-2-methoxybenzene, 1-hydroxynaphthalene, 2-hydroxynaphthalene, 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene and 1,5-dihydroxynaphthalene. It is particularly advantageous to use the adduct of 1 mole of ethylene oxide to 1-hydroxy-2-chlorobenzene and to 1-hydroxy-4-chlorobenzene.

The component (d) may be added to the liquor or paste preferably in an amount of 5 to 40 parts by weight with reference to 1000 parts by weight of liquor or paste. Whereas the efficacy of the agent gradually subsides below the preferred range, it is not deleterious to use larger amounts. The limits are determined by economic considerations.

The liquor or paste may also contain the conventional additives, as for example acids, such as acetic acid, swelling agents, such as benzyl alcohol, solubilizers, such as low molecular weight alcohols, glycols and butyrolactone, antifoaming agents, such as high molecular weight aliphatic alcohols, and thickeners. It is preferable, however, to use liquors which do not contain a thickener. When dyeing with dyes which are capable of reacting with suitable metals with the formation of complexes, for example the so-called chrome dyes, the mixture of assistants may be salted out by the addition of the agents supplying metal, for example chromium fluoride or chromium acetate; this causes separation into two layers and ineffectiveness of the system. This can be prevented by adding chelate-forming agents, as for example α-cyanocyclopentanone, β-diketo compounds or β-keto esters, such as acetylacetone, α-acetylbutrolactone, pentanone-2-carboxylic esters or acetoacetic esters. The complex-forming metal is thus bound and loses the property of salting out the assistant system from the solution. It is not necessary to bind the metal ions completely, but about 1 mole of the chelating agent to 1 mole of the metal salt used, for example chromium fluoride, is sufficient. It should however be taken into consideration that hydrogen ions are liberated by the chelate formation and contribute to the acidity of the liquor. Less acid is therefore required.

The salting-out action of the agents supplying metal on the assistant mixture may surprisingly also be suppressed by using the dye, which is to react with the metal to form the complex, in dispersed form, the usual dye dispersing agents, such as alkali metal salts of ligninsulfonic acids or naphthalenesulfonic acid-formaldehyde reaction products, being coemployed. The fact that finely divided dyes may be used brings with it the further advantage that even in the case of sparingly soluble chrome dyes, a colloidal solution may be obtained by scattering into warm water and this, after adding the assistants according to this invention and chromium salts, may be used immediately, whereas when dyes which are not finely divided are used, the suspension has to be boiled before the assistants and chromium salts are added and the remaining additives cannot be added until cooling has taken place.

Application of the dye liquor to the material to be dyed may be carried out by printing, coating or spraying. It is preferable, however, to use the padding method. Among the printing methods, the vigoureux printing of tops has proved to be especially suitable.

The temperature is kept below that at which all the dyes present would be absorbed. The absorption temperature is that at which the dye migrates from the aqueous dye solution to the material being dyed to an appreciable extent within the usual times of treatment; as used in the specification, the term absorption temperature means the temperature at which half of the dye originally present in the dye solution will migrate onto the material to be dyed within half an hour. It is advantageous to bring the dye liquor onto the material to be dyed at a temperature which is as much as possible below the absorption temperature; it has proved to be particularly suitable to use temperatures in the neighborhood of room temperature, i.e. at about 10° to 40° C.

Fixing of the dye may be carried out in the conventional way by treatment with steam at about 100° to 120° C. Another known measure for fixing the dye is treatment in a hot acid liquor. It is advantageous to introduce the material impregnated with the dye liquor into the acid liquor at a temperature of 80° to 98° C. It has proved to be particularly suitable to subject the material to be dyed first to a short steam treatment in order that the dye may be partly fixed and then to complete fixation of the dye in the hot acid liquor. Acids which are suitable for the acid liquor are inorganic and organic acids and also acid salts, examples being sulfuric acid, phosphoric acid, hydrochloric acid, formic acid, acetic acid, sodium hydrogen sulfate, potassium hydrogen sulfate and ammonium chloride. The acids or acid salts are advantageously used in such an amount that the acid liquor has a pH value of 3 to 4. Organic acids are preferred, particularly formic acid. In some cases it is useful to add water-soluble salts, preferably calcium salts, to the acid liquor.

After the dye has been fixed, the material may be washed, rinsed and dried in the usual way.

The process according to this invention may be carried out batchwise or continuously.

As compared with the prior art methods described earlier in this specification, the process aucording to the invention is distinguished by the fact that the steps of the process can be varied to a great extent; moreover the possibility of working in the absence of thickeners is particularly valuable. Thickeners may soil the apparatus used, for example the steamer, to such a degree that when the dye is changed it is necessary to carry out a cleaning of the apparatus lasting several hours. When the present process has been used without thickeners, a simple spraying out of the apparatus with water is sufficient to clean it.

Examples of polyamide fibers which may be dyed or printed according to the invention are wool and other animal hair, silk, protein fibers and synthetic polyamide fibers, such as those from ε-caprolactam, from adipic acid and hexamethylene diamine and from ω-aminoundecanic acid. They may be dyed or printed according to the invention alone as mixtures with each other or as mixtures with other fibers.

The present process is very well suited for dyeing tufted carpets of synthetic polyamide fibers. Whereas it has not been possible by prior art methods to dye these carpets continuously in a satisfactory manner, this is possible without difficulty by the process according to this invention; satisfactory dyeings are obtained even with 1:2 metal-complex dyes, which tend to give very streaky dyeings on tufted goods.

For dyeing and printing synthetic polyamide fibers it has proved to be particularly suitable to add to the dyeing or printing mixtures, adducts of more than 10 moles, preferably up to 80 moles, of ethylene oxide to 1 mole of an oxalkylatable compound containing a hydrophobic grouping in the molecule. Oxalkylatable compounds suitable as starting materials for these adducts are particularly aliphatic alcohols having ten to twenty carbon atoms, alkylphenols having ten to twenty carbon atoms, saturated and unsaturated fatty acids having ten to twenty carbon atoms, their glycerides and their reaction products with alkanolamines and primary and secondary alkylamines having ten to twenty carbon atoms. Examples of such adducts are: the adduct of 40 moles of ethylene oxide to 1 mole of castor oil or to 1 mole of the reaction product of a fatty acid, such as oleic acid or stearic acid, with diethanolamine. Addition of 2 to 4 parts by weight of these products to 1000 parts by weight of an impregnating liquor is usually sufficient.

The invention is illustrated by the following examples. The parts are parts by weight.

EXAMPLE 1

30 parts of finely divided dye C.I. No. 15,675 is dissolved in 500 parts of water, then 20 parts of the triethanolamine salt of p-n-decylbenzenesulfonic acid, 15 parts of the adduct of 6 moles of ethylene oxide to 1 mole of isodecanol, 10 parts of p-chlorophenyl monoethylene glycol ether (i.e. the adduct of 1 mole of ethylene oxide to 1 mole of 1 hydroxy-4-chlorobenzene) and 15 parts of glacial acetic acid are added and the whole is made up to 1000 parts with water.

This padding liquor is used to impregnate wool tops at a temperature of 30° to 35° C.; the tops are then squeezed out to a liquor retention of about 110%. The material is then steamed at 100° to 102° C. with saturated steam for fifteen minutes and then washed in warm water at about 40° to 45° C.

A deep bluish red dyeing is obtained which does not exhibit any grey streaks.

An equally good result is obtained when the wool tops, after impregnation and squeezing out, are treated for only ten minutes with saturated steam at 100° to 102° C., then brought into a boiling bath containing 5 g./l. of formic acid and having a pH value of 3.5 for five minutes and then washed.

A similar result is obtained when the adduct of 6 moles of ethylene oxide to 1 mole of isodecanol is replaced by an equal amount of an adduct of 3 moles of ethylene oxide to 1 mole of n-hexanol, or of 6 moles of ethylene oxide to 1 mole of pentadecanol or of 8 moles of ethylene oxide to 1 mole of n-octadecanol.

EXAMPLE 2

35 parts of the finely divided dye C.I. No. 15,710 is dissolved in 600 parts of water and then 20 parts of the diethanolamine salt of p-n-dodecylbenzene sulfonic acid, 20 parts of the adduct of 4 moles of ethylene oxide to 1 mole of isononanol, 10 parts of p-chlorophenyl monoethylene glycol ether, 25 parts of chromium fluoride and 20 parts of glacial acetic acid are added and the whole is made up to 1000 parts with water.

Wool tops are impregnated with this padding liquor, squeezed out and steamed in an atmosphere of saturated steam for forty-five minutes at 100° to 102° C. After the dyed material has been washed with water, a black dyeing is obtained which is fast to rubbing and exhibits no streaks.

Deep black dyeings which are fast to rubbing are similarly obtained by using the following compounds instead of the adduct of 4 moles of ethylene oxide to 1 mole of isononanol:

(a) 15 parts of an adduct of 2 moles of ethylene oxide to 1 mole of p-isononylphenol;

(b) 20 parts of the adduct of 6 moles of ethylene oxide to 1 mole of isodecanol;

(c) 20 parts of the adduct of 6 moles of ethylene oxide to 1 mole of isotridecanol;

(d) 15 parts of the adduct of 4 moles of ethylene oxide to 1 mole of isooctanol;

(e) 25 parts of the adduct of 3 moles of ethylene oxide to 1 mole of p-n-hexylphenol;

(f) 25 parts of the adduct of 4 moles of ethylene oxide to 1 mole of m-n-dodecylphenol or p-n-dodecylphenol;

(g) 30 parts of the adduct of 6 moles of ethylene oxide to 1 mole of p-isopentadecylphenol.

EXAMPLE 3

30 parts of finely divided dye C.I. No. 15,675 is dissolved in 500 parts of water and then 20 parts of the sodium salt of the sulfuric acid hemiester of oleyl alcohol, 20 parts of the adduct of 4 moles of ethylene oxide to 1 mole of isononanol, 10 parts of p-chlorophenyl monoethylene glycol ether and 15 parts of glacial acetic acid are added and the whole is made up to 1000 parts with water. Wool tops are impregnated with this padding liquor, squeezed out and steamed for fifteen minutes at 100° to 102° C. in an atmosphere of saturated steam.

A deep bluish red dyeing is obtained which is fast to rubbing and does not exhibit any streaks is obtained after washing.

Deep dyeings which are fast to rubbing are obtained in the same way by using the following anion-active compounds instead of the sodium salt of the sulfuric acid hemiester of oleyl alcohol:

(a) 20 or 40 parts of the sodium salt of the sulfuric acid hemiester of an adduct of 2 or 4 moles of ethylene oxide to 1 mole of nonylphenol;

(b) 20 parts of the sodium salt of an alkylsulfonic acid having fourteen carbon atoms;

(c) 20 parts of sodium monobenzylnaphthalene sulfonate;

(d) 25 or 50 parts of triethylammonium diisopropylnaphthalene sulfonate;

(e) 20 parts of the sodium salt of oleic tauride;

(f) 20 parts of the sodium salt of isohexylisopropylnaphthalene sulfonic acid.

EXAMPLE 4

20 parts of the finely divided dye C.I. No. 12,715 is dissolved in 500 parts of water and then 10 parts of triethanolammonium n-decylbenzene sulfonate, 12 parts of the adduct of 4 moles of ethylene oxide to 1 mole of isononanol, 5 parts of p-chlorophenyl monoethylene glycol ether, 10 parts of the adduct of 40 moles of ethylene oxide to 1 mole of castor oil and 5 parts of glacial acetic acid are added and the whole is made up to 1000 parts with water.

Textured nylon-6 fibers, tufted onto a jute fabric, are impregnated with the said solution, squeezed out with a padding machine and steamed for twenty minutes at 100° to 102° C. in an atmosphere of saturated steam.

After the fibers have been washed with water a deep bluish red nylon tufted material is obtained, the jute component exhibiting only a slight dyeing.

In the same way:

(a) 20 parts of the dye C.I. No. 18,690 gives a reddish yellow dyeing;

(b) 20 parts of a dye obtained by mixing chroming of 1 mole of unchromed dye C.I. No. 12,715 and 1 mole of unchromed dye C.I. No. 12,174 gives a yellowish red dyeing; and

(c) 1 part of a dye obtained by mixed chroming of 1 mole of unchromed dye C.I. No. 12,195 and 1 mole of unchromed dye C.I. No. 12,197 gives a level pale grey dyeing.

EXAMPLE 5

20 parts of dye C.I. No. 61,135 is dissolved in 500 parts of water and then 20 parts of the triethanolamine salt of n-decylbenzenesulfonic acid, 20 parts of the adduct of 6 moles of ethylene oxide to 1 mole of isodecanol, 10 parts of p-chlorophenylmonoethylene glycol ether and 10 parts of glacial acetic acid are added and the whole is made up to 1000 parts with water.

A wool tufted carpet which has not yet been coated is impregnated with the said solution and squeezed out on a padding machine. It is then steamed for twenty minutes at 100° to 102° C. with saturated steam and washed with water. A greenish blue tufted material is obtained which exhibits very good levelness and penetration of the dye.

Equally good results are obtained by replacing the p-chlorophenyl monoethylene glycol ether by the following substances:

(a) 10 parts of o-chlorophenyl monoethylene glycol ether;

(b) 15 parts of phenyl monoethylene glycol ether;

(c) 20 parts of phenyldiethylene glycol ether;

(d) 15 parts of p-methylphenyl monoethylene glycol ether;

(e) 30 parts of β-naphthyl diethylene glycol ether;

(f) 40 parts of the adduct of 1 mole of ethylene oxide to 1 mole of 1,2-dihydroxybenzene; or

(g) 40 parts of the adduct of 2 moles of ethylene oxide to 1 mole of 1,5-dihydroxynaphthalene.

We claim:

1. A process for dyeing and printing fibers of natural or synthetic polyamides by application of an aqueous solution which contains (a) at least one anionic dye and (b), in 1000 parts by weight, 5 to 60 parts by weight of at least one anion-active dyeing assistant to the fibers at a temperature which is lower than the absorption temperature of all the dyes present, said anion-active dyeing assistant being a water-soluble salt of a sulfuric acid hemiester of an aliphatic alcohol having ten to twenty carbon atoms, of a sulfuric acid hemiester of an adduct of an alkylphenol having six to twelve carbon atoms in the alkyl radical to a 1 to 5 molar amount of ethylene oxide, of an alkyl or alkylaryl sulfonic acid with ten to twenty carbon atoms or of N-acyltaurines having 10 to 20 carbon atoms in the acyl radical, and finishing off the dyeing or print by steaming with or without treatment with a hot aqueous acid liquor, wherein the dye solution also contains in each each 1000 parts by weight: (c) 5 to 30 parts by weight of at least one adduct of 2 to 8 moles of ethylene oxide to 1 mole of an aliphatic alcohol having six to eighteen carbon atoms or of 2 to 6 moles of ethylene oxide to 1 mole of an alkylphenol having six to fifteen carbon atoms in the alkyl radical; and (d) 5 to 40 parts by weight of at least one monophenyl ether or mononaphthyl ether of ethylene glycol or diethylene glycol which may bear on the aromatic nucleus a halogen atom, a hydroxyl group, a phenyl group, an alkyl group having up to five carbon atoms or an alkoxy group having up to five carbon atoms.

2. A process as claimed in claim **1** in which components (b) and (c) are used in the weight ratio 0.25:1 to 2:1.

3. A process as claimed in claim **1** in which 2 to 4 parts by weight of an adduct of 10 to 80 moles of ethylene oxide to 1 mole of an aliphatic alcohol having ten to twenty carbon atoms, an alkylphenol having ten to twenty carbon atoms, a fatty acid having ten to twenty carbon atoms or a glyceride thereof or a reaction product thereof with an alkanolamine or an alkylamine having ten to twenty carbon atoms, is added to 1000 parts by weight of dye solution

4. A process as claimed in claim **1** wherein p-chlorophenyl ethylene glycol ether is used as component (d).

5. A process as claimed in claim **1** in which at least one adduct of 3 to 6 moles of ethylene oxide to 1 mole of a branched alcohol having six to fifteen carbon atoms is used as component (c).

6. A process as claimed in claim **1** in which at least one adduct of 2 to 4 moles of ethylene oxide to 1 mole of an alkylphenol having eight to ten carbon atoms in the alkyl radical is used as component (c).

7. A process as claimed in claim **1** wherein a dye solution is used which consists of ingredients (a) through (d) in water.

8. An assistant mixture for carrying out the process of claim **1** and comprising the following components: (i) 5 to 60 parts by weight of at least one anion-active dyeing assistant, said assistant being a water-soluble salt of a sulfuric acid hemiester of an aliphatic alcohol having ten to twenty carbon atoms, of a sulfuric acid hemiester of an adduct of an alkylphenol having six to twelve carbon atoms in the alkyl radical to a 1 to 5 molar amount of ethylene oxide, of an alkyl or alkylaryl sulfonic acid with ten to twenty carbon atoms or of N-acryltaurines having 10 to 20 carbon atoms in the acyl radical; (ii) 5 to 30 parts by weight of at least one aduct of 2 to 8 moles of ethylene oxide to 1 mole of an aliphatic alcohol having six to eighteen carbon atoms or of 2 to 6 moles of ethylene oxide to 1 mole of an alkylphenol having six to fifteen carbon atoms in the alkyl radical; and (iii) 5 to 40 parts by weight of at least one monophenyl ether or mononaphthyl ether of ethylene glycol or diethylene glycol which may bear on the aromatic nucleus a halogen atom, a hydroxyl group, a phenyl group, an alkyl group having up to five carbon atoms or an alkoxy group having up to five carbon atoms.

References Cited

UNITED STATES PATENTS

3,334,960 8/1967 Abel.
3,363,972 1/1968 Ulrich et al.

NORMAN G. TORCHIN, *Primary Examiner.*

J. E. CALLAGHAN, *Assistant Examiner.*

U.S. Cl. X.R.

8—93