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STABLE SOLUTION FOR PRODUCING ICE COLORS

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This invention relates to the production of solutions of ice color compositions and more particularly to the provision of stable aqueous solutions suitable for producing ice colors on the fiber.

In the azoic dyeing and printing of fibrous materials such as textile fibers, leather and the like, a diazotizable aromatic or heterocyclic primary amine, usually called the azoic diazo base, devoid of water-solubilizing groups such as carboxylic and sulfonic acid groups, is diazotized and coupled on the fiber with an azoic coupling component, also devoid of solubilizing groups. The diazo may be in the form of a freshly prepared diazo or as a pre-stabilized diazo. In some cases wherein the diazonium salt is relatively stable, it may be as the sulfate or chloride, but more often it is stabilized as a double salt with a compound such as zinc chloride, or as a diazoamino compound with a stabilizing amine.

The stabilizing amines are primary, or more preferably, secondary amines; they may be alkyl, aryl or heterocyclic; they contain solubilizing groups which solubilize the diazoamino compound, such as sulfonic, carboxylic, polyoxy and the like groups, and at least one replaceable hydrogen atom attached to an amino nitrogen atom.

One usual method of producing fabrics colored with azoic dyes is to print the material with an alkaline paste which contains both the diazoamino compound and the coupler and then develop the color in situ by treatment with a weak acid, in some few cases with steam, but preferably with acidified steam. A representative composition which comprises a diazoamino compound and an azoic coupler is available on the market under the trademark "Rapidogen" (General Aniline & Film Corporation), and such term, as used herein, is used in reference to this type of composition.

For the most part Rapidogens have been produced and sold in powder form, but there has been of late increased interest in Rapidogens in solution form. Such stabilized ice color solutions are, however, subject to certain objections. Over extended periods of time in storage, the diazo compound decomposes somewhat with evolution of nitrogen so that there is a danger of pressure developing in the container. Furthermore, formation of the dye prior to use by premature coupling may occur which leads to turbid solutions or the formation of a sediment. This is not only detrimental from an esthetic sense but causes difficulty in handling, since the liquor must be free of sediment in order to give level prints. Further, as a result of this deterioration, the intensity of the color developed on the fiber is reduced, and duller prints are obtained. This tendency towards deterioration is particularly serious in the case of such solutions containing diazoamino compounds which are especially sensitive to precoupling, namely those derived from aromatic amines nuclearly substituted by acylamido (e.g. aroylamido) groups, and formulated to produce blue and violet prints, the tendency being aggravated by higher temperatures prevalent in various locations and seasons.

It is an object of this invention to provide an aqueous aklaline solution suitable for producing ice colors on the fiber which will not be subject to the above disadvantages. Another object of this invention is the provision of a stable aqueous alkaline solution containing an ice color diazo compound stabilized and solubilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, and an ice color coupling component. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which includes an aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, an ice color coupling component, and about 0.5 to 5% by weight of a nonionic surface active agent having the formula

$$R[(OC_2H_4)_nOH]_m$$

wherein R is a hydrophobic radical selected from the group consisting of (A) an aliphatic hydrocarbon radical of at least 12 carbon atoms, (B) an alkylated phenyl radical containing at least 1 alkyl radical and a total of at least 7 alkyl carbon atoms, and (C) a polyether radical having a molecular weight of about 300 to 3000 and 3 to 8 carbon atoms per recurring ether unit, n has a value of at least 4, and m is 1 when R is (A), 1 when R is (B) and 2 when R is (C). It has been found that the above defined compositions of the instant invention are surprisingly stable and resistant to sedimentation and deterioration, even at elevated temperatures up to 120° F. or more. In the above formula, the upper limit of n is generally about 70.

The nonionic surface active agents employed in the instant invention are well known in the art and are in general produced by reacting an appropriate hydrophobic aliphatic alcohol, alkylated phenol or polyglycol of the type defined by R above, with the required number of moles of ethylene oxide under the proper conditions, preferably in the presence of an alkaline catalyst such as potassium hydroxide or sodium hydroxide and heat and pressure, to introduce hydrophylic polyoxyethylene groups therein. General methods for carrying out the polyoxyethylation reaction with the aliphatic alcohols, alkylated phenols and polyglycols are adequately set forth in U.S. Patents 1,970,578, 2,213,477 and 2,674,619. Generally, the number of moles of ethylene oxide combined with the hydrophobe R in the surface active agents used in this invention will vary with the molecular weight of the hydrophobe with which it is reacted, and will usually vary from about 4 to 140 moles per mole of hydrophobe, depending upon the desired water-dispersibility and surface activity properties.

As examples of nonionic surface active agents employed in the instant invention, in which R is (A), namely an aliphatic hydrocarbon radical of at least 12 carbon atoms, there may be mentioned the reaction products of 1 mole of lauryl alcohol with 4 moles and 15 moles of ethylene oxide, 1 mole of hexadecyl alcohol with 12 moles and 20 moles of ethylene oxide, 1 mole of octadecyl alcohol with 20 moles of ethylene oxide, 1 mole of oleyl alcohol with 20 moles of ethylene oxide, and 1 mole of Oxotridecyl alcohol (as derived from tetrapropylene or triisobutylene by the Oxo process) with 7 moles, 10 moles and 15 moles of ethylene oxide, and the like. These aliphatic alcohols employed for reaction with ethylene oxide may be straight or branched, saturated or unsaturated, and primary, secondary or tertiary. Those preferred are branched chain primary aliphatic alcohols, which group includes 2,4,5,5,7-pentamethyl-1-octanol, 2,5,7,9-tetramethyl-1-decanol, and the like. Within this group, alcohols are preferably employed which are prepared by the catalytic reaction of a poly-

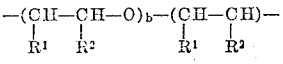
olefin such as tetrapropylene, pentapropylene, triisobutylene, tetraisobutylene, tributene and the like with carbon monoxide and hydrogen to form an aldehyde followed by catalytic reduction of this aldehyde to a primary alcohol. This two-stage process is known as the Oxo process and alcohols produced by such process may be designated as Oxo alcohols. Reference is made to British Patent No. 719,445 for a disclosure of suitable branched chain primary aliphatic alcohols and reaction products thereof with ethylene oxide to produce nonionic surface active agents useful in the instant invention.

As examples of nonionic surface active agents employed in the instant invention in which R is (B), namely an alkylated phenyl radical, there may be mentioned the reaction products of 1 mole of octylphenol with 4 moles of ethylene oxide, 1 mole of nonylphenol with 10 moles and 20 moles of ethylene oxide, 1 mole of dinonylphenol with 17 moles of ethylene oxide, 1 mole of didecylphenol with 40 moles of ethylene oxide, 1 mole of dodecylphenol with 15 moles of ethylene oxide, 1 mole of hexadecylphenol with 25 moles of ethylene oxide, and 1 mole of octadecylphenol with 30 moles of ethylene oxide and the like.

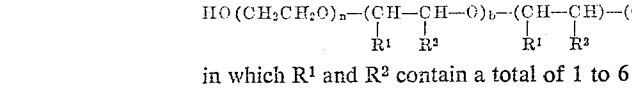
Where R is (C) in the above formula, *m* has a value of 2 so that these nonionic surface active agents are characterized by the formula

$$HO(CH_2CH_2O)_n—R—(OCH_2CH_2)_nOH$$

wherein R is a polyether radical having a molecular weight of about 300 to 3000 and 3 to 8 carbon atoms per recurring ether unit. More particularly, when R is (C) it is characterized by the formula



the formula for the nonionic surface active agent then being



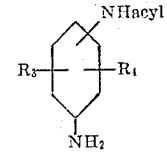
in which R^1 and R^2 contain a total of 1 to 6 carbon atoms and are selected from the group consisting of H, lower alkyl and phenyl, and, when taken together, the carbon atoms necessary to complete a carbocycle; and *b* has a value such that said polyether radical R has a molecular weight of about 300 to 3000. In this formula, *n* will generally have a value such that the nonionic surface active agent contains about 20 to 90% by weight of combined ethylene oxide. It will be understood that the values of *n*, *b*, R^1 and R^2, are interdependent and should be selected to provide a proper balance between the hydrophobe portion R and the hydrophilic polyoxyethylene groups. Thus, in the preferred embodiment wherein R^1 is H and R^2 is methyl, *b* may range from about 15 to 50 and preferably about 18 to 30 so that the polypropylene oxide portion of the molecule is water-insoluble. In this preferred embodiment, *n* will have a value of about 4 to 65. As the number of carbon atoms in the R^1 and R^2 groups increase, the value of *b* may be decreased so that when R^1 and R^2 in the portion R contain 6 carbon atoms, *b* can be 3 or 4. For a given hydrophobe portion R, the lower values of *n* within the above range will yield a liquid agent, and higher values of *n* will yield an agent of more viscous nature tending towards a solid state.

The nonionic surface active agents described in the foregoing paragraph may be prepared in known manner as described for example in U.S. Patent No. 2,674,619. In preparing such agents, a suitable 1,2-alkylene oxide or substituted alkylene oxide, as for example butylene oxide, amylene oxide, phenyl ethylene oxide (oxystyrene) cyclohexene oxide, cyclooctene oxide, or preferably propylene oxide, is polymerized in the presence of an alkaline catalyst such as sodium hydroxide, preferably at elevated temperatures and pressures, to produce the corresponding water-insoluble polypropylene glycol or substituted polypropylene glycol having a molecular weight of about 300 to 3000. Said polyglycol is then reacted under similar conditions with the required number of moles of ethylene oxide to yield the desired nonionic surface active agents. Such agents should generally have a molecular weight ranging from about 1200 to 15,000 and preferably about 2000 to 10,000.

As specific examples of nonionic surface active agents useful in the instant invention in which R is (C) as described above, there may be mentioned the reaction product of 30 moles of ethylene oxide with 1 mole of a polypropylene glycol having a molecular weight of about 2000, the reaction product of 1 mole of a polypropylene glycol having a molecular weight of about 1500 to 1800 with 20 to 30%, by weight of the reaction product, of ethylene oxide, the reaction product of 1 mole of a polypropylene glycol having a molecular weight of about 1500 to 1800 with 40 to 50%, by weight of the reaction product, of ethylene oxide, the reaction product of 1 mole of a polypropylene glycol having a molecular weight of about 1000 to 1200 with 40 to 50%, by weight of the reaction product, of ethylene oxide, and the reaction product of 1 mole of a polypropylene glycol having a molecular weight of about 1500 to 1800 with 80 to 90%, by weight of the reaction product, of ethylene oxide.

The ice color diazo components operative in the compositions of the instant invention are well known in the art and in general include diazotizable primary amine compounds devoid of solubilizing groups such as carboxylic or sulfonic acid groups. Included among such compounds are such aromatic and heterocyclic amines as anilines, xenylamines, naphthylamines, benzidines, aminocarbazoles, aminofuranes, aminothiazoles, aminoarylsulfones, aminodiphenyl ethers, aminobenzophenones, aminofluorenones, aminoazo compounds, and the like. As specific examples of some suitable ice color diazo components, there may be mentioned aminoazo toluene, 4-chloro-2-nitroaniline, 5-chloro-o-toluidine, 4-nitro-o-toluidine, 2,5-dichloroaniline, 4 - amino-m-anisidine, 4 - nitro-o-anisdine, 4 - chloro-o-anisdine, 1 - aminonaphthalene, 1-aminoanthraquinone, dianisidine, 5-chloro-4-nitro-o-anisidine, aminobenzophenone, aminodiphenylsulfone, 2,6-dichloro-1,4-phenylenediamine, benzidine, 4,4′-diaminostilbene, and the like.

As indicated above, the instant invention is particularly advantageous when using as ice color diazo components those particularly sensitive to precoupling which are derived from diazotizable aromatic primary amine compounds containing a nuclearly substituted acylamido group, and having the formula



wherein R^3 and R^4 are selected from the group consisting of H, lower alkyl such as methyl and ethyl, lower alkoxy such as methoxy and ethoxy, and halogen such as chlorine or bromine. As examples of such particularly sensitive diazos, there may be mentioned those derived from 4-benzoylamino-5-methyl-o-anisidine, 4 - benzoylamino-2,5-diethoxyaniline, 4 - benzoylamino-2,5-dimethoxyaniline, 4-benzoylamino-6-chloro-m-anisidine, 4-benzoylamino-2,6-dimethylaniline, 4 - toluylamino-2,5-dimethoxyaniline.

Prior to incorporation in the solutions of the instant invention, the ice color diazo component is diazotized in known manner as by treatment with sodium nitrite and dilute hydrochloric acid, and the resulting ice color diazo compound solubilized and stabilized against axoic coupling on the alkaline side in known manner by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom

attached to an amino nitrogen atom. The resulting stabilized ice color diazo compounds are often referred to as diazoamino, diazoimino, and diazoamidine compounds and the like, and generically under the term diazoamino compounds. The organic amines employed for such stabilization are well known and are reacted with the ice color diazo compound in proportions sufficient to react with all the diazo groups therein. As representative of such stabilizing organic amines, there may be mentioned by way of example, N-methyl taurine, sarcosine, 4-sulfo-2-aminobenzoic acid, 5-sulfo-2-methylaminobenzoic acid, 5-sulfo-2-ethylaminobenzoic acid, 1 - aminobenzoic - 3,6 - disulfonic acid, alpha-naphthylamine-2,4-disulfonic acid, beta-naphthylamine-4,6,8-trisulfonic acid, proline, pyrrolidine-alpha-sulfonic acid, glucamine, methyl glucamine, guanyl urea-N-sulfonic acid, guanyl taurine, N-nitro-guanyl urea, 2-biguanidyl naphthalene-1-sulfonic acid, creatine, cyanamide, and the like. Carboxylic and sulfonic acid groups are preferred as the solubilizing groups, but other groups are known such as ammonium salt groups and polyalcohol radicals and the like.

In general, the stabilized ice color diazo compounds employed in the solutions of the instant invention are formed by the reaction of the diazo derivative of a strongly basic diazotizable primary amine with a stabilizing amine of weak basicity. Such stabilized compounds do not undergo a coupling reaction in alkaline media in the presence of an ice color coupling component, but in the presence of acidic reagents, they split, permitting coupling of the ice color diazo compound with the ice color coupling component.

The ice color coupling components operative in the instant invention, also well known in the art, are devoid of solubilizing groups such as carboxylic or sulfonic acid groups. In general, these coupling components may be characterized as compounds having an active methylene group, an enolizable keto group or an aromatic hydroxy group inducing coupling, usually in ortho- or para-position, preferably the former, to said hydroxy group. Such compounds are typified by the acylacetarylides (e.g. anilides, etc.), the pyrazolones, and aromatic hydroxy compounds capable of coupling. As acylacetarylides there may be mentioned acetoacetic acid arylides, furoyl acetic acid arylides, terephthaloyl-bis-acetic acid arylides, and the like. As pyrazolones, there may be mentioned 1-phenyl-3-methyl-5-pyrazolone, 1-p-tolyl-3-methyl - 5 - pyrazolone, 3-methyl-5-pyrazolone, 5-pyrazolone, 1,3-dimethyl-5-pyrazolone, 1-(p-chlorophenyl)-3-methyl-5-pyrazolone, 1-(p-nitrophenyl)-3-methyl-5-pyrazolone, 1-(o-methoxyphenyl) - 3 - methyl-5-pyrazolone, 1 - (m-aminophenyl)-3-methyl-5-pyrazolone, 1-methyl - 5 - pyrazolone, 1 - phenyl - 5 - pyrazolone, 1 - phenyl-5-pyrazolone-3-carboxylic acid methyl ester, 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester, and other 5-pyrazolones either unsubstituted or substituted in the 1- and/or 3-positions by non-solubilizing radicals. The aromatic (carbocyclic or heterocyclic) hydroxy compounds useful as coupling components herein generally include phenols, resorcinols, 1- and 2-naphthols, benzonaphthols, hydroxy-benzofluorenones, hydroxy-azo compounds such as (o-hydroxyaniline→resorcinol) coppered and aniline→8-amino-2-naphthol and the like, in addition to arylides of beta-hydroxy aromatic and heterocyclic carboxylic acids. Illustratively, examples of such arylides (e.g. anilides, etc.) which may be employed in the process of the instant invention are 3-hydroxy-2-naphtholic acid arylides, 3-hydroxy-2-anthroic acid arylides, 3-hydroxy-2-carbazole carboxylic acid arylides, 3-hydroxy-2-furane carboxylic acid arylides, 2-hydroxy-11H-benzo(a)carbazole-3-carboxylic acid arylides, hydroxydibenzothiophene carboxylic acid arylides and the like. These and other such ice color coupling components operative herein are disclosed in Diserens, "Chemical Technology of Dyeing and Printing," volume 1, pages 213 to 224 (Reinhold Publishing Corp., 1948), Lubs, "Chemistry of Synthetic Dyes and Pigments," pages 182 through 192 (Reinhold Publishing Corp., 1955), and Adams, "Journal of the Society of Dyers and Colorists," volume 67 (1951), beginning at page 223.

The solutions of the instant invention should contain in known manner approximately equivalent proportions of the stabilized ice color diazo component and ice color coupling component whereby substantially no unreacted components remain after coupling has taken place on the fiber. The instant solutions are preferably of concentrations near the saturation point and usually contain from about 10 to 25% by weight of the Rapidogen (combined weight of stabilized diazo compound and coupling component). As stated above, improved and unexpected results of the instant invention are attained by incorporating into these solutions about 0.5 to 5% by weight of the above-described water-soluble nonionic surface active agents or mixtures thereof. The stabilized solutions of the instant invention are employed for the azoic printing of fibrous materials in known manner and there is accordingly no need to further describe their manner of application.

The solutions of the instant invention may be prepared in any desired manner and the components mixed in any desired order. It is preferred, however, to employ an auxiliary organic solvent in a concentration of about 5 to 50% by weight in the solution to assist in solubilizing the components of the solution, such solvent being usually an alcohol such as ethylene glycol, diethylene glycol, propylene glycol and 1,4-butanediol, and their methyl, ethyl, propyl, and butyl ethers, methanol, ethanol, propanol, butanol, cyclohexanol, and mixtures thereof and the like. Generally, the stabilized ice color diazo compound and the ice color coupling component are added to an aqueous alkaline solution containing the organic solvent, the said water-soluble nonionic surface active agent added, and an additional amount of water then added to yield a clear stable solution. If desired, known assistants, thickening agents, dispersing agents and the like may be included. The pH of the instant solutions should be more than 7 and preferably about 9 to 13.

The following examples, in which parts are by weight unless otherwise indicated, are illustrative of the instant invention and are not to be regarded as limitative.

Example 1

37 g. of the diazoamino from 4-benzoylamino-5-methyl-o-anisidine, diazotized and stabilized with sarcosine, 27 g. 3-hydroxy-2-naphthanilide and 1 g. 3-hydroxy-2-naphth-m-nitranilide are added to a mixture of 40 g. Cellosolve, 100 g. water and 6.2 g. KOH at a temperature below 40° C. and stirred to solution. 10 g. of the reaction product of 1 mole of Oxo tridecyl alcohol (from tetrapropylene by the Oxo process) with 7 moles of ethylene oxide are then added. The solution is then made up to 200 g. with water, stirred to solution and filtered.

A control solution is made up in similar manner, but excluding the said reaction product.

Samples of these solutions when tested for shade and strength by printing and developing on cotton in usual manner, are found to be commensurate with each other. Other samples of these solutions are placed in a 40° C. incubator for 7 months. The incubated sample with the nonionic additive is clear and gives a good print whereas the incubated sample without the additive contains considerable violet-colored sediment and prints 10–15% weaker and also duller in shade.

Example 2

The procedure of Example 1 is repeated, except that 10 g. of the reaction product of 1 mole of the same Oxo tridecyl alcohol with 10 moles ethylene oxide is substituted for the additive of Example 1, with commensurate results.

Example 3

The procedure of Example 1 is repeated, except that 10 g. of the reaction product of 1 mole of the same Oxo tridecyl alcohol with 15 moles ethylene oxide is substituted for the additive of Example 1, with commensurate results.

Example 4

The procedure of Example 1 is repeated, except that 10 g. of the reaction product of 1 mole of lauryl alcohol with 15 moles of ethylene oxide is substituted for the additive of Example 1, with commensurate results.

Example 5

The procedure of Example 1 is repeated, but employing 10 g. of the reaction product of 1 mole of nonylphenol with 10 moles of ethylene oxide instead of the additive of Example 1, with commensurate results.

Example 6

The procedure of Example 1 is repeated, but employing 10 g. of the reaction product of 1 mole of octadecylphenol with 30 moles ethylene oxide instead of the additive of Example 1, with commensurate results.

Example 7

The procedure of Example 1 is repeated, but employing 10 g. of the reaction product of 1 mole of dinonylphenol with 17 moles ethylene oxide instead of the additive of Example 1, with commensurate results.

Example 8

The procedure of Example 1 is repeated, but employing 10 g. of the reaction product of 30 moles of ethylene oxide with 1 mole of a polypropylene glycol having a molecular weight of about 2000 instead of the additive of Example 1, with commensurate results.

Example 9

The procedure of Example 1 is repeated, but employing 10 g. of the reaction product of 124 moles of ethylene oxide with 1 mole of a polypropylene glycol having a molecular weight of about 1500 instead of the additive of Example 1, with commensurate results.

Example 10

10.5 g. of the diazoamino from 4'-amino-2',5'-diethoxybenzanilide, diazotized and stabilized with N-methyltaurine, 6.1 g. of the diazoamino from dianisidine, tetrazotized and stabilized with N-methyltaurine and 18.8 g. 3-hydroxy-2-naphth-o-toluidide are added to a mixture of 30 g. Cellosolve, 10 g. diethyleneglycol and 7 g. KOH. To this is added 2 g. of the reaction product of 1 mole of nonylphenol with 20 moles of ethylene oxide and the solution made up to 200 g. with water. After stirring to solution, the solution is filtered.

At the end of 3 months storage at 110° F. this solution shows no signs of sedimentation whereas a control, made up without the said reaction product shows signs of sedimentation after 1½ weeks.

Example 11

20.8 g. of the diazoamino from dianisidine, tetrazotized and stabilized with N-methyl taurine and 20.8 g. 3-hydroxy-2-naphth-o-toluidide are mixed into 27 g. Cellosolve, 9 g. diethyleneglycol and 11.8 g. KOH at a temperature below 40° C. To this is added 1 g. of the reaction product of 1 mole of dinonylphenol with 17 moles of ethylene oxide. The solution is made up to 200 g. with water, stirred to solution and filtered.

At the end of three months storage at 110° F. this solution shows no signs of sedimentation whereas a control, made without the said reaction product, contains sediment after 2 weeks.

Example 12

A solution is made up as described in Example 11 above using:

11.6 g. diazoamino from 4'-amino-2',5'-diethoxybenzanilide, diazotized and stabilized with N-methyltaurine,
7.3 g. diazoamino from 4'-amino-2',5'-dimethoxybenzanilide, diazotized and stabilized with N-methyltaurine,
13.4 g. 3-hydroxy-2-naphthoic acid alpha-naphthalide,
45 g. Cellosolve,
15 g. diethyleneglycol,
6.5 g. KOH, and
3 g. reaction product of 1 mole of dodecylphenol with 15 moles of ethylene oxide,
Water to make up 200 g. of solution.

A storage test of this solution in comparison to a control which does not contain said reaction product shows this solution to be much more stable.

Example 13

131 g. diazoamino from 2,5-dichloroaniline diazotized and stabilized with 5-sulfo-2-ethylaminobenzoic acid is added to a mixture of 100 g. Cellosolve, 50 g. diethylene glycol, 200 g. water and 31 g. solid KOH. 95 g. 3-hydroxy-2-naphth-o-phenetidide is added, together with 30 g. of the reaction product of 1 mole of nonylphenol with 10 moles of ethylene oxide. The solution is made up to 1,000 g. with water. The solution shows no sedimentation after an extended period in storage.

Example 14

45 g. diazoamino from 3-amino-N,N-dimethyl-p-toluene-sulfonamide diazotized and stabilized with 5-sulfo-2-methylaminobenzoic acid is added to a mixture of 100 g. water, 75 g. Cellosolve, 25 g. diethylene glycol and 20 g. KOH. 20.2 g. 3-hydroxy-2-naphth-1,3-xylidide and 10.2 g. 3-hydroxy-2-naphth-m-nitroanilide are added. 10 g. of the reaction product of 1 mole of nonylphenol with 20 moles of ethylene oxide is then added, and the solution made up to 500 g. The solution shows no sedimentation after an extended period in storage.

Example 15

20 parts of the Rapidogen solution produced in Example 6 is mixed with 15 parts caustic soda 40° Be. and pasted with 65 parts neutral starch tragacanth.

Cotton cloth is printed with this paste by means of a roller and color developed by passing through a chamber containing steam acidified with acetic and formic acid vapors for 2–4 minutes. A violet print is produced.

This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

We claim:

1. A substantially clear, stable aqueous alkaline solution comprising an ice color diazo compound solubilized and stabilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of a nonionic surface active agent having the formula

$$R—\{(OC_2H_4)_nOH\}_m$$

wherein R is a hydrophobic radical selected from the group consisting of (A) an aliphatic hydrocarbon radical of at least 12 carbon atoms, (B) an alkylated phenyl radical containing at least 1 alkyl radical and a total of at least 7 alkyl carbon atoms, and (C) a polyether radical having a molecular weight of about 300 to 3000 and 3 to 8 carbon atoms per recurring ether unit, *n* has a value of at least 4, and *m* is 1 when R is (A), 1 when R is (B) and 2 when R is (C), said diazo compound and coupling

component being devoid of solubilizing carboxylic and sulfonic acid groups and being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

2. A solution as defined in claim 1 in which R in said nonionic surface active agent is an aliphatic hydrocarbon radical of at least 12 carbon atoms.

3. A solution as defined in claim 1 in which R in said nonionic surface active agent is the Oxo tridecyl radical in the alcohol derived from tetrapropylene by the Oxo process.

4. A solution as defined in claim 1 in which R in said nonionic surface active agent is an alkylated phenyl radical containing at least 1 alkyl radical and a total of at least 7 alkyl carbon atoms.

5. A solution as defined in claim 1 in which R in said nonionic surface active agent is a nonylphenyl radical.

6. A solution as defined in claim 1 in which R in said nonionic surface active agent is a dinonylphenyl radical.

7. A solution as defined in claim 1 in which R in said nonionic surface active agent is a dodecylphenyl radical.

8. A solution as defined in claim 1 in which R in said nonionic surface active agent is a polyether radical having a molecular weight of about 300 to 3000 and 3 to 8 carbon atoms per recurring ether unit.

9. A solution as defined in claim 8 in which said polyether radical is a polyoxypropylene radical.

10. A solution as defined in claim 1 in which said diazo compound contains a nuclearly substituted acylamido radical.

11. A substantially clear, stable aqueous alkaline solution comprising the diazo compound of 4-benzoylamino-5-methyl-o-anisidine solubilized and stabilized against azoic coupling on the alkaline side by reaction with sarcosine, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of the reaction product of 7 moles of ethylene oxide with one mole of the tridecyl alcohol derived from tetrapropylene by the Oxo process, said coupling component being devoid of solubilizing carboxylic and sulfonic acid groups and said diazo compound and coupling component being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

12. A substantially clear, stable aqueous alkaline solution comprising the diazo compound of 4-benzoylamino-5-methyl-o-anisidine solubilized and stabilized against azoic coupling on the alkaline side by reaction with sarcosine, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of the reaction product of 1 mole of a polypropylene glycol having a molecular weight of about 2000 with 30 moles of ethylene oxide, said coupling component being devoid of solubilizing carboxylic and sulfonic acid groups and said diazo compound and coupling component being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

13. A substantially clear, stable aqueous alkaline solution comprising the diazo compound of 4-benzoylamino-5-methyl-o-anisidine solubilized and stabilized against azoic coupling on the alkaline side by reaction with sarcosine, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of the reaction product of 1 mole of dinonylphenol with 17 moles of ethylene oxide, said coupling component being devoid of solubilizing carboxylic and sulfonic acid groups and said diazo compound and coupling component being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

14. A substantially clear, stable aqueous alkaline solution comprising the diazo compound of 4'-amino-2',5'-diethoxybenzanilide solubilized and stabilized against azoic coupling on the alkaline side by reaction with N-methyl taurine, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of the reaction product of 1 mole of nonylphenol with 20 moles of ethylene oxide, said coupling component being devoid of solubilizing carboxylic and sulfonic acid groups and said diazo compound and coupling component being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

15. A substantially clear, stable aqueous alkaline solution comprising the diazo compound of 4'-amino-2',5'-dimethoxybenzanilide solubilized and stabilized against azoic coupling on the alkaline side by reacton wth N-methyl taurine, an ice color coupling component, and, as substantially the sole surface active agent, about 0.5 to 5% by weight of the reaction product of 1 mole of dodecylphenol with 15 moles of ethylene oxide, said coupling component being devoid of solubilizing carboxylic and sulfonic acid groups and said diazo compound and coupling component being present in approximately equivalent proportions which, combined, amount to at least about 10% by weight in the solution.

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