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3,741,902

LAUNDRY PRESPOTTER COMPOSITION

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9 Claims

ABSTRACT OF THE DISCLOSURE

Laundry prespotter free of water and applicable to dampened fabrics without gelling consisting essentially of a liquid nonionic detergent, an organic liquid miscible therewith selected from certain alcohols, alkylene glycols, alkylene glycol alkyl or phenyl ethers, alkylene glycol esters, alkoxy ethanols and propanols and alkoxy triglycols, and optionally, an enzyme ingredient comprising alkaline or neutral protease or amylase; the prespotter can be packaged in an aerosol container for user convenience.

BACKGROUND OF THE INVENTION

This invention has to do with laundry prespotters and more particularly to liquid laundry products useful for prespotting of clothes, prior to regular washing thereof. As such, the invention is concerned with provision of a laundry prespotter which is effective in use, low in cost and liquid for easy application, e.g. by spray or aerosol delivery.

Prior art

Laundry prespotters are known. Typically a liquid detergent may be recommended for application directly onto heavily soiled areas. In other cases, a detergent containing powder may be applied as a concentrated solution in water to spots expected to be difficult to remove in a normal wash cycle. Enzyme containing prespotters have been marketed, in powder form typically, and are highly effective against protein based soil, e.g. blood stain. Such products are necessarily dry until used because the enzymes used, protease and amylase, tend to be self-destructive in aqueous environments. See U.S. Pat. 3,472,783 to Smille et al.; U.S. Pat. 3,451,935 to Roald et al.; and U.S. Pat. 3,519,379 to Blomeyer et al.

Liquid prespotters relying on detergents for cleansing power have encountered the problem of gelling of the liquid detergent on mixing with water. A gelled prespotter is not highly effective.

SUMMARY OF THE INVENTION

Accordingly, it is a major objective of the present invention to provide a laundry prespotter containing a liquid detergent which is non-gelling on admixture with water in use and which as well is a suitable environment for enzymes and amenable to convenience packaging, e.g. in aerosol containers.

This and other objectives of the invention, to become apparent hereinafter, are realized in a laundry prespotter according to the invention which consists essentially of a mixture free of water and glycerine and containing per 100 parts by weight from 5 to 20 parts of a liquid nonionic detergent and an organic liquid miscible therewith in an amount sufficient to prevent gelling of the detergent on water contact between 95 and 20 parts selected from certain alcohols, alkylene glycols, alkylene glycol ethers and esters, alkoxy ethanols and propanols, ketones and alkoxy triglycols. The mixture is a favorable environment for protease and amylase enzyme, e.g. in weight concentrations of 0.05 to 5% of the mixture, where the mixture is free of organic solvents for the enzymes, hereinafter enumerated. In fact, such mixtures have been demon-

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strated stable, i.e. efficacious for periods over one year when stored at 130° F. The mixture with or without the enzyme may be aerosol packaged with suitable propellant, particularly for foamed application to premoistened soil on fabric.

Thus, the invention provides as well method of maintaining ungelled a liquid nonionic detergent which is sprayed onto a water wet surface, e.g. of fabric, which includes coapplying to the surface with the detergent an organic liquid miscible with the detergent as identified herein. In aerosol delivery applications, the method further includes dissolving a normally gaseous but liquefiable propellant in the mixture under pressure in an aerosol dispensing can in an amount between 1 and 5% by weight of the mixture, to foam the coapplied components of the mixture upon application to the surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As indicated, the present invention is concerned with improved gelation behavior in liquid nonionic detergents which enables their use effectively as prespotters. This result is achieved in water free mixtures of liquid nonionic detergents and organic liquids miscible therewith.

The term "nonionic detergent" herein includes those produced by the introduction of alkylene oxide group into an organic hydrophobic compound or group having an aliphatic or aromatic structure. The hydrophobic organic group generally contains at least 8 carbon atoms and up to about 30 carbon atoms. Condensed with the hydrophobic group are at least 5 and preferably up to about 50 alkylene oxide groups. It is preferred to use the polyoxyethylene condensates derived from ethylene oxide. It is preferred to use the polyalkylene oxide condensates of alkyl phenol, such as the polyoxyethylene ethers or alkyl phenols having an alkyl group of at least about six, and usually about 8 to 12 carbons, and an ethylene oxide ratio (No. of moles per phenol) of about 7.5, 8.5, 11.5 or 20, though the number of ethylene oxide groups will be usually from about 8 to 18. The alkyl substituent on the aromatic nucleus may be di-isobutylene, diamyl, polymerized propylene, dimerized C₆-C₇ olefin, and the like.

Further suitable nonionic detergents are the polyoxyalkylene esters of organic acids, such as the higher fatty acids, rosin acids, tall oil acids, or acids from the oxidation of petroleum, et cetera. These polyglycol esters will contain usually from about 12 to about 30 moles of ethylene oxide or its equivalent and about 8 to 22 carbons in the acyl group. Suitable products are refined tall oil condensed with 16 or 20 ethylene oxide groups, or similar polyglycol esters of lauric, stearic, oleic acids, etc.

Additional nonionic detergents are the polyalkylene oxide condensates with higher fatty acid amides, such as the higher fatty acid primary amides, mono- and di-ethanolamides. Suitable agents are coconut acid fatty amide condensed with about 10 to 50 moles of ethylene oxide. The fatty acyl group will have similarly about 8 to 22 carbons, and usually about 10 to 18 carbon atoms, in such products. The corresponding sulfonamides may be used also if desired.

Other suitable polyether nonionic detergents are the polyalkylene oxide ethers of high aliphatic alcohols. Suitable fatty alcohols having a hydrophobic character, preferably 8 to 22 carbons, are lauryl, myristyl, cetyl, stearyl and oleyl alcohols which may be condensed with an appropriate amount of ethylene oxide, such as at least about 6, and preferably about 10 to 30 moles. A typical product is oleyl alcohol condensed with about 12, 15 or 20 moles of ethylene oxide. The corresponding higher alkyl mercaptans or thioalcohols condensed with ethylene oxide are suitable in the present invention also. The water-sol-

uble polyoxyethylene condensates with hydrophobic polyoxypropylene glycols may be employed also.

Further suitable nonionic detergents are the higher fatty acid alkanolamides, such as the monoethanolamides, diethanolamides and isopropanolamides wherein the acyl radical has about 10 to 14 carbon atoms and amine oxides. Examples are coconut (or equivalent lauric), capric and myristic diethanolamide, monoethanolamide and isopropanolamide, dodecyl dimethyl amine oxide and dimethyl acetoxymethylamine oxide where alkyl is C_{11} - C_{14} .

Intimately mixed with the above mentioned detergents are organic liquids miscible therewith. Suitable co-liquids include:

(1) Alcohols having 1 to 13 carbon atoms, e.g. alcohols selected from methanol, ethanol, propanols, butanols, pentanols, hexanols, heptanols, iso-octanols, iso-decanols, trimethyl-4-nonanol and tridecanol;

(2) Alkylene glycols having molecular weights up to 600, e.g. selected from ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, polyethylene glycols having molecular weights between 190 and 600, 2-methyl-2-ethyl-1,3 propanediol, 2-ethyl-1,3-hexanediol, and tetraethylene glycol;

(3) Alkylene glycol alkyl or phenyl ethers, e.g. having molecular weights up to 207 in which the alkyl group or phenyl group contains up to 6 carbon atoms. Among others these ethers may be mentioned: diethylene glycol diethyl ether, diethylene glycol monomethyl ether, diethylene glycol dibutyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, and dipropylene glycol monomethyl ether;

(4) Ethylene glycol alkyl esters having molecular weights up to 205, in which the ester group contains from 2 to 4 carbon atoms inclusive, e.g. diethylene glycol monomethyl ether acetate, and diethylene glycol monobutyl ether acetate;

(5) Alkoxy ethanol or propanols having a molecular weight up to 201 and in which the alkoxy group contains up to 4 carbon atoms, e.g. 2-ethoxyethanol, methyl-2-ethoxyethanol, isobutyl-2-ethoxyethanol, butyl-2-ethoxyethanol, hexyl-2-ethoxyethanol, phenyl-2-ethoxyethanol, 1-butoxyethoxy-2-propanol, n-butoxy-2-propanol and n-propoxy-2-propanol;

(6) Ketones having a molecular weight up to 185, e.g. selected from the group consisting of acetone, methyl-ethyl ketone, methylisobutyl ketone, cyclohexanone, methyl-n-amyl ketone, methylisoamyl ketone, ethylbutyl ketone, diisobutyl ketone, isobutylheptyl ketone, mesityl oxide, isophorone, acetyl acetone and diacetone alcohol; and

(7) Alkoxy triglycols having a molecular weight up to 207 and in which the alkoxy group contains up to 4 carbon atoms inclusive, e.g. selected from methoxytriglycol, ethoxytriglycol and butoxytriglycol.

The laundry prespotter typically employs the mentioned nonionic detergents and organic liquids in proportions per 100 parts by weight of their mixture of 5 to 80 parts of detergent and correspondingly 20 to 95 parts of the organic liquid. In preferred formulations at least 40 parts by weight of detergent is employed.

The above mixture may also include a thickening agent, e.g. from 0.25 to 10% by weight of a polyethylene glycol having a molecular weight between 1000 and 20,000.

The described compositions form highly desirable vehicles for enzymes to be used as prespotters. Suitable enzymes are described in detail in U.S. Pat. 3,451,935 above mentioned, which is hereby incorporated by reference. Particularly preferred are neutral or alkaline protease and amylase enzymes, suitably having an average particle size of from 1 to 100 microns. Amounts of enzymes employed may range between 0.05 and 5 percent by weight, or higher if economics permit, e.g. to 15%, by weight based on the weight of the mixture of detergent and organic liquid. Solvents for enzyme ingredients should be excluded from the formulations, thus, water, glycerine,

ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and dipropylene glycol liquids are not to be used in enzyme compositions according to the invention. Thickening agents such as those mentioned above may be used in the enzyme versions of the invention compositions, and in the above-mentioned amounts. While pH of the enzyme prespotter is not narrowly critical, it is desirably on the near to neutral to alkaline side, i.e. between 6 and 10.

The just described compositions are liquid and highly adapted to spray application onto premoistened spots on fabric. Local application thusly means economy in use. Alternatively the prespotter may be poured onto spotted areas or added to water for soaking or incorporated in wash water in a conventional washing machine.

Maximum benefit is realized through spray application, e.g. by pumping through a nozzle or preferably by aerosol spray application.

In a highly preferred embodiment, there is provided an aerosol package comprising a pressure resistant can having a dispensing nozzle and containing the nonionic detergent-organic liquid mixture or the nonionic organic liquid-enzyme mixtures mentioned, as well as a conventional aerosol propellant, e.g. nitrogen, carbon dioxide, nitrous oxide, an inert hydrocarbon having up to five carbon atoms or halogenated hydrocarbon having up to four carbon atoms, which is normally gaseous, but liquefiable at container pressure below 75 pounds/square inch gauge at 25° C., and preferably one which is at least partially soluble in the mixtures mentioned in an amount sufficient to cause foaming of the liquid on discharge from the container through the nozzle, e.g. soluble enough to form 1% to 50% solutions in the liquid mixture.

EXAMPLES

In the examples following all parts and percentages are by weight unless otherwise indicated.

Enzyme I herein is a blend of neutral and alkaline protease and -amylase sold by Monsanto Company under the name Enzyme AP.

Enzyme II herein is a blend of alkaline protease and -amylase sold by Rohm and Haas Company under the name Protease 57.

Enzyme III is a blend of alkaline protease and amylase sold by Wallerstein under the name Alkaline Protease 201-HA.

Detergent A is a linear C_{11} - C_{15} secondary alcohol with 9 moles of ethylene oxide (Tergitol 15-S-9).

Detergent B is a linear secondary C_{12} - C_{15} alcohol with 9 moles of ethylene oxide (Tergitol 25-S-9).

Detergent C is a linear secondary C_{14} - C_{15} alcohol with 12 moles of ethylene oxide (Tergitol 45-S-12).

Detergent D is a linear primary C_{12} - C_{15} alcohol with 7 moles of ethylene oxide (Neodol 25-7).

Detergent E is a nonyl phenoxy poly(ethyleneoxy)ethanol (Igepal CO630).

Example 1

A prespotter composition was prepared by blending 0.5 part of Enzyme I, 49 parts of hexylene glycol, 49 parts of Detergent B and 1.5 parts of Polyethylene Glycol 6000. Even after three months of storage at 140° F., the composition effectively removed blood and carbohydrate stains from test cloths as well as grease and ball point pen ink stains therefrom.

Example 2

Example 1 was duplicated using 65 parts of Detergent B and 33 parts of Glycol 6000. The composition was similarly effective as a stain remover and prespotter before and after storage.

Example 3

Example 1 was duplicated using 59.5 parts of Detergent C, 40 parts of dioxane as the organic liquid, and omitting

the Glycol 6000. The composition was similarly effective as a stain remover and prespotter before and after storage.

Example 4

An aerosol package was made up by packaging under pressure in a dispensing container. Enzyme I, 0.25 part, Detergent A, 52.65 parts, hexylene glycol 26.35 parts, Polyethylene Glycol 6000, 0.5 part, Freon 12 (dichlorodifluoromethane), 20 parts, and perfume 0.25 part. The composition is effective as a prespotter sprayed directly onto areas of cloths previously stained with blood, spinach, starch, grease and ball point pen ink. The composition was tested again after 13 months of storage at 130° F. and again found effective.

Example 5

Example 4 was duplicated substituting Detergent D for Detergent A. The composition was similarly effective and stable.

Example 6

Example 4 was duplicated substituting Detergent E for Detergent A. The composition was similarly effective and stable.

Example 7

A non-gelling nonionic prespotter composition free of enzyme was prepared using Detergent C, 50 parts, and dioxane, 50 parts. The composition was an effective prespotter against grease and ball point pen ink, but not as effective against protein stain as the preceding examples.

Example 8

Example 7 was duplicated substituting hexylene glycol for dioxane. The composition was similarly effective as the prespotter in Example 7 and non-gelling.

Example 9

Example 7 was duplicated substituting propoxy propanol for dioxane. The composition was similarly effective as the prespotter in Example 7 and non-gelling.

Example 10

Example 7 was duplicated using Detergent E for Detergent C and mesityl oxide for the dioxane. The composition was similarly effective as the prespotter in Example 7 and non-gelling.

Example 11

Test cloths were written upon with ball point pens and grease stained. The fabric was moistened with water and treated with the composition of Example 1, delivered from an aerosol dispenser. The ink and grease stains were effectively removed. Similar effectiveness against premoistened protein and carbohydrate soil was also found. No gelling of the applied detergent was noted in the tests.

Example 12

A liquid mixture containing 0.5% Enzyme I, and 99.5 parts of a 60:40 mixture of a detergent (Tergitol 45-S-10) and dioxane was added to a washing machine load comprising blood and carbohydrate soiled test cloths at a level of 0.25 cup/60 liters of wash water (ca. 0.10% by weight) and effectively removed the indicated soil.

Control I

Detergent A is sprayed onto moistened cloth containing test soil specimens of blood and chocolate. The detergent gells and does not remove the stain or facilitate its removal in a normal washing cycle.

Control II

Example 1 is duplicated substituting ethylene glycol for hexylene glycol. The solution is evaluated for stain removal every day. After seven days storage at 70° F. the enzyme dropped to one-third its original removal rate.

Example 13

Example 1 is duplicated substituting a coconut fatty acid amide condensed with 10 moles of ethylene oxide for Detergent A. The composition is an effective prespotter.

Example 14

Example 1 is duplicated substituting oleyl alcohol condensed with 15 moles of ethylene oxide for Detergent A. The composition is an effective prespotter.

Example 15

Example 1 is duplicated substituting myristic diethanolamide for Detergent A. The composition is an effective prespotter.

I claim:

1. Laundry prespotter free of water and glycerine and consisting of a mixture containing per 100 parts by weight from 5 to 80 parts of a liquid nonionic detergent and an organic liquid miscible therewith in an amount sufficient to prevent gelling of the detergent on water contact between 95 and 20 parts, said organic liquid being selected from the group consisting of alcohols having 1 to 13 carbon atoms selected from the group consisting of methanol, ethanol, propanols, butanols, pentanols, hexanols, heptanols, iso-octanols, iso-decanols, trimethyl-4-nonanol, and tridecanol; alkylene glycols having molecular weights up to 600 selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, polyethylene glycols having molecular weights between about 190 and 600, 2-methyl-2-ethyl 1,3-propanediol, 2-ethyl-1, 3-hexanediol, and tetraethylene glycol; alkylene glycol alkyl ether selected from the group consisting of diethylene glycol diethyl ether, diethylene glycol monomethyl ether, diethylene glycol dibutyl ether, diethylene glycol monobutyl ether, diethylene glycol monophenyl ether, propylene glycol monomethyl ether and dipropylene glycol monomethyl ether; or phenyl ethers having molecular weights up to 207, alkylene glycol alkyl esters having molecular weights up to 205, selected from the group consisting of diethylene glycol monoethyl ether acetate and diethylene glycol monobutyl ether acetate; alkoxy ethanols and alkoxy propanols having molecular weights up to 201 selected from the group consisting of 2-ethoxyethanol, methyl-2-ethoxyethanol, isobutyl-2-ethoxyethanol, butyl-2-ethoxyethanol, hexyl-2-ethoxyethanol, phenyl-2-ethoxyethanol, 1-butoxy-2-propanol, n-butoxy-2-propanol and n-propoxy-2-propanol; ketones having molecular weights up to 185 selected from the group consisting of acetone, methylethyl ketone, methylpropyl ketone, methylisobutyl ketone, cyclohexanone, methyl-n-amyl ketone, methylisoamyl ketone, ethylbutyl ketone, diisobutyl ketone, isobutylheptyl ketone, mesityl oxide, isophorone, acetyl acetone and diacetone alcohol; and alkoxy triglycols having molecular weights up to 207 selected from the group consisting of methoxytriglycol, ethoxytriglycol and butoxytriglycol.

2. Prespotter according to claim 1 including also from 0.25 to 10% by weight based on the weight of the mixture of a polyethylene glycol having a molecular weight between 1000 and 20,000 as a thickening agent.

3. Prespotter according to claim 1 including also from 0.05 to 5 percent by weight of a solid, particulate enzyme selected from the group consisting of alkaline protease, neutral protease and amylase, based on the weight of nonionic detergent and organic liquid combined, with the proviso that said prespotter is additionally free of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and dipropylene glycol solvents for the enzyme.

4. Prespotter according to claim 3 in which said enzymes have an average particle size of from 1 to 100 microns.

5. Prespotter according to claim 3 in which said prespotter has a pH between 6 and 10.

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6. Prespotter according to claim 3 including also from 0.25 to 10% by weight based on the weight of the mixture of a polyethylene glycol having a molecular weight between 1000 and 20,000, as a thickening agent.

7. Aerosol package comprising a pressure resistant can having a dispensing nozzle and containing the laundry prespotter defined in claim 1 and a propellant for dispensing the same, said propellant comprising a normally gaseous but liquefiable material at least partially soluble in the mixture in an amount sufficient to cause foaming of the prespotter liquid on discharge from the container through said nozzle.

8. Aerosol package comprising a pressure resistant can having a dispensing nozzle and containing the laundry prespotter defined in claim 3 and a propellant for dispensing the same, said propellant comprising a normally gaseous but liquefiable material at least partially soluble in the mixture in an amount sufficient to cause foaming of the prespotter liquid on discharge from the container through said nozzle.

9. Aerosol package comprising a pressure resistant

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can having a dispensing nozzle and containing the laundry prespotter defined in claim 6 and a propellant for dispensing the same, said propellant comprising a normally gaseous but liquefiable material at least partially soluble in the mixture in an amount sufficient to cause foaming of the prespotter liquid on discharge from the container through said nozzle.

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