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3,822,145 FABRIC SOFTENING Marvin Liebowitz, Edison, Neil M. McHugh, Bridgewater, and Henry D. Cross III, Colts Neck, N.J., assignors to Colgate-Palmolive Company, New York, N.Y. No Drawing. Filed Nov. 15, 1971, Ser. No. 199,010 Int. Cl. C08j 1/44; D06m 13/00, 15/26 US CI 117-139.5 A 21 Claims

ABSTRACT OF THE DISCLOSURE

Poly-lower alkylenes, such as polyethylene, are applied to tumbling fabrics to be softened. Preferably, such application is in the form of a stable foam, dispensed from a pressurized container, polyethylene is emulsified in such 15 foam, the fabrics treated are of damp, recently washed laundry and the conditioning is effected in an automatic laundry dryer while the laundry is being dried.

20 This invention relates to softening fabrics, such as those which are made of cotton or synthetic fibers or mixtures thereof. More particularly, it relates to softening such materials with preparations, preferably in stable foam form, which contain poly-lower alkylenes and preferably, such compositions also include other surface active softening agents, such as the anionic, nonionic and amphoteric synthetic organic detergents. The invention is also of the foams made, the pressurized compositions from which they are produced and a method of producing the foams $_{30}$ by discharging such compositions.

It is known to treat fabrics, yarns, threads, manufactured textiles, articles made from them, such as clothing and laundry to impart desirable properties to such materials. The compositions for effecting such treatments 35 have been produced in a wide variety of physical forms, including emulsions, sprays, solids, coated papers and fabrics, sponges, and liquids, and applications of these to fabrics and fibers have been made at different temperatures and under various conditions so as to produce 40 the best softening, antistatic properties, bactericidal actions, and other treatments.

Softening agents, bactericides and antistatic chemicals have been deposited on laundry being washed in an automatic washing machine, in which a moving baffled tub $_{45}$ or a tub-agitator combination maintains circulation of the washing and rinsing liquids in the horizontal and vertical types of machines, respectively. Usually, to be applied in the washing machine, the treating agents have to be substantive. Substantive cationic fabric softeners have 50 been incorporated in detergent compositions or have been dissolved in the wash water or rinse water. The most effective softening, which has been obtained with cationic softening agents, often of the quaternary ammonium salt type, has been by addition of such substantive chem-55 icals in the rinse water, from which they are attracted to the laundry and are held tightly to it. Thus, after rinsing is completed, the softening compounds are still present on the laundry fibers and exert their conditioning effects thereon. As is well known, the use of softeners is 60 inconvenient for the consumer because she must make a special trip to the laundry, which is often located in the basement or other remote or inaccessible part of a residence, to add the softener. Also, she must make this trip at a precise time; otherwise, the washer may have passed the rinse cycle or she may have to wait for it to reach such point. In recent years, such inconveniences have been avoided by having softeners added to the laundry after it has been transferred to an automatic dryer. Thus, softening agents have been sprayed onto the laun-70 dry and onto dryer interior parts, from where they are subsequently transferred to the laundry. They have been

incorporated in cellulosic substrates and have been applied to the laundry from the surfaces of papers, cardboard, wood and plastic articles. Additionally, they have been discharged from aerosol containers as sprays or foams and have been applied to the laundry in such physical states.

Conditioning operations in the dryer are more advantageous than the methods which require addition of softening agent to the rinse water because they allow the use of non-substantive softening and antistatic agents, do not waste such agents in discharged rinse water and are more convenient to employ. However, due to application to the laundry in somewhat concentrated form, in some cases the deposits of conditioning agents are not uniform and often stains or greasy spots are apparent on the laundry, especially if pressurized conditioners are discharged directly onto the materials to be treated and are allowed to soak into them before there is an opportunity for them to be spread over the surfaces of the laundry in thin films. Attempts to solve such problems resulted in the inventions described in previous patent applications S.N. 109,691 for Fabric Conditioning, by Roberts et al., filed in the U.S. Patent Office on January 25, 1971, and S.N. 194,549 Liebowitz et al., entitled Fabric Conditioning. In both 25 such applications foam compositions for use in conditioning laundry in an automatic laundry dryer were described. In the latter application, examples were given in which the poly-lower alkylene conditioning agents of the present invention were utilized together with the betaines found by Liebowitz et al. to be especially useful fabric softeners.

The present invention is of new compositions, foams and methods for their manufacture and the use thereof which give improved non-staining fabric conditioning. The conditioned laundry is not objectionably "waterproofed" by softening agent, contrasted with the situation when cationic softeners are employed. Additionally, the present products are economical to manufacture and use and permit commercial marketing of aerosol foam fabric softeners intended for use in the dryer, without the necessity for overpricing the product and thereby diminishing its market appeal, and without the need to develop new chemicals which are non-toxic and non-irritating, to satisfy governmental regulations, and are of acceptable costs.

In accordance with the present invention a method of softening fibrous materials comprises tumbling such materials into repeated contacts with a source of poly-lower alkylene, so as to transfer to surfaces of the fibrous materials a sufficient quantity of poly-lower alkylene to soften such materials. Preferably, the fibrous materials being softened are polymeric textile fibers such as cottons, nylons, polyesters, acrylics, acetates, Dacron and mixtures thereof, softening is effected in an automatic laundry dryer while drying the damp laundry, the poly-lower alkylene is polyethylene of a molecular weight averaging from 1,000 to 3,000 and it is present in a foam matrix from which it is rubbed onto the surfaces of the fibers of the materials being dried during tumbling thereof in the laundry under dryer conditions, e.g., 20 to 60% water in the laundry to be dried, 10 to 100 revolutions of the dryer drum per minute, and a hot air temperature of 40 to 90° C. Also within the invention are fabric conditioning compositions in pressurized dispensers, which also comprise a poly-lower alkylene softening agent and a pressurizing means sufficient to generate a dispensing and foaming pressure in the container. Such compositions preferably include 4 to 20% of a polyethylene of a molecular weight in the range of 1,000 to 3,000, 0.5 to 10% of synthetic surface active agent which is either anionic, nonionic or amphoteric or a mixture thereof, 20 to 60% of water and 20 to 70% of liquefied gas propellant. The

novel foams and methods of producing them from the described compositions are also within the invention.

The poly-lower alkylene may be a random or block copolymer of lower alkylenes, such as those of 2 to 4 carbon atoms. However, it is preferred to employ poly-5 ethylene or polypropylene or polymers made from mixtures of ethylene and propylene. Most preferably, the polymeric material is made solely from ethylene. When butylene or isobutylene is present, it will normally be to a minor extent, generally from 1 to 20% of the weight 10of the polymer. Similarly, the proportion of propylene in the polymer, by weight, will be less than 40%, if it is present at all, and if present at least 1% will normally be used. The molecular weight of the poly-lower alkylene will be less than 5,000 under almost all circumstances and 15 will preferably be less than 4,000, with a preferred range of 1,000 to 3,000. Most preferably, the polyethylene will have a molecular weight in the 2,000-2,200 range. The ranges given are for average molecular weights but it usually is preferred that substantially all (over 90%) of 20 the polymer should be within such molecular weight ranges.

The molecular weight of the polyethylene is sufficiently high that it might be expected to be in solid form. However, because it is very finely divided and is usually em- 25 ployed in the presence of surface active agents and suitable solvent systems, it readily forms an emulsion or pseudo-emulsion and has the properties of such. For example, in a most preferred form of the polyethylene, as it is employed in making the composition of the present in- 30 vention, it is classified as an aqueous nonionic emulsion, comprising 32% of polyethylene of a molecular weight averaging (and also with over 90% being) in the range of 2,000-2,200. The composition includes 8% of a nonionic synthetic organic detergent or surface active agent 35 are not supposed to be as effective as the quaternaries, of the alkyl phenol polyoxyethylene ethanol type. A preferred chain length for the polyethoxy chain is from 6 to 20 ethylene oxides, preferably about 15 ethylene oxides. The alkyl is a "middle" alkyl, usually of 7 to 10 carbon atoms, preferably of 8 or 9 carbon atoms, typically nonyl 40 or isooctyl. The alkyl substitution is usually para to the hydroxyl of the phenol. Other nonionics such as those subsequently described may be used in partial or complete replacement of the Igepal type. Also, anionics and amphoterics and surfactant mixtures are also suitable 45 under the same conditions. Such an emulsion has a Brookfield viscosity, using the Brookfield RVF spindle No. 1, of 75±40 centipoises at 20 r.p.m. and 80° F. It's pH is $7.9 \pm .3$ and it appears transparent, after the emulsion is allowed to dry out on a glass plate. The color of the emul-50 sion is a slightly yellowish off-white and it appears thick to the eye, with a characteristic wax-like odor. No more than a trace amount of solids is retained on a U.S. Standard Sieve Series No. 270 stainless steel sieve, through which the emulsion is passed at 80° F. 55

The suitable poly-lower alkylene, in emulsion form, as described above, is available under the trade name Poly-Pel N-40 of Scher Brothers, Clifton, New Jersey. A similar product is also available from Chemical Corporation of Âmerica, East Rutherford, New Jersey, under their 60 name Chemcor PEN 40.

The textile fibers, fabrics, articles of apparel, white goods, and other articles, threads, yarns and cloth to be softened will be cotton for the most part but may also include nylons, polyesters, acrylics, acetates, Dacron and 65 all the other synthetics and natural fibers and mixtures thereof normally employed in the manufacture of textiles. Although these are of different tendencies to sorb or hold various conditioning agents, all may be benefited by application of the present softeners to them.

As has been described in the other patent applications previously referred to herein, various synthetic organic detergents or other surface active agents of the anionic, nonionic and amphorteric types are useful to condition fabrics. In some cases it may also be desirable to utilize 75 soaps in which the lower alkanol is of 1 to 5 carbon

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some cationic materials, such as the quaternary ammonium halides, e.g., distearyl dimethyl ammonium chloride, cetyl trimethyl ammonium bromide, benzethonium chloride, stearyl pyridinium halides and imidazolinium methosulfates, as softening agents, especially because such materials will also posses antibacterial properties, but usually they are avoided because of excess substantivities to textiles and a continuing buildup of such materials on the fabrics being treated, which produces a hydrophobic or "waterproofing" effect, and a greasy feel, which are often undesirable. Although lengthy descriptions of the anionic, nonionic and amphoteric surface active agents and synthetic organic detergents may be found in the texts, Surface Active Agents and Detergents, volumes I and II, by A. M. Schwartz, J. W. Perry and J. Berch, published in 1958 by Interscience Publishers, Inc., and Detergents and Emulsifiers 1969 Annual by John W. McCutcheon, a listing of some such representative compounds will be given herein. The anionic surface active agents include the sulfuric reaction products having a higher alkyl or acyl radical thereon. Some of these are the higher alkyl benzene sulfonates, preferably with the alkyls being linear; the higher fatty acyl taurides and isethionates; higher fatty acid monoglyceride sulfates and sulfonates; and more specifically, tallow alcohol sulfate, coconut oil monoglyceride sulfate and n-dodecyl benzene sulfonate, as the sodium salts. Amphoteric conditioners used include the complex fatty amido compounds, e.g., those sold as Soromines AT and AL, the higher alkyl betaalanines, the N-higher alkyl aspartic acids and the Miranols.

Also within this group and preferred are the amphoterics recited in the Liebowitz et al. application previously mentioned. These are betaines which, although they in the present compositions, especially when combined with alkanolamine soaps, appear to be exceedingly effective as softening agents and have the additional advantage of not causing any staining or greasy feel of the materials treated. Such amphoterics are preferably higher $(C_{10}-C_{20})$ fatty alkyl di-lower (C_{1-4}) alkyl glycines or higher fatty acylamido-lower alkyl di-lower alkyl glycines or similar derivatives of other amino acids of the glycine type. For example, coconut oil fatty alkyls amine of dimethyl glycine and coconut oil fatty acids amidopropyl dimethyl glycine are preferred examples of such compounds. Among other preferred surface active fabric softeners are the nonionic surfactants and detergents which include the polyoxy-lower alkylene higher alkyl ether, e.g., polyoxyethylene lauryl ether having four ethoxy groups (Brij 30); higher alkyl phenoxy poly(lower alkoxy) lower alkanols, e.g., nonyl phenoxy polyethoxy ethanol (Igepal CO 880) and balanced hydrophilic-lipophilic compounds made by the condensation of lower alkylene oxides with organic hydrophobic materials, e.g., Pluronics F-68 and L-44. Such nonionic softeners usually include lipophilic groups having higher alkyl components, generally of 8 to 20 carbon atoms, and hydrophilic components which are poly-lower alkylene oxides of 4 to 100 moles of lower alkylene oxide per mole of compound. Preferred lower alkylene oxides are those of 2 to 3 carbon atoms, most preferably, ethylene oxide. The nonionics do not react with the dimethyl glycine derivatives, the polyethylene softeners or the lower alkanolamine soaps, which are also often present in these compositions and therefore, the nonionics are preferred supplementary conditioning agents for use with the polyethylenes, especially when anionic, amphoteric or cationic conditioners are also there.

The lower alkanolamine higher fatty acid soaps which are the most useful in combination with the poly-lower alkylenes and which, together with them produce softening and antistatic compositions of greatly improved properties, are usually lower alkanolamine higher fatty acid atoms, preferably 1 to 3 carbon atoms and most preferably, is ethanol. The higher fatty acid portion of the molecule is of 10 to 20 carbon atoms and is preferably of 16 to 20 carbon atoms, with the 16 to 18 carbon atoms range being most preferred. The best embodiment of the 5 fatty acid moiety of the alkanolamine soap is commercial stearic acid, double pressed, comprising stearic, palmitic and oleic acids, or triple pressed stearic acid, comprising stearic and palmitic acid. Of course, the pure stearic or palmitic acids may be employed, if the cost thereof is 10 no serious detriment. The alkanolamines of the alkanolamine soaps may be mono-, di-, or tri-alkanolamines and of these, the trialkanolamines are most preferred. Generally, they are of the same alkanol radicals but mixed alkanolamines are also used. Instead of the alkanola-15 mines, in some cases the lower alkyl amines may be employed, usually in mixture with the alkanolamine soaps. Examples of the alkanolamine soaps are the most preferred triethanolamine stearate, triethanolamine palmitate, triethanolamine tallowate, triisopropanolamine co-20 cate, tri-t-butanolamine laurate, diethanolamine stearae and monoisopropanolamine palmitate. The ordinary higher (C10-C20) fatty acid soaps of alkali metals, such as sodium and potassium, alkaline earth metals, such as calcium, and the ammonium and magnesium soaps may be 25 used alone or in mixture, together with the alkanolamine soaps but the proportions thereof will normally be held to less than 30% of the total higher fatty acid soap content.

Amine oxides may be present in the compositions and 30 are useful in softening laundry. These are normally higher alkyl di-lower alkyl amine oxides wherein the higher alkyl is of 8 to 20 carbon atoms, preferably of 12 to 18 carbon atoms, and the lower alkyl is of 1 to 4 carbon atoms, preferably being methyl. Mixtures of alkyls may 35 also be employed. The amine oxides help to distribute the other required conditioning agents satisfactorily over the materials being treated, contribute to non-staining properties and help to remove the conditioning agent on subsequent launderings, aiding in preventing the treated 40textiles or fabric from becoming hydrophobic or waterproofed. Their utility in the present compositions is somewhat surprising in view of the fact that the polyethylene emulsions themselves are expected to possess sufficient leveling properties to be satisfactorily distributed over 45 the textiles being treated.

Small proportions of higher fatty acid lower alkanolamides, especially di-lower alkanolamides, also aid in conditioning and in producing and maintaining a stable foam. Such compounds are of higher fatty acids of 10 to 50 20 carbon atoms, preferably of 12 to 18 carbon atoms and most preferably, of 12 to 14 carbon atoms, and of lower alkanols, such as those of 1 to 4 carbon atoms, especially ethanol and isopropanol. Examples of suitable alkanolamides include lauric myristic diethanolamide, the 55 preferred compound; lauric diisopropanolamide; stearic monoethanolamide; myristic diethanolamide; palmitic monoisopropanolamide; and lauric dimethanolamide. Instead of the same alkanol being employed, different alkanols of the types mentioned may be used, as in lauric 60 myristic ethanol isopropanolamide. The alkanolamides are especially useful for imparting antistatic effects to the laundry being treated.

It has been found that the presence of a plasticizing, humectant or emollient type compound such as a suitable 65 dihydric, trihydric or polyhydric lower alkanol, e.g., glycols, glycerol, lower alkylene glycol, dialkylene glycol, or polyalkylene glycol, such as propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, sorbitol and mannitol, and equivalent such compounds and 70 substituted derivatives thereof, make satisfactory compounds of the present compositions and appear to toughen the stable foam produced, so as to make it better able to resist the shocks and forces encountered in tumbling with humid materials during the conditioning operation. 75 type or mixtures thereof, may be variable, to obtain the

With the plasticizer or humectant it is sometimes also advisable to include in the present compositions other strengthening agents and a lubricant. Materials which improve the strength of the foam include resinous or polymeric compounds, such as gums and synthetic organic compounds, but these sometimes have the undesirable effect on the treated fabrics of forming flakes or apparent deposits thereon, even when employed in small quantities.

The propellants used may be any suitable type, including compressed gases such as nitrogen, carbon dioxide, nitrous oxide and air but usually those that are most satisfactory for producing foams will be organic compounds, generally lipophilic in nature and low boiling, usually being liquids near atmospheric pressures, which are referred to as liquefied gases. These will preferably be cyclic or acyclic lower chlorocarbons, fluorocarbons, chloro-fluoro carbons, or hydrocarbons of carbon contents of 1 to 4. Although such compounds may contain free hydrogens the best of them are saturated and completely halogenated. Examples of suitable propellants are those commercial products known as Propellants 11, 12, 14, 21, 22, 114, etc. Perhaps the most useful of the liquefied gas propellants are dichlorodifluoromethane, monofluorotrichloromethane, dichlorotetrafluoroethane, octafluoropropane, octafluorocyclobutane, propane, butane, isobutane, cyclobutane, methylene chloride, and tetrafluoromethane. The propellants will usually be employed in mixture, with the mixture being such as to generate a pressure in a gas-tight container of about 10 to 100 lbs./sq. in. gauge, preferably from 20 to 70 lbs./sq. g. at 70° F. They will also be chosen for compatibility with the rest of the formula and for assisting and maintaining the stability of the foams generated. If flammable propellants are used, considering that the nature of the present product is such as to require its employment in conjunction with laundry dryers, they will usually be formulated with non-flammable materials or other propellants so as to avoid any danger of combustion in use. In preferred propellant formulations there will be employed from 10 to 90% of a "high pressure" propellant and from 90 to 10% of a "diluent" propellant. For example, 60 parts of dichlorodifluoromethane may be used with 40 parts of dichlorotetrafluoroethane to make a propellant or gas portion of a conditioning composition. Preferably such ratios will be from 70 to 30% of the "high pressure" propellant and 30 to 70% of the "low pressure" diluent. The water employed in the conditioning compositions, if present at all, will preferably be deionized or other water of low hardness, under 50 parts per million of hardness, calculated as calcium carbonate. It will usually be undesirable for it to contain dissolved salts to

an extent of more than 0.1%. Of course, with the other constituents there may be present various adjuvants such as coloring agents (dyes and water dispersible pigments), perfumes, fluorescent dyes or optical brighteners, bactericides, fungicides, soil repellents, synthetic and natural gums and colloids, and solvents, all for their obvious functions. Usually, the total of such materials will be less than 20% of the composition weight and preferably, will be less than 5% thereof, with no material being present in an amount greater than 5%.

The fabric conditioning poly-lower alkylene of the mentioned molecular weight will comprise from about 2 to 20% of the pressurized composition, preferably about 3 to 10% thereof. With less than 2% of the polyethylene or other poly-lower alkylene present, the softening effects are not sufficiently pronounced to make a satisfactory product based prinicpally on the poly-lower alkylene. With more than 20% present the product tends to be over-waxy in nature and can cause staining, even when applied in a nonionic emulsion form. Although the weight of the synthetic organic surface active agent or detergent present, of the anionic, amphoteric or nonionic best softening and leveling effects, generally from 0.5 to 20%, preferably 1 to 10%, and most preferably 1 to 4%, of such material will be present, in total, in the pressurized foaming composition. Such amounts give useful conditioning and aid in producing the desired foam. When only one synthetic surface active agent (including soaps for the purpose of this description) is employed it will preferably be a nonionic of the ethoxylated fatty alcohol or ethoxylated alkyl phenol type, having an ethylene oxide content of 50 to 85% preferably 60 to 80%. However the surface active component will usually include an alkanolamine soap, as described, to make the softener more effective.

Foams may be made without water but they are not as useful as those which contain some water, to assist 15in the formation of desirable and stable emulsions. The proportion of water present will often be within the 10 to 70% range, preferably 20 to 60% and most preferably from 30 to 50%. Other solvents, such as lower alkanols, aldehydes and ketones may replace part of 20 the water but usually will be present to no greater extent than 5% in the final product. To obtain pressurized compositions that will be dispensable to the atmosphere through an ordinary aerosol valve to form a stable foam, which has at least 10% of its weight still in foam form 25 after three minutes of tumbling with a load of damp laundry in an automatic laundry dryer, there will be used from 15 to 75% of a liquefied gas or pressurized gas propellant, preferably 35 to 65%, and most preferably from 40 to 60%. The propellant will create a pressure 30 in the range previously described herein. It will be emulsified with the softener, surface active agent and water or may have the softener dissolved in it.

The triethanolamine higher fatty acid soap will be from 0.5 to 30%, preferably 1 to 10% and most prefer-35 ably from 1 to 5% of the composition. It is preferred that the ratio of poly-lower alkylene:soap should be in the range of 10:1 to 1:5. The proportion of higher fatty acid alkanolamide present will be from 0.05 to 2%, preferably from 0.1 to 0.5%. That of humectant 40 or plasticizer (glycerol or other polyol) will be from 0.1 to 20%, preferably from 0.5 to 5%. Too much alkanolamide makes the product objectionably thick and interferes with uniform dispensing, whereas too much of the plasticizer can make the product unacceptably 45sticky. The amine oxides, if employed, constitute from 0.5 to 20% of the composition, preferably from 1 to 5% thereof.

The proportions of materials mentioned above are those which are found to give useful softening and anti-50 static effects, while still producing the described foams in useful form, preferably sufficiently stable to last long enough in the dryer so as to distribute the active conditioning agent(s) evenly over the surfaces of the fabrics being treated in a laundry dryer. The useful composi-55 tions within the invention do not stain laundry, deposit greasy spots thereon nor make the fabric hydrophobic after repeated treatments, unlike the cationic softeners. Although one of skill in the art will be able to modify the various materials and proportions to obtain useful 60 softeners, generally, when the proportions are changed so to be outside of the limits recited, or the compounds are similarly altered, the properties of the compositions will be modified so that a less acceptable product, generally unacceptably poor in foaming and conditioning 65 characteristics, results.

The stable foams of this invention are made by discharging the pressurized composition to the atmosphere through an ordinary dispensing value. Discharge may be very quick, usually occurring in less than ten seconds, 70 and the foam produced, which is of essentially the same composition as the pressurized product before dispensing, with the propellant expanding to produce the foam, resists breakdown or drainage, even during use. The propellant almost completely volatilizes during dis- 75

pensing, although a small proportion thereof, the lower pressure or "solvent" fraction, may be present as a liquid film in the foam, and some of the higher pressure propellant may escape. Thus, the foam will be constituted of all the original components except for a part of the propellant mixture, usually less than 20%, preferably less than 10%, which may be lost. For the purpose of this discussion, it will be considered that the composition of the foam is that of the pressurized product, although it will be recognized that there may be some losses of propellant, in which case the proportion of each constitutent in the foam will be increased by the multiplier 100/100-X, wherein X is the percent of propellant lost in dispensing.

The present aerosol compositions are easily made and require no special procedures or apparatuses. If desired, the soaps and surface active agents may be made in situ or may be mixed with the rest of the ingredients, except for the propelants, and the compositions may subsequently be pressurized, usually by having the gaseous propellant added through a discharging valve. Normally, initial mixing of the materials is at room temperature and in some cases they may be warmed slightly, sufficiently to produce a homogeneous product. Also, in addition to pressure filling, refrigerated liquid propellant may be added to the container, after which a dispensing valve may be affixed and the container sealed. In the making of the triethanolamine stearate in situ, triethanolamine and stearic acid may be blended together initially or at a suitable later time when the composition is being formulated. With respect to heating to make the mixture homogeneous so as to promote in situ reactions of the types described, it will normally not be required to heat to a temperature greater than 50° C. and of course, in the presence of materials such as perfume and solvents, addition thereof will be at as low a temperature as feasible to avoid excessive evaporation losses. The products may be made at various pH's but usually the pH will be from 6 to 10, preferably from 7 to 9 and most preferably from 7 to 8, at a one percent concentration in water.

To use the pressurized composition one needs only to press the discharge valve button of the aerosol dispenser to release the desired amount of conditioning foam. For best results the can should be shaken immediately after manufacture and also before use to make sure that the composition is uniform before dispensing. This also will prevent undesired increases in pressure due to separation of the propellant from the rest of the product. The foam may be discharged directly into the dryer onto fabrics or laundry to be conditioned, usually in a single "mass" or charge. It need not be first discharged externally of the dryer and then transferred to the fabrics. Tumbling of the laundry and the drying thereof may be commenced immediately after adding of the foam. Because the density of the foam will usually be about constant for a particular composition, the consumer can judge by volume or dispensing time when the appropriate amount of foam has been generated.

The amount of conditioning composition employed will usually be sufficient to provide about 0.05 to 1 gram of the poly-lower alkylene softener per pound of dry laundry and most preferably, about 0.1 to 0.5 gram per pound will be used. Thus, for the usual eight pounds of dry laundry in the dryer from 0.4 to 8 grams of conditioning agent will be used, usually corresponding to from 5 to 100 grams of conditioning composition, preferably from 10 to 50 grams thereof. Such relatively small amounts are convenient to handle, pack and dispense, and with the usual aerosol container several applications are available from a single package. Of course, the amounts to be employed will depend on the effectiveness of the particular conditioning composition being considered. The amounts of softening agent and supplemental softeners, leveling agents, antistatic compounds, etc., present in the formula

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may also be adjusted so as to allow for a certain desired number of uses of the product per container. Similarly, container size may be adjusted, e.g., from three ounces to two pounds per container.

The laundry treated will normally contain from 20 to 70%, most often from 30 to 60% of water, with the balance usually being of mixed cotton, cotton-polyester, nylon, acetate, acrylic and Dacron textiles. Although such materials may be treated with the present foams outside the automatic laundry dryer, conditioning in the dryer 10 appears to be far superior, apparently due to the tumbling effects, the wetness of the laundry, the humid atmosphere, the air blowing and the presence of heat, and therefore is highly preferred.

Although the present stable foams will maintain their 15 shapes indefinitely if not subjected to external forces, when added to the damp laundry in an automatic laundry dryer the foams are slowly abraded or worn down so that the softening materials in them are spread over the surfaces of the laundry. Although foams have been employed 20 in which such spreading was reported to have taken place within 1 to 5 turns of the dryer drum (about 0.5 to 15 seconds) or longer, the superior properties of the present compositions are thought to be due in significant part to the particular softening agent, its built-in leveling effect 25 and the supplemental action of the alkanolamine soaps, when present. Thus, the foam is spread in thin films over the laundry and does not deposit greasy spots or stains thereon. For example, in a drum which may revolve at a speed of from 10 to 100 r.p.m., most often from 10 to 60 30 r.p.m., and with drying air at a temperature from room temperature to as high as about 100° C., most of the time at from 40 to 70 or 90° C., the present foams will not be completely spread over the laundry within a three minute period. In other words, some of the foam will 35 still be present in the dryer after this period of time and normally at least 10% of the formula will still be in such form. The tumbling and drying operations will continue longer, from five minutes to an hour total time, and within such period all the foam will be distributed. Apparently the good distribution is also attributable in part to the moisture on the fabric that is to be conditioned and the particular components of the foam, which, in combination, spread the conditioning agent over the laundry, softening it and making it less likely to accumulate static 45 charges when subjected to friction.

After treatment of the laundry according to the invention examination indicates no spotting, greasy or oily stains or other objectionable uneven distribution of the softening agent. The laundered items dried are soft and 50 often are also antistatic, especially when alkanolamides are present in the formulations. They do not become "waterproofed," even after repeated treatments, apparently because the polyethylene is removed in subsequent washings, which removal is facilitated by the method of 55 application to the laundry and the other components of the pressurized composition.

The following examples illustrate various embodiments of the invention. Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

EXAMPLE 1

A second s		Parts	
Polyethylene emulsion ¹		25.0	.,
Polyethoxylated fatty alcohol ²		2.0	65
Triethanolamine stearate		1.5	
Glycerine		1.0	
Lauric/myristic diethanolamide		0.1	
Water		20.4	70
Dichlorodifluoromethane		30.0	10
Dichlorotetrafluoroethane		20.0	
¹ 32% polyethylene of molecular weight of phenol polyethoxy ethanol (75% ethylene	of 2,000, 8% oxide) and	nonyl 60%	
water.			75

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A pressurized softening and antistatic composition for the treatment of damp laundry in an automatic laundry dryer is made of the above formula by mixing the mentioned constituents, except for the dichlorodifluoromethane and dichlorotetrafluoroethane, in known manner, at atmospheric pressure and temperature, after which the mixture is placed in gas-tight dispensing containers of six and sixteen ounces capacities and the containers are pressurized by addition through the valves of the 60:40 mixture of Propellants 12 and 114. Upon completion of the filling operation the containers are shaken and tested for leaks and internal pressure and are ready for use. In some cases the triethanolamine stearate is made by the reaction of approximately stoichiometric quantities of triethanolamine and stearic acid (double pressed) at a temperature of about 50° C., either in the presence of the glycerol and diethanolamide and some of the water or in the presence of part of the water only. The polyethylene emulsion employed is that sold under the trade name Poly-Pel N-40, of Scher Brothers, Clifton, N.J. but Chemcor PEN 40, of Chemical Corp. of America, East Rutherford, N.J., may also be employed, as may be other polyethylene emulsions which are based on Grade 629 Polyethylene Nonionic Emulsion of Allied Chemical Corporation. The polyethylene emulsion used is of an offwhite or slightly yellow color, in thick emulsion form, having a Brookfield RVF Spindle No. 1 viscosity of 75±40 cps. at 20 r.p.m. and 80° F. The emulsion can be filtered through a No. 270 stainless steel mesh U.S. Standard Sieve Series sieve at 80° F. with no more than a trace amount (less than 0.1%) of solid retained.

The product made is a sufficiently stable emulsion, as may be observed by packing it in glass containers. However, for best use the product is shaken within five minutes of discharge. Its pH stays at about 7.5 during storage.

Twenty grams of pressurized composition are discharged onto damp laundry in a dryer from a 16 oz. container of the product as a stable foam having a density of about 0.02 gram per cubic centimeter. The internal pressure of the composition in the container, about 55 p.s.i.g., pro-duces a voluminous foam, about a liter in volume. When the proportion of propellants employed are changed, e.g., to 30:70 P12:114, or the amount thereof is diminished, so that the pressure is about 25 p.s.i.g., the density of the foam made is higher, e.g., 0.04 to 0.1 g./cc., and the volume is diminished. When desired, the foam may be discharged as separate sections or balls thereof, with from two to four of these being used to furnish the nineteen or twenty grams of conditioning composition (there may be some loss of propellant, usually of Propellant 12).

The foam discharged from the pressurized container is a stable foam, which for the purpose of this specification and example is considered to be a "solid". Although it may be abraded and reduced in size by tumbling with damp laundry, the foam is form-retaining if not subjected to external contacts or pressures and hence, is a solid. After discharging onto the top of an eight pound (dry basis) charge of mixed damp laundry, (approximately 45% moisture content), composed approximately half of cotton and half of synthetic fabrics, and almost always within one minute after such charging, the dryer is started. The synthetics charged include a major proportion, about 35% of the total charge, of permanent or durable press polyester-cotton blends in 65:35 or 70:30 proportions, Dacron, acetates, acrylics and nylons. For test purposes, some of the permanent press fabric is a light blue in color so that oily or greasy deposits of excessive amounts of materials, such as fabric softeners, can be readily discerned thereon, especially after the products are pressed with a hot iron.

The dryer, started in motion almost immediately after addition of the conditioning foam, utilizes drying gas at about 70 to 90° C. and revolves at about 30 to 40 r.p.m. After three minutes of operation the dryer is halted and ²C₁₂-C₁₃ higher fatty alcohol, 60% ethylene oxide content. 75 the drying foam is observed, at which time it is noted that

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Donto

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approximately 10% of the foam has not been deposited on laundry and is still visible. After an additional two minutes, with the outlet air being at 45° C. because of heat being absorbed from the drying air due to vaporization of water, the contents of the dryer are again inspected and no foam is seen. Subsequently, drying is continued for another 40 to 50 minutes, until all the laundry is thoroughly dried and has had the softening composition distributed over it.

After the cooling of the laundry, which is partially 10effected in the dryer by blowing unheated air over it for a few minutes after completion of the normal drying cycle, it is checked for softening and antistatic properties. It is found that each of the treated articles is pleasantly soft to the touch and is noticeably of a lower tendency to hold 15 static electricity charges than controls not treated with the softening foam. No oily or greasy stains are found on any of the items treated, even after pressing with a hot iron, despite the fact that polyethylene is a hydrocarbon and could be expected in such an application to cause some 20spotting of the laundry.

The treating procedure is varied so as to apply portions of the foam at different times during the drying cycle, with half of it being applied immediately, a quarter after five minutes and another quarter after an additional ten min- 25 utes. No significant differences in product properties are seen to result and, because of the inconvenience of partial applications a preferred method of application is at the beginning of the drying process, as previously described.

In modifications of the above formula, the proportion 36 of polyethylene, 8% in the present formula, is varied over the range from 2 to 20%. At 3% and 5% concentrations softening is obtainable, although less than with the 8% of polyethylene and at 15 and 20% concentrations greater softening effects result. However, at the higher concentrations, especially at the 20% concentration, sometimes the foam is thicker than wanted and at concentrations above 20% spotting or grease spots may be found on the treated laundry. The variations in polyethylene content are compensated for by corresponding changes in mositure and 40 propellant concentrations. Thus, when the polyethylene content is reduced to 3%, with a corresponding diminution in moisture and emulsifier contents, too, water is added to compensate for the moisture decrease and more propellant system is utilized. When the content of the 45polyethylene is increased, the amount of water added is decreased so as to compensate for that added in the polyethylene emulsion and the proportion of propellant is decreased similarly, to compensate for the additional emulsifier. In the various changes of the formula that are 50 made, the moisture content is maintained within the twenty to sixty percent range. In similar experiments, the average molecular weight of the polyethylene product is changed to 1,500 to 2,800, and good softening effects are also the result. The preferred method of addition of the poly-55ethylene is as a nonionic or other emulsion but it may also be added to the present pressurized composition in liquid or dissolved form.

In addition to the nonionic surface active agent present in the emulsion, there is added to the present composition 60 at the expense of the water, from 1 to 5% of an anionic or amphoteric surface active agent, including lauryl alcohol sulfate, coconut oil fatty acids monoglyceride sulfate, higher olefin sulfonate, or higher alkyl dimethyl glycine, all preferably in salt form such as the sodium or triethanolamine salt, or acid. Such additions improve the spreading power of the foam over the damp laundry contacted and also add conditioning effects of their own. When the content of triethanolamine stearate is increased to 3% or decreased to 0.5%, good products are also obtained. Simi- 70 larly, when the alkanolamide is changed to coconut oil fatty acids diethanolamide and the content thereof is increased to 0.4%, a good softening foam is made, and when the glycerine content is changed to 3%, the plasticizing effect thereof is more noticeable. Addition of 1% 75 and anionic surface active agents, products obtained are

distearyl dimethyl amine oxide produces a good softening foam, too. Stable foams result when the quantity of the propellant mixture is increased to 60% or diminished to 40%, with adjustments in the water content being made accordingly. When 1% of a perfume is added, which may be accompanied by from 1 to 4% of a solvent for it, such as ethanol, the softening action is not inhibited and the clothes are also left scented. When the pH is varied over the range of 6 to 9, as by addition of acids, alkalis or buffers, the softening properties are not adversely affected. Similarly, when the liquefid gas mixture is replace by a mixture of Propellants 11 and 12, 21 and 22 or propane and isobutane, a good softening foam is also made. This is also the case when a minor proportion of liquefied gas is replaced by a non-liquefied pressurized gas.

In addition to changing the proportions of the various components of the compositions and the types thereof and making several such changes in one formulation, the weights of active conditioning agents applied may also be altered. Thus, useful softening is obtained by employing enough foam, e.g., 10, 20 or 40 grams, to deposit 0.5, 2 and 4 grams of active softening polyethylene or polylower alkylene per eight pounds of laundry. Generally, the smallest amount of the polyalkylene which gives good softening will be employed.

EXAMPLE 2

		Parts	
_		A	В
0	Coconut oil fatty alkyls dimethyl glycine ¹ Coconut oil fatty acids amidopropyl dimethyl glycine ¹	9.6	9.6
	Triethanolamine stearate Glycerine	0.7 0.5	0.7 0.5
	Lauric myristic diethanolamide Polyethylene emulsion, aqueous ²	0.1 10	0.1 10
5	Water, deionized. 60:40 mixture of Propellant 12 (dichlorodifluoromethane)	8.7 50	8.7 50
	and Propellant 114 (dichlorotetrafluoroethane)		

v.5% sait and amine and ² See Example 1.

The above pressurized softening and antistatic compositions are made according to the techniques described in Example 1 and are tested by the methods thereof. Instead of employing the full amount of one of the dimethyl glycine derivative compounds described, a mixture of equal parts thereof may be utilized.

When such materials are tested by the method of Example 1 the products are found to be very satisfactorily softened and also, are antistatic. The softness noted is similar to the softness obtained with cationic softening agents. Furthermore, the present compositions do not objectionably stain laundry treated with them and do not waterproof" such laundry upon repeated applications, as sometimes results from cationics being employed. Laundered articles treated with the present compositions in an automatic laundry dryer during regular drying operations are noticeably superior to control laundry items not so treated.

In variations of the above formulas, when myristyl dimethyl glycine and palmityl amidoethyl dimethyl glycine are employed in place of the respective alkyl and fatty acid amido compounds desired softening effects are obtained. Also, in such formulas and the primary formulas of this example, when 30% of the triethanolamine stearate is replaced by sodium or potassium stearate, good softening is still obtained and the leveling actions of the triethanolamine stearate, nonionic surface active agent, and polyethylene are not appreciably diminished. Changes in the propellant types, to a mixture of Freons 11 and 12 or isobutane and propane (85:15), do not change the good quality of the foam, although its density may be varied somewhat in the 0.01 to 0.1 g./cc. range.

In the above formulations, when each is modified so as to exclude non-essential components, such as glycerine, lauric myristic diethanolamide and nonionic, amphoteric 5

still good foams sufficiently stable to be employed satisfactorily and soften the laundry treated.

The invention has been described with respect to various disclosures and illustrative examples thereof. It is not to be so limited since it should be apparent to one of skill in the art that substitutions may be made and equivalents may be employed without departing from the spirit of the invention.

What is claimed is:

1. A method of softening fibrous textile laundry material in a tumble dryer which comprises applying directly to such material an aqueous, substantially stable foam composition containing emulsified poly-lower alkylene, said lower alkylene containing from 2 to 4 carbon atoms, said poly-lower alkylene having a molecular weight of from about 1,000 to 3,000 tumbling said fabric whereby to transfer to surfaces of the fibrous material a quantity of poly-lower alkylene sufficient to soften such material.

2. A method according to claim 1 wherein the laundry being softened initially contains from 20 to 60% water, $_{20}$ drying is effected in an automatic laundry dryer containing a rotating drum which makes from 10 to 100 revolutions per minute and which is inclined from the vertical and hot air at a temperature of 40 to 90° C. is blown into said dryer during operation thereof. $_{25}$

3. A method according to claim 2 wherein the foam is of such stability that at least 10% is left after tumbling three minutes in the dryer and none is left after 10 minutes and the drying and softening operation continues for a period of 5 to 10 minutes to one hour.

4. A method of softening fibrous textile laundry material in a tumble dryer which comprises applying directly to such material an aqueous, substantially stable foam composition containing poly-lower alkylene, said lower alkylene containing from 2 to 4 carbon atoms, said poly-lower 35 alkylene having a molecular weight of from about 1,000 to 3,000 and organic detergent selected from the group consisting of anionic, nonionic, amphoteric and cationic detergents, and wherein the ratio of poly-lower alkylene to detergent is from about 40:1 to 1:10, and tumbling 40 said fabric whereby to transfer to surfaces of the fibrous material a quantity of foam composition sufficient to soften said fabric.

5. A method according to claim 4 wherein said detergent is selected from the group consisting of (A) poly- 45 ethoxylated C₈-C₂₀ alkyl alcohol containing from 4 to 100 moles of ethylene oxide, (B) C₇-C₁₀ alkyl phenol polyoxyethylene ethanol containing from 6 to 20 moles of ethylene oxide and mixtures of (A) and (B).

6. A method according to claim 4 wherein said foam composition is dispensed from a pressurized container, the composition in said container comprising from about 2 to 20% of said poly-lower alkylene, from about 0.5 to 20% of said detergent, from about 10 to 70% water and from about 15 to 75% of liquefied gas propellant. 55

7. A method according to claim 6, wherein said polylower alkylene is polyethylene.

8. A method according to claim 6, wherein said polylower alkylene contains from 1 to 20% based on the weight of the polymer of butylene or isobutylene.

9. A method according to claim 6, wherein said polylower alkylene contains from 1 to 40% based on the weight of the polymer of propylene.

10. A method according to claim 6, wherein said propellant is at least one material selected from the group consisting of cyclic or acyclic lower chlorocarbons, flu-

orocarbons, chlorofluorocarbons and hydrocarbons containing from 1 to 4 carbon atoms.

11. A method according to claim 6, wherein said composition comprises, by weight, about 8 parts of polyethylene, 1.5 parts of triethanolamine stearate, 2 parts of an ethoxylated higher fatty alcohol of 12 to 18 carbon atoms in the higher alkyl or alkenyl group thereof and containing about 60% of ethylene oxide, 2 parts of polyethoxylated nonyl phenol of about 75% ethylene oxide content, 37 parts of water, 30 parts of dichlorodifluoromethane

and 20 parts of dichlorotetrafiuoroethane.12. A method according to claim 6, wherein said com-

position further contains from 0.1 to 20% of humectant or plasticizer.

13. A method according to claim 6, wherein the amount of foam composition employed is sufficient to provide about 0.05 to 1 gram of alkylene polymer per pound of dry laundry.

14. A method according to claim 6 wherein said foam composition further contains from 0.5 to 30% of lower alkanolamine higher fatty acid soap in which the lower alkanol is of 1 to 5 carbon atoms, and the higher fatty acid portion is of 10 to 20 carbon atoms.

15. A method according to claim 6, wherein said composition further contains from 0.5 to 20% amine oxide.

16. A method according to claim 15, wherein said amine oxide is higher alkyl, di-lower alkyl amine oxide wherein the higher alkyl contains 8 to 20 carbon atoms and the lower alkyl contains from 1 to 4 carbon atoms.

17. A method according to claim 6 wherein said detergent comprises nonionic detergent and amphoteric detergent selected from the group consisting of C_{10} - C_{20} fatty alkyl di- C_1 - C_4 alkyl glycines and C_{10} - C_{20} fatty acylamido- C_1 - C_4 alkyl, C_1 - C_4 dialkyl glycines.

18. A method according to claim 17 wherein said amphoteric detergent is coconut oil fatty alkyls dimethyl glycine.

19. A method according to claim 17 wherein said amphoteric detergent is coconut oil fatty acids amidopropyl dimethyl glycine.

20. A method according to claim 6 wherein said foam composition further contains from 0.5 to 2% of C_{12} - C_{18} fatty acid, C_1 - C_4 alkanolamide as foam stabilizer.

21. A method according to claim 20 wherein said foam stabilizer is lauric/myristic diethanolamide.

References Cited

UNITED STATES PATENTS

3,442,692 5/1969 3,686,025 8/1972 3,676,199 7/1972 3,245,831 4/1966 1,948,568 2/1934 2,023,013 12/1935 2,655,480 10/1953	Gaiser 117-120 Morton 252-8.8 X Hewitt et al 117-139.5 X Shippee 117-139.5 Faber et al 8-138 X Faber et al 8-149.1 X Spitzer et al 252-305 X
2,655,480 10/1953 3,650,816 3/1972	

OTHER REFERENCES

⁶⁰ Rosenbaum; Article in American Dyestuff Reporter, May 18, 1959, pp. 46–49.

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117-109, 120, 139.5 CQ; 252-8.6, 8.8, 305

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