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3,686,025

TEXTILE SOFTENING AGENTS IMPREGNATED INTO ABSORBENT MATERIALS

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No Drawing. Filed Dec. 30, 1968, Ser. No. 788,102

Int. Cl. D06m 13/00; D21h 1/34

U.S. Cl. 117-140 R

8 Claims

ABSTRACT OF THE DISCLOSURE

Softening agents can be impregnated into absorbent materials, especially absorbent paper and non-woven cloth, and such compositions are useful and effective for softening textile fabrics in a standard, automatic, clothes dryer, as well as in an automatic washer.

BACKGROUND OF THE INVENTION

Certain chemical compounds have long been known in the art to possess the desired quality of imparting softness to textile fabrics. The quality of softness or being soft is well defined in the art and, as used herein, means that quality of a treated fabric whereby its handle or texture is smooth, pliable, and fluffy, and not rough or scratchy to the touch. Known generally as "softening agents," "fabric softeners," or "softeners," these compounds have long been used by housewives in the laundry and by the textile industry to soften a finished fabric.

Additionally, many of these compounds act to reduce the "static cling" of the treated fabrics. Static cling is, generally, the phenomenon of one fabric adhering to another or to parts of itself as a result of static electrical charges located on the surface of the fabric. It can also involve the adherence of lint, dust, and other similarly undesired substances to a fabric due to these static charges. It is noticeably present in fabrics that are freshly washed and dried in an automatic dryer. By softening and reducing the static cling of a fabric, it is more comfortable when worn. Such treated fabrics additionally are easier to iron, and have fewer hard-to-iron wrinkles.

Softening agents are usually employed in liquid formulations, and powder, tablet, and granular formulations are known. However, all such softening compositions have in common their limitation to use in the laundry or fabric washing or rinsing process.

Use of these compositions results in many inconveniences. For example, housewives very often forget to add the softening agent during the rinse cycle of the washing process, thereby necessitating repeated rinse cycles until the softener is timely remembered and added. Additionally, these softening compositions are not generally pre-measured; the result is that the housewife often uses an amount insufficient to adequately soften the fabrics or she wastes the softening composition by using excessive amounts or by spillage.

The prior art suggests the coating or impregnation of cellulosic materials with a softening agent with the objective of softening or otherwise treating the cellulosic material itself; thus, only small amounts (5% or less by weight of the dry cellulosic material) of the softening agent have been used for this purpose. Recently suggested is the use of substantially larger amounts of a softening agent coated onto paper for use as a dryer-added softening composition. However, this composition has the serious disadvantage of causing marked staining of the treated fabrics due to its too rapid release of the softener from the paper substrate. The prior art has failed to recognize the importance of controlling release of softener

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from the substrate by controlling the absorbency of the material used as a substrate.

Therefore, it is an object of this invention to provide a novel fabric softening composition which can be used in a standard automatic clothes dryer and which eliminates or substantially reduces fabric staining.

Additionally, it is an object of this invention to provide softening compositions which are pre-measured and which need not be limited to use in the rinse cycle of an automatic washer.

Further, it is an object to provide a composition which can be used to impart anti-static qualities to a variety of fabric materials, especially synthetic fabrics from which automobile and some furniture upholstery are generally made.

Also, it is an object to provide a composition which can be used as a surfactant to cleanse articles made of wood (furniture), plastic, and the like.

BRIEF SUMMARY OF THE INVENTION

These and other objects, readily apparent to those skilled in the art, are achieved by the invention herein, which is a softening composition consisting essentially of a fabric softener impregnated into an absorbent material which is also referred to herein as a substrate. Preferably, the absorbent substrate is cellulosic, particularly a multi-ple, absorbent paper or an absorbent non-woven cloth. The term "cloth" herein shall mean a woven or non-woven fabric or cloth used as a substrate, in order to distinguish said component from the term "fabric" which is intended herein to mean the textile fabric which is desired to be softened. Large amounts, generally in excess of 200% by weight of the dry substrate, of the softening agent are required.

The softening compositions herein, while effective when used to soften fabrics in rinse water, particularly in the rinse cycle of a standard automatic clothes washer, find particular application in effectively softening fabrics in a standard, automatic clothes dryer.

Preferably, the softening composition comprises a softening agent impregnated into absorbent paper or non-woven cellulosic cloth and made up into a tubular roll or individual sheets. A desired length of the treated paper is torn off the or a sheet removed from its package and placed into the clothes dryer wherein the fabrics to be treated have been loaded. The dryer is then operated in customary fashion, and softening occurs as the fabrics directly contact the treated substrate, whereby the softening agent is transferred from the absorbent substrate to the fabric. The necessary contact between the fabric and the softener-impregnated substrate is effected by the spinning or tumbling action of a standard, automatic clothes dryer.

If the softening composition is used in a washer, a sheet is removed from the package or a desired length torn off the roll and placed into the rinse water, e.g., of the final rinse cycle. The softening agent disperses into the rinse water and is then absorbed by the fabrics.

DETAILED DESCRIPTION OF THE INVENTION

Essential to the invention herein is the use of an absorbent substrate. It is known that most substances are able to absorb a liquid substance to some degree; however, the term "absorbent," as used herein, is intended to mean a substance with an absorbent capacity (i.e., values representing a substrate's ability to take up and retain a liquid) from 5.5 to 12, preferably 7 to 10, times its weight of water.

Determination of absorbent capacity values is made by using the capacity testing procedures described in

U.S. Federal Specifications UU-T-595b modified as follows:

- (1) tap water is used instead of distilled water;
- (2) the specimen is immersed for 30 seconds instead of 3 minutes;
- (3) draining time is 15 seconds instead of 1 minute; and
- (4) the specimen is immediately weighed on a torsion balance having a pan with turned-up edges.

Absorbent capacity values are then calculated in accordance with the formula given in said specification. Based on this test, one-ply, dense bleached paper (e.g., kraft or bond having a basis weight of about 32 pounds per 3,000 square feet, has an absorbent capacity of 3.5 to 4; commercially available household one-ply toweling paper has a value of 5 to 6; and, commercially available two-ply household toweling paper (a paper structure preferred herein) has a value of 7 to about 9.5.

Using a substrate with an absorbent capacity of less than 5.5 tends to cause too rapid release of the softening agent from the substrate resulting in several disadvantages, one of which is poorer softening of the fabrics. Using a substrate with an absorbent capacity over 12 is undesirable, inasmuch as too little of the softening agent is released to adequately soften the fabrics.

The substrate of this invention can also be defined in terms of "free space." Free space, also called "void volume," as used herein is intended to mean that space within a structure that is unoccupied. For example, certain multiply paper structures comprise plies embossed with protuberances, the ends of which are mated and joined; this paper structure has a void volume or free space between the unembossed portions of the plies, as well as between the fibers of the paper sheet itself. A non-woven cloth also has such space between each of its fibers. The free space of non-woven cloth or paper, having designated physical dimensions, can be varied by modifying the density of the fibers of the paper or non-woven cloth. Substrates with a high amount of free space generally have low fiber density; high density substrates generally have a low amount of free space. The substrates of the invention herein have from about 40% to about 90%, preferably about 55%, free space based on the overall volume of the substrate's structure. This free space is directly connected with, and a result of, the substrate having an absorbency value of 5.5 to 12.

The use of dense, one-ply or ordinary kraft or bond paper as a softening agent substrate, as suggested in the prior art, causes staining of the treated fabrics. Applicant has discovered that this staining is caused by the low absorbent capacity of the paper substrate. Thus, the softening agent on such paper is rapidly released in excessive quantities when subjected to customary dryer temperatures, with the result that treated fabrics become stained at points of contact with the softener-coated paper. Applicant has further discovered the fabric staining can be eliminated altogether or substantially reduced by employing a substrate having an absorbent capacity in the range of 5.5 to 12, such that less of the softening agent is released at any given point of time and on contact with a fabric to be treated.

Accordingly, suitable materials which can be used as a substrate in the invention herein include, among others, sponges, paper, and woven and non-woven cloth, all having the necessary absorbency requirements defined above. The preferred substrates of the softening compositions herein are cellulosic, particularly multi-ply paper and non-woven cloth.

Specifically, the preferred paper substrate is a compressible, laminated, calendered, multi-ply, absorbent paper structure. Preferably, the paper structure has 2 or 3 plies and a total basis weight of from 14 to 90 pounds per 3,000 square feet and absorbent capacity values within the range of 7 to 10. Each ply of the preferred paper structure has a basis weight of about 7 to 30 pounds, per 3,000

square feet, and the paper structure can consist of plies having the same or different basis weights. Each ply is preferably made from a creped, or otherwise extensible, paper with a creped percentage of about 15% to 40% and a machine direction (MD) tensile and cross-machine (CD) tensile of from about 100 to 1,500, grams per square inch of paper width. The two outer plies of a 3-ply paper structure or each ply of a 2-ply paper structure are embossed with identical repeating patterns consisting of about 16 to 200 discrete protuberances per square inch, raised to a height of from about 0.010 inch to 0.40 inch above the surface of the unembossed paper sheet. From about 10% to 60% of the paper sheet surface is raised. The distal ends (i.e., the ends away from the unembossed paper sheet surface) of the protuberances on each ply are mated and adhesively joined together, thereby providing a preferred paper structure exhibiting a compressive modulus of from about 200 to 800 inch-grams per cubic inch and Handle-O-Meter (HOM) MD and CD values of from about 10 to 130.

Suitable adhesives are known in the art and commonly include, among others, water, starches, wet-strength resins, and polyvinyl acetates. A particularly suitable adhesive is prepared by heating from about 2 to about 4 parts by weight of substantially completely hydrolyzed polyvinyl alcohol resin in from about 96 to about 98 parts by weight of water. Preferably, about 0.03 pound of adhesive solids are used to join 3,000 square feet of the embossed plies, with the adhesive being applied to the distal surfaces of the protuberances of one or all plies.

The compressive modulus values which define the compressive deformation characteristics of a paper structure compressively loaded on its opposing surfaces, the HOM values which refer to the stiffness or handle of a paper structure, the MD and CD HOM values which refer to HOM values obtained from paper structure samples tested in a machine and cross-machine direction, the methods of determining these values, the equipment used, and a more detailed disclosure of the paper structure preferred herein, as well as methods of its preparation, can be found in Edward R. Wells, U.S. Pat. 3,414,459, issuing on Dec. 3, 1968, the full disclosure of which is hereby incorporated hereinto.

The preferred non-woven cloth substrates useable in the invention herein can generally be defined as adhesively bonded fibrous or filamentous products, having a web or carded fiber structure (where the fiber strength is suitable to allow carding) or comprising fibrous mats, in which the fibers or filaments are distributed haphazardly or in random array (i.e., an array of fibers in a carded web wherein partial orientation of the fibers is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibers or filaments can be natural (e.g., wool, silk, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g., rayon, cellulose ester, polyvinyl derivatives, poly-olefins, polyamides, or polyesters).

Methods of making non-woven cloths are not a part of this invention and being well known in the art, are not described in detail herein. Generally, such cloths are made by air- or water-laying processes in which the fibers or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fiber-laden air or water is passed. The deposited fibers or filaments are then adhesively bonded together, dried, cured, and otherwise treated as desired to form the non-woven cloth. Non-woven cloths made of polyesters, polyamides, vinyl resins, and other thermoplastic fibers can be spun-bonded, i.e., the fibers are spun out onto a flat surface and bonded (melted) together by heat or by chemical reactions.

The absorbent properties required herein are particularly easy to obtain with non-woven cloths and are provided merely by building up the thickness of the cloth, i.e., by superimposing a plurality of carded webs or mats

to a thickness adequate to obtain the necessary absorbent properties, or by allowing a sufficient thickness of the fibers to deposit on the screen. Any diameter or denier of the fiber (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fiber that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which, further, makes the non-woven cloth especially suitable for impregnation with a softening agent by means of intersectional or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

The choice of binder-resins used in the manufacture of non-woven cloths can provide substrates possessing a variety of desirable traits. For example, the absorbent capacity of the cloth can be increased, decreased, or regulated by respectively using a hydrophilic binder-resin, a hydrophobic binder-resin or a mixture thereof in the fiber bonding step. Moreover, the hydrophobic binder-resin, when used singly or as the predominant compound of a hydrophobic-hydrophilic mixture, provides non-woven cloths which are especially useful as substrates when the softening compositions herein are used in the rinse cycle of an automatic washer.

When the substrate of the softening compositions herein is a non-woven cloth made from fibers deposited haphazardly or in random array on the screen, the compositions exhibit excellent strength in all directions and are not prone to tear or separate when used in the washer or the dryer.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibers, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant. Preferably, the fibers are from $\frac{3}{16}$ " to 2" in length and are from 1.5 to 5 denier. Preferably, the fibers are at least partially oriented haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. Preferably, the cloth comprises about 70% fiber and 30% binder-resin polymer by weight and has a basis weight of from about 20 to 24 grams per square yard.

The absorbent substrates, which are used in the softening compositions herein, can take a variety of forms. For example, the substrate can be in the shape of a ball or puff, or it may be a sheet or swatch of woven or non-woven cloth. When the substrate is paper or cloth, individual sheets of desired length and width can be used, or, if paper, a continuous roll of desired width from which a measured length is torn off can be employed.

The fabric softeners of the softening compositions herein can be used singly or, in admixture with one or more compatible fabric softeners. The terms "softener," "fabric softener," or "softening agent," are used interchangeably herein and are intended to include such admixtures. The fabric softeners, as more particularly described hereinafter, used in the softening compositions herein can be selected from the following broadly denoted classes of compounds which contain at least one long chain group:

- (1) cationic quaternary ammonium salts including quaternary imidazolium salts;
- (2) nonionic compounds, such as tertiary phosphine oxides, tertiary amine oxides and ethoxylated alcohols and alkylphenols;
- (3) anionic soaps, sulfates and sulfonates, e.g., fatty acid soaps, ethoxylated alcohol sulfates and sodium alkyl sulfates, alkyl sulfonates, sodium alkylbenzene sulfonates, and sodium or potassium alkylglyceryl ethersulfonates;
- (4) Zwitterionic quaternary ammonium compounds;
- (5) ampholytic tertiary ammonium compounds; and
- (6) compatible mixtures of one or more compounds of these classes.

Essential to the compositions herein is the use of a fabric softener that exhibits a softening point (hereinafter also designated "s.p.") below the temperature of about 170° F.

The term "softening point," as used herein, means the temperature at which the fabric softener, impregnated into the absorbent substrate, becomes completely liquefied or sufficiently liquefied to adhere to fabrics contacting the softener-impregnated substrate in the dryer.

Determination of softening points of fabric softener impregnated into the absorbent substrates herein is made by continuously passing water, and temperature of which is constantly measured by a thermometer or temperature gauge, through a 1" diameter metal pipe which has a thoroughly cleaned and polished surface and about which a sheet of a softener-impregnated substrate (i.e., a softening composition herein) has been tightly wrapped. The surface of the pipe equilibrates with the water temperature, and the water temperature is raised until a marked change is observed in the composition sheet. This change is characterized by the composition sheet being damp to the touch, by the ability to now slide the sheet along the pipe, and by the pipe feeling "lubricated" on removal of the composition sheet. The water temperature at which this change is observed is the softening point of the fabric softener.

To insure adequate softening of fabrics in a dryer, the fabric softener must have a softening point within the temperature ranges of a standard, automatic clothes dryer. Dryer temperatures start at room temperature (about 75° F.) and reach up to about 170° F., i.e., automatic, electric dryers, containing an average load of fabrics (about $5\frac{1}{2}$ pounds dry and about $9\frac{3}{4}$ pounds wet), reach up to about 150° F. to about 160° F. with maximum temperatures occurring very near the end of the drying cycle; gas dryers reach even higher temperatures, about 170° F. Accordingly, the fabric softener used must have a softening point below about 170° F., preferably below about 150° F.; particularly useful are fabric softeners which exhibit softening points at temperatures occurring early in the drying cycle, i.e., from room temperature (75° F.) to about 140° F.

Many fabric softeners have softening points above the necessary ranges; however, the softening points of these fabric softeners can be lowered to a desired temperature by the addition of a liquid, such as ethyl alcohol, isopropyl alcohol, or an isopropyl alcohol/water mixture. Where necessary, the softener's softening point is lowered to a temperature in the above ranges. Preferably, the softener should have a softening point, or its softening point should be lowered, no lower than about 100° F. It is desirable that the compositions herein be suitable for storage on the shelf until use and, further, that the compositions aer not runny or do not drip, but rather, are substantially solid at temperatures below about 100° F. The above mentioned liquids are especially suitable for the purpose of lowering a softener's softening point where necessary, inasmuch as they are highly evaporative compounds. Thus, large amounts (e.g., from about 10% to 300% by weight of the fabric softener) can be added to the softener which is then impregnated into an absorbent substrate, and, upon drying the treated substrate a suitable length of time, all but a residual amount (e.g., from about 0.1% to 7% by weight of the softener) evaporates, leaving a substantially solid softening composition of the invention herein. This residual amount is sufficient to reduce the fabric softener's softening point to within the necessary range.

Particularly preferred softening agents of the softening compositions herein are the cationic quaternary ammonium salts which have the general formula



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wherein X is an anion, preferably a halide and more particularly, a chloride ion. Suitable other anions can include acetate, phosphate, nitrite, and methyl sulfate radicals. Additionally, in the above formula, R and R₁ represent benzyl or an alkyl containing from 1 to 3 carbon atoms, R₂ represents benzyl, or an alkyl containing from 1 to 3 carbon atoms, or an alkyl of from 12 to 20 carbon atoms, or alkoxypropyl or hydroxy substituted alkoxypropyl radicals wherein the alkoxy contains 12 to 20 carbon atoms, and R₃ represents an alkyl containing from 12 to 20 carbon atoms. The carbon chains of R₃ and R₂, whenever R₂ represents a chain of from 12 to 20 carbon atoms, can be straight or branched, and saturated or unsaturated.

Because of their known softening efficacy, the most preferred cationic softening agents are dialkyl dimethyl ammonium chloride or alkyl trimethyl ammonium chloride wherein the alkyl contains from 12 to 20 carbon atoms and are derived from long chain fatty acids, especially from hydrogenated tallow. The terms "tallow" and "tallowalkyl," used herein, are intended to mean alkyls containing from 16 to 18 carbon atoms. The term "tallowalkoxy," used herein, means an alkyl ether radical wherein the alkyl contains from 16 to 18 carbon atoms. Specific examples of the particularly preferred cationic softening agents include the following:

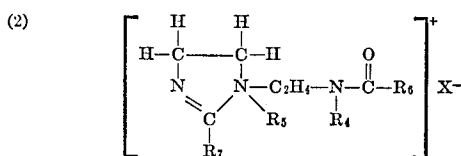
tallowtrimethyl ammonium chloride,
tallowdimethyl (3-tallowalkoxypropyl) ammonium chloride,
ditallow dimethyl ammonium chloride,
ditallow dimethyl ammonium methyl sulfate,
eicosyltrimethyl ammonium chloride, and
dieicosyldimethyl ammonium chloride.

Examples of other preferred cationic softening agents suitable for use in the invention herein include the following:

dodecyltrimethyl ammonium chloride,
didodecyldimethyl ammonium chloride,
tetradecyltrimethyl ammonium chloride,
ditetradecyldimethyl ammonium chloride,
pentadecyltrimethyl ammonium chloride,
dipentadecyldimethyl ammonium chloride,
didodecyldiethyl ammonium chloride,
didodecyldipropyl ammonium chloride,
ditetradecyldiethyl ammonium chloride,
ditetradecyldipropyl ammonium chloride,
ditallowdiethyl ammonium chloride,
ditallowdipropyl ammonium chloride,
tallowdimethyl benzyl ammonium chloride,
tallowdiethyl benzyl ammonium chloride,
dodecyltrimethyl ammonium methyl sulfate,
didodecyldiethyl ammonium acetate,
tallowtrimethyl ammonium acetate,
tallowdimethyl benzyl ammonium nitrite, and
ditallowdipropyl ammonium phosphate.

Other cationic softening agents of Formula 1 are known and include variables wherein R and R₁ can also represent a phenyl radical or a hydroxy substituted alkyl of from 1 to 3 carbon atoms.

Cationic quaternary imidazolium compounds are also preferred as softening agents in the compositions herein. These compounds conform to the formula



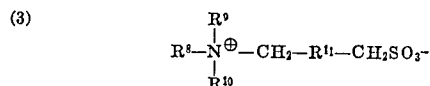
wherein R₅ is an alkyl containing from 1 to 4, preferably from 1 to 2, carbon atoms, R₆ is an alkyl containing from 1 to 4 carbon atoms or a hydrogen radical, R₇ is an alkyl containing from 8 to 25, preferably at least

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15, carbon atoms, R₄ is hydrogen or an alkyl containing from 8 to 25, preferably at least 15, carbon atoms, and X is an anion, preferably methyl sulfate or chloride ions. Other suitable anions include those disclosed with reference to the cationic softening agents of Formula 1. Particularly preferred are those compounds of Formula 2 in which both R₄ and R₇ are alkyls of from 16 to 25, especially 16 to 18 and 20 to 22, carbon atoms.

Many other cationic quaternary ammonium softening agents, which are useful herein, are known; for example, alkyl [C₁₂ to C₂₀]-pyridinium chlorides, alkyl [C₁₂ to C₂₀]-alkyl [C₁ to C₃]-morpholinium chlorides, and quaternary derivatives of amino acids and amino esters.

Other preferred softening agents include Zwitterionic quaternary ammonium compounds which have the formula



wherein R₉ and R₁₀ are each methyl, ethyl, n-propyl, isopropyl, 2-hydroxyethyl or 2-hydroxypropyl, R₈ is a 20 to 30 carbon atom alkyl or alkenyl and wherein said alkyl or alkenyl contains from 0 to 2 hydroxyl substituents, from 0 to 5 ether linkages, and from 0 to 1 amide linkage, and R₁₁ is an alkylene group containing from 1 to 4 carbon atoms with from 0 to 1 hydroxyl substituents; particularly preferred are compounds wherein R₈ is a carbon chain containing from 20 to 26 carbon atoms selected from the group consisting of alkyls and alkenyls and wherein said alkyls and alkenyls contain 0 to 2 hydroxyl substituents. Specific examples of the particularly preferred compounds of this class include the following:

3-N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-eicosyl-N,N-di(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-docosyl-N,N-bis-(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-tetracosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tetracosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-tetracosyl-N,N-bis-(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-hexacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-hexacosyl-N,N-dimethylammonio)-propane-1-sulfonate

Examples of other preferred compounds of this class are as follows:

3-(N-eicosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tetracosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-heneicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tricosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tricosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tricosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-(N-pentacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate

- 3-[N-(2-methoxydocosyl)-N,N-dimethylammonio]-2-hydroxypropane-1-sulfonate
 3-(N-heptacosyl-N,N-dimethylammonio)-propane-1-sulfonate
 3-(N-octacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
 3-(N-nonacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
 3-(N-1-triacontyl-N,N-dimethylammonio)-propane-1-sulfonate
 3-[N-(3,5-dioxatetracosyl)-N,N-dimethylammonio]-2-hydroxypropane-1-sulfonate

The compounds of Formula 3 are disclosed more particularly in a copending application entitled "Textile Treating Compounds, Compositions and Processes for Treating Textiles," by Charles B. McCarty, Ser. No. 648,527, filed June 5, 1967, the disclosure of which provides methods of preparing these compounds and is fully incorporated hereinto.

Other Zwitterionic compounds useful as softening agents in compositions herein are known and include Zwitterionic synthetic detergents as represented by derivatives of aliphatic quaternary ammonium compounds wherein one of the four aliphatic groups has about 8 to 20 carbon atoms, another contains a water-solubilizing group (e.g., carboxy, sulfato or sulfo groups), and any of which are straight or branched. A more detailed disclosure of these compounds can be found in Francis Diehl, U.S. Pat. 3,213,030, issued Oct. 19, 1965.

Nonionic tertiary phosphine oxide compounds are also preferred softening agents for use in the novel softening compositions herein. These compounds have the generic formula



wherein R_{12} is alkyl, alkenyl, or monohydroxy alkyl having a chain length of from 20 to 30 carbon atoms, and wherein R_{13} and R_{14} are each alkyl or monohydroxy alkyl containing from 1 to 4 carbon atoms; particularly preferred are tertiary phosphine oxides in which R_{12} is alkyl, alkenyl, and monohydroxy alkyl having a chain length of from 20 to 36 carbon atoms, and wherein R_{13} and R_{14} are each methyl, ethyl or ethanol.

Specific examples of particularly preferred softeners of this class include the following:

eicosyldimethylphosphine oxide,
 eicosyldi(2-hydroxyethyl)phosphine oxide,
 docosyldimethylphosphine oxide,
 docosyldi(2-hydroxyethyl)phosphine oxide
 tetracosyldimethylphosphine oxide,
 hexacosyldimethylphosphine oxide,
 eicosyldiethylphosphine oxide,
 docosyldiethylphosphine oxide, and
 tetracosyldi(2-hydroxyethyl)phosphine oxide.

Examples of other preferred tertiary phosphine oxides of this class are as follows:

eicosylmethylethylphosphine oxide,
 heneicosyldimethylphosphine oxide,
 β -hydroxyeicosyldimethylphosphine oxide,
 β -hydroxydocosyldimethylphosphine oxide,
 heneicosylmethylethylphosphine oxide,
 docosylmethylethylphosphine oxide,
 tricosyldiethylphosphine oxide,
 tricosyldimethylphosphine oxide,
 tetracosyldi(2-hydroxyethyl)phosphine oxide,
 pentacosyldimethylphosphine oxide,
 eicosylmethyl-2-hydroxybutylphosphine oxide,
 eicosyldibutylphosphine oxide,
 docosylmethyl-3-hydroxybutylphosphine oxide,
 hexacosyldiethylphosphine oxide,
 heptacosyldimethylphosphine oxide,
 octacosyldiethylphosphine oxide, and
 triacontyldimethylphosphine oxide.

The C_{20} to C_{30} nonionic tertiary phosphine oxides are disclosed more particularly in the aforementioned McCarty application, wherein methods of preparing these compounds are also given.

- 5 Other nonionic tertiary phosphine oxides useful herein are known and include the nonionic synthetic detergents having the same formula as that of Formula 4 above wherein R_{12} is an alkyl, alkenyl, or monohydroxyalkyl of from 10 to 20 carbon atoms, and wherein R_{13} and R_{14} are each alkyl or monohydroxyalkyl of from 1 to 3 carbon atoms. The C_{10} to C_{20} tertiary phosphine oxides are more particularly described in the aforementioned Diehl patent.

10 Nonionic tertiary amine oxides are also known to be useful as softening agents and can be utilized in the compositions of the present invention. These nonionic compounds have the formula



20 wherein R_{15} represents a straight or branched chain alkyl or alkenyl containing from 20 to 30 carbon atoms and from 0 to 2 hydroxyl substituents, from 0 to 5 ether linkages, there being at least one moiety of at least 20 carbon atoms containing no ether linkages, and 0 to 1 amide linkage, and wherein R_{16} and R_{17} are each alkyl or monohydroxy alkyl groups containing from 1 to 4 carbon atoms and wherein R_{16} and R_{17} can be joined to form a heterocyclic group containing from 4 to 6 carbon atoms; particularly preferred are those wherein R_{15} is a straight or branched alkyl, alkenyl, or monohydroxy alkyl containing 20 to 26 carbon atoms and wherein R_{16} and R_{17} are each methyl, ethyl, or ethanol.

Specific examples of the particularly preferred compounds of this class are as follows:

- 35 eicosyl-bis-(β -hydroxyethyl) amine oxide,
 eicosyldimethylamine oxide,
 docosyldimethylamine oxide,
 docosyl-bis-(β -hydroxyethyl) amine oxide
 tetracosyldimethylamine oxide,
 tetracosyl-bis-(β -hydroxyethyl) amine oxide,
 40 hexacosyldimethylamine oxide, and
 hexacosyl-bis-(β -hydroxyethyl) amine oxide.

Examples of other preferred tertiary amine oxides of this class are as follows:

- 45 2-hydroxyeicosyldimethylamine oxide,
 eicosylmethylethylamine oxide,
 eicosyldiethylamine oxide,
 2-hydroxyeicosyldiethylamine oxide,
 50 heneicosyldimethylamine oxide,
 heneicosyldiethylamine oxide,
 docosyldiethylamine oxide,
 tricosyldimethylamine oxide,
 tricosyldiethylamine oxide,
 tetracosyldiethylamine oxide,
 55 β -hydroxytetracosyldimethylamine oxide,
 pentacosyldimethylamine oxide,
 hexacosyldiethylamine oxide,
 eicosylmethyl(2-hydroxypropyl) amine oxide,
 60 docosylbutylmethylamine oxide,
 2-docosenyldimethylamine oxide,
 2-methoxydocosyldimethylamine oxide,
 heptacosyldimethylamine oxide,
 octacosylmethylethylamine oxide,
 65 octacosyldiethylamine oxide,
 nonacosyldimethylamine oxide,
 triacontyldiethylamine oxide,
 3,6-dioxaoctacosyldimethylamine oxide,
 2-hydroxy-4-oxatetracosyldimethylamine oxide,
 70 6-stearamidohexyldimethylamine oxide.

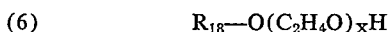
The tertiary amine oxides of this class and methods of their preparation are also disclosed more particularly in the aforementioned McCarty application.

- 75 Other tertiary amine oxides useful herein are known and include compounds corresponding to Formula 5 above

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wherein R_{15} is an alkyl of 8 to 20, particularly 16 to 18, carbon atoms, and R_{16} and R_{17} are methyl or ethyl radicals; the C_8 to C_{20} nonionic tertiary amine oxides are disclosed in more detail in the above-referenced Diehl patent.

Nonionic ethoxylated alcohol compounds are also known as softening agents and are preferred in the softening compositions herein. These compounds have the generic formula



wherein R_{18} represents an alkyl of from 20 to 30 carbon atoms, and X is an integer of from 3 to 45.

The particularly preferred ethoxylated alcohol compounds of this class are the condensation products of reacting from 3 moles to 45 moles of ethylene oxide with one mole of eicosyl alcohol, heneicosyl alcohol, tricosyl alcohol, tetracosyl alcohol, pentacosyl alcohol, or hexacosyl alcohol. Specific examples of the particularly preferred ethoxylated alcohols include the following reaction products of:

3 moles ethylene oxide+1 mole of heneicosyl alcohol,
9 moles ethylene oxide+1 mole eicosyl alcohol
12 moles ethylene oxide+1 mole hexacosyl alcohol,
15 moles of ethylene oxide+1 moles tetracosyl alcohol,
20 moles of ethylene oxide+1 mole pentacosyl alcohol,
and
30 moles of ethylene oxide+1 mole tricosyl alcohol.

Other preferred ethoxylated alcohols are the condensation products of from 3 moles to 45 moles of ethylene oxide with one mole of heptacosyl, octacosyl, nonacosyl, or triacontyl alcohols. Specific examples include the condensation products of the following:

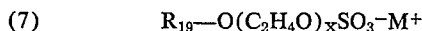
5 moles of ethylene oxide+1 mole of nonacosyl alcohol,
6 moles of ethylene oxide and 1 mole of heptacosyl alcohol,
9 moles of ethylene oxide+1 mole of octacosyl alcohol,
20 moles of ethylene oxide+1 mole of heptacosyl alcohol,
30 moles of ethylene oxide+1 mole of triacontyl alcohol,
and
40 moles of ethylene oxide+1 mole of nonacosyl alcohol.

These compounds and methods of their preparation are more particularly disclosed in the above-mentioned McCarty application.

Also suitable for use as softening agents in the compositions herein are nonionic synthetic detergents as represented by the polyethylene oxide condensates of aliphatic alcohols containing from 8 to 20 carbon atoms and alkylphenols wherein the alkyl contains from 8 to 20 carbon atoms. Particularly preferred are the condensation products of 1 mole of tallow alcohol with 20 moles and with 30 moles of ethylene oxide, hereinafter designated TAE₂₀ and TAE₃₀ respectively. The Diehl patent discloses these compounds in more detail.

Also preferred as softening agents in the compositions herein are anionic ethoxylated alcohol sulfates and anionic sulfonates.

The preferred ethoxylated alcohol sulfates have the generic formula



wherein X is an integer of from 1 to 20, M is an alkali metal (e.g., Na, K, Li), ammonium or substituted ammonium cations, and wherein R_{19} is an alkyl containing from 20 to 30 carbon atoms.

The particularly preferred anionic ethoxylated alcohol sulfate softening compounds are the sodium and potassium salts or the monoethanol, diethanol, or triethanol ammonium salts of the sulfated condensation product of from 1 to about 20 moles of ethylene oxide with one mole of eicosyl alcohol, heneicosyl alcohol, tricosyl alcohol, tetracosyl alcohol, pentacosyl alcohol, or hexacosyl alcohol. Specific examples of these particularly preferred anionic

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softening compounds include the salts of the sulfated condensation products of the following:

1 mole of ethylene oxide+1 mole of tetracosyl alcohol
3 moles of ethylene oxide+1 mole of hexacosyl alcohol,
9 moles of ethylene oxide+1 mole of tricosyl alcohol,
12 moles of ethylene oxide+1 mole of eicosyl alcohol,
16 moles of ethylene oxide+1 mole of pentacosyl alcohol,
and
29 moles of ethylene oxide+1 mole of heneicosyl alcohol.

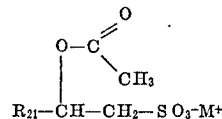
Other preferred anionic ethoxylated sulfate compounds are the sodium or potassium salts or monoethanol, diethanol, or triethanol ammonium cations of the sulfated condensation products of from 1 to 20 moles of ethylene oxide with one mole of heptacosyl alcohol, octacosyl alcohol, nonacosyl alcohol, and triacontyl alcohol.

Anionic synthetic detergents as represented by alkyl sulfates of the formula



wherein M is an alkali metal and R is an alkyl of from 8 to 20 carbon atoms are also useful as softening agents herein. These compounds are more particularly disclosed in the above-referenced Diehl patent.

The preferred anionic sulfates have the general formula (9)



wherein M is an alkali metal or a substituted ammonium cation, and R_{21} is an alkyl containing from 20 to 30 carbon atoms. The particularly preferred anionic sulfonates are those in which R_{21} is an alkyl containing from 20 to 26 carbon atoms. Examples of the particularly preferred compounds include:

sodium or potassium 2-acetoxycocoylsulfonate,
ammonium 2-acetoxycocoylsulfonate,
diethanolammonium 2-acetoxycocoylsulfonate,
sodium or potassium 2-acetoxycocoylsulfonate,
sodium or potassium 2-acetoxytetracosylsulfonate,
sodium or potassium 2-acetoxypentacosylsulfonate,
sodium or potassium 2-acetoxylhexacosylsulfonate,
sodium or potassium 2-acetoxylheptacosylsulfonate and
sodium or potassium 2-acetoxyoctacosylsulfonate

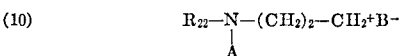
Other preferred anionic sulfonates include sodium or potassium:

2-acetoxynonacosylsulfonate,
2-acetoxyltriacontylsulfonate,
2-acetoxylheneitriacontylsulfonate, and
2-acetoxyldotriacontylsulfonate.

The anionic ethoxylated alcohol sulfates and the anionic sulfonates mentioned above can be prepared by the method disclosed in the aforementioned McCarty application, wherein said compounds are more particularly disclosed.

Other anionic sulfonates useful as softening agents herein are the synthetic detergents as represented by, among others, sodium or potassium alkylbenzenesulfonates and sodium alkylglycerylethersulfonates having the configuration of Formula 9 above, wherein R_{21} is an alkylbenzene or alkylglycerylether with the alkyl containing from 10 to 20 carbon atoms. These compounds are more particularly described in the above-mentioned Diehl patent.

Additionally, ampholytic synthetic detergents of the formula



wherein R_{22} is an alkyl of from 8 to 18 carbon atoms, A is R_{22} or hydrogen, and B is a water-solubilizing group

(particularly SO_3^-), can be used as softening agents in the compositions herein. These compounds are more particularly disclosed in the above-referenced Diehl patent.

The admixture of one or more softening agents of one class with one or more compatible softening agents of another class can be used in the compositions herein; when such admixtures are used herein, the amount of softener of any one class can range from 1% to 99%, as desired, by weight of the admixture. Examples of admixtures suitable for use herein include the following, wherein all percentages are by weight of the admixture:

	Percent
Ditallowdimethyl ammonium chloride -----	65
Tallowdimethylphosphine oxide -----	35
Eicosyltrimethyl ammonium chloride -----	30
Hexacosyldimethylamine oxide -----	70
Eicosyltrimethyl ammonium chloride -----	60
TAE ₃₀ -----	40
Ditallowdimethyl ammonium chloride -----	45
3-(N-eicosyl - N,N - dimethylammonio)-2-hydroxypropane-1-sulfonate -----	55
Ditallowdimethyl ammonium chloride -----	60
Eicosyldimethylamine oxide -----	40
Ditallowdimethyl ammonium chloride -----	50
3 - (N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate -----	50
Eicosyltrimethyl ammonium chloride -----	50
3 - (N-docosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate -----	50
Sulfated condensation product of 9 moles of ethylene oxide+1 mole of eicosyl alcohol -----	50
Condensation product of 9 moles of ethylene oxide+1 mole eicosyl alcohol -----	50
Sodium 2-acetoxydocosylsulfonate -----	40
TAE ₂₀ -----	60
Sodium 2-acetoxydocosylsulfonate -----	60
Tetracosyldimethylphosphine oxide -----	40
Diethanolammonium 2-acetoxydocosylsulfonate -----	75
Dodecyldimethylamine oxide -----	25
Dodecylbenzenesulfonate -----	45
TAE ₂₀ -----	55
3 - (N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate -----	70
Condensation product of 30 moles of ethylene oxide+1 mole tricosylalcohol -----	30
3 - (N-docosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate -----	65
TAE ₃₀ -----	35
3-(N-tetracosyl - N,N - dimethylammonio)-2-hydroxypropane-1-sulfonate -----	45
Tetracosyldimethyl phosphine oxide -----	55
3 - (N-tetracosyl)-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate -----	75
Tallowdimethylamine oxide -----	25

Other admixtures can be formulated from the compounds and in the amounts disclosed hereinabove.

Anionic soaps, i.e., the sodium salts of long-chain fatty acids, such as lauric, myristic, palmitic, stearic, and arachidonic acids, can also be used as a softening agent in the compositions herein, and many such compounds are known in the art.

The fabric softeners disclosed above provide a comprehensive list from which a single fabric softener or an admixture of softeners can be chosen to obtain the property of exhibiting a softening point in the 100° F. to about 170° F. range.

Other additives can also be used in combination with a softening agent. Although not essential to the invention herein, certain of these additives are particularly desirable and useful, e.g., perfumes and brightening agents; shrinkage controllers, anti-static agents, and spotting agents are also useful.

While not essential, liquids which serve as a carrier for the softening agent can be employed. Such liquids aid in releasing the softening agent from the absorbent substrate and in promoting adherence of the softener to the fabric contacting the softener-impregnated substrate. Further, the liquid carrier can be used to more evenly impregnate the absorbent substrate with the softening agent, or it can be used, where necessary, to lower the softening point of a softening agent below 170° F. preferably below 150° F. and no lower than 100° F., necessary for proper softening of fabrics in a standard, home clothes dryer. When a liquid carrier is so used, it should preferably be inert or stable to the fabric softener. Moreover, the liquid carrier should be substantially evaporated at room temperatures, and the residue (i.e., the softening agent) should then be sufficiently hardened so as not to run or drip off the substrate or cause the substrate to stick together when folded. Isopropyl alcohol or isopropyl alcohol/water mixtures are the preferred liquid carriers for these purposes; methanol, ethanol, or acetone can also be used.

Other additives can include anti-creasing agents, finishing agents, fumigants, lubricants, fungicides, and sizing agents. Specific examples of possible additives disclosed herein can be found in any current Year Book of the American Association of Textile Chemists and Colorists. Any additive used should be compatible with the softening agent.

The amounts of many additives (e.g., perfume and brighteners) that can be used in combination with a softening agent are generally small, being in the range of from 0.01% to 3% by weight of the softening agent.

The softening compositions herein comprise a softening agent impregnated into an absorbent substrate. The impregnation can be done in any convenient manner, and many methods are known in the art. For example, the softener, in liquid form, can be sprayed onto a substrate or be added to a wood-pulp slurry from which the substrate is manufactured.

Impregnation, rather than coating, the substrate with a softener is essential. The term "coating" connotes the adjoining of one substance to the surface of another; "impregnation" is intended to mean the permeation of the entire substrate structure, internally as well as externally. One factor affecting a given substrate's absorbent capacity is its free space. Accordingly, when a softening agent is applied to an absorbent substrate, it penetrates into the free space; hence, the substrate is deemed impregnated. The free space in a substrate of low absorbency, such as a one-ply kraft or bond paper, is very limited; such a substrate is, therefore, termed "dense." Thus, while a small portion of the softening agent penetrates into the limited free space available in a dense substrate, a rather substantial balance of the softener does not penetrate and remains on the surface of the substrate so that it is deemed a coating. The difference between coating and impregnation is believed to explain why the softener-impregnated absorbent substrate of the invention herein eliminates or substantially reduces the staining of fabrics observed when a softener-coated dense substrate is utilized.

In a preferred method of making the softener-impregnated absorbent substrate, the softener is applied to absorbent paper or non-woven cloth by a method generally known as padding. The softening agent is preferably applied in liquid form to the substrate; thus, softeners which are normally solid at room temperature should first be melted and/or solvent-treated with one of the liquid carriers mentioned hereinbefore. Methods of melting the

softener and/or of treating the softener with a solvent are known and can easily be done to provide a satisfactory softener treated substrate.

In another preferred method, the softening agent, in liquid form, is placed into a pan or trough which can be heated, if necessary, to maintain the softener in liquid form. To the liquid softener is then added any desired additives. A roll of absorbent paper is then set up on an apparatus so that it can unroll freely. As the paper unrolls, it travels downwardly and, submersed, passes through the pan or trough containing the liquid softener at a slow enough speed to allow sufficient impregnation. The absorbent paper then travels, at the same speed, upwardly and through a pair of rollers which squeeze off excess bath liquid and provide the absorbent paper with 11 to 12 grams of the softening agent per foot length of 11" wide paper. The impregnated paper is then cooled to room temperature, after which it can be folded, cut or perforated at uniform foot lengths, and subsequently packaged and/or used.

The rollers used resemble "squeeze rolls" used by those in the paper and paper-making art; they can be made of hard rubber or steel. Preferably, the rollers are adjustable, so that the orifice between their respective surfaces can be regulated to control the amount of the softener liquid on the paper.

In another method of impregnation, the softening agent, in liquid form, is sprayed onto absorbent paper as it unrolls and the excess softener is then squeezed off by the use of squeeze rollers or by a doctor-knife. Other variations include the use of metal "nip" rollers onto the leading or entering surfaces of which the softening agent is sprayed; this variation allows the absorbent paper to be treated, usually on one side only, just prior to passing between the rollers wherein excess softener is squeezed off; this variation additionally involves the use of metal rollers which can be heated to maintain the softener in the liquid phase. A further method is separately treating a desired number of the individual plies of a multi-ply paper and subsequently adhesively joining the plies with a known adhesive-joinder compound; this provides a composition which can be untreated on one of its outer sides, yet contains several other plies, each of which is treated on both sides.

In applying the softening agent to the absorbent substrate, the amount of softener impregnated into the absorbent substrate is in the ratio range of 10:1 to 2:1 by weight of the dry untreated substrate. Preferably, the amount of the softening agent impregnated is from about 4:1 to about 2:1, particularly 3:1, by weight of the dry untreated substrate. When the softening agent is a condensation product of fatty alcohol with 1 to 45 moles of ethylene oxide, the ratio of softener to substrate is preferably from 3:1 to 2:1 by weight of the dry substrate to insure optimum non-staining characteristics.

The composition weight ratios indicated above particularly apply to the amount of softener present in each foot length of the substrate, the amount of softener impregnated being dependent upon the weight of one foot length of the substrate, regardless of width. Thus, for example, a foot length of a substrate 11" wide requires more impregnated softener than does one foot length of a substrate 8½" wide in order to obtain a given softener-substrate ratio. Generally, the amount of softener ranges from about 3 grams to about 37 grams per foot length of a substrate no more than 11" wide, with small amounts of softener being used on light-weight substrates, such as non-woven cloths, and large amounts of heavy substrates, such as multi-ply paper.

The following examples will serve to further illustrate the preparation of the novel softening compositions of this invention:

In Examples I, II, III, IV, V, VI, and VII, the absorbent substrate is a paper structure having the particularly preferred characteristics of the specifically preferred paper

substrates disclosed hereinbefore and prepared in the manner of Example I of the aforementioned Wells patent. More particularly, the substrate is a compressible, laminated and calendered absorbent paper structure comprising two extensible paper sheets; each sheet (or ply) has a basis weight of about 16 pounds per 3,000 square feet and a MD value about 660, a CD value about 380, and a 20% dry-crepe. Each sheet is embossed with identical raised patterns consisting of about 70 inwardly directed discrete protuberances per square inch, raised about 0.02 inch above the surface of the paper sheets. The protuberances constitute about 45% of the surface of each sheet and are mated and adhesively joined with polyvinyl alcohol resin. The paper structure exhibits a compressive modulus of about 340 together with HOM MD/CD values of about 36/31 and has an absorbent capacity of about 7. This paper is a particularly preferred paper substrate herein and weighs about 3.7 grams for a 12" x 11" sheet and about 2.8 grams for a 12" x 8½" sheet.

The non-woven cloths used as substrate in Example VIII have been more generally described above. More particularly, Stock A is an air-laid, non-woven cloth comprising 70% regenerated cellulose (American Viscose Corporation) and 30% hydrophobic binder-resins (Rhoplex HA-8 on one side of the cloth, Rhoplex HA-16 on the other; Rohm & Haas, Inc.). The cloth has a thickness of 4 to 5 mils, a basis weight of about 24 grams per square yard, and an absorbent capacity of 6. One foot length of the cloth, 8½" wide, weighs about 1.78 grams. The fibers are ¼" in length, 1.5 denier, and are oriented substantially haphazardly. The fibers were lubricated with sodium oleate.

Stock B is a water-laid, non-woven cloth commercially available from C. H. Dexter Co., Inc. The fibers are regenerated cellulose, about ¾" in length, about 1.5 denier, and are lubricated with a similar standard textile lubricant. The fibers comprise about 70% of the non-woven cloth by weight and are oriented substantially haphazardly; the binder-resin (HA-8) comprises about 30% by weight of the cloth. Stock B is about 4 mils thick, and it has a basis weight of about 24 grams per square yard and an absorbent capacity of 5.7. One foot length of the cloth, 8½" wide, weighs about 1.66 grams.

The trade-named fabric softeners used in the examples herein were used as commercially obtained. "Adogen 448" and "Arquad 2HT-75" are substantially solid formulations of 75 parts cationic fabric softener, ditallowdimethyl ammonium chloride, 18 parts isopropyl alcohol, and 7 parts water (parts are expressed by weight). "Aliquat 264" is a liquid formulation of (in parts by weight) 18 parts isopropyl alcohol, 6 parts water, and 76 parts cationic fabric softener di-tall oil dimethyl ammonium chloride wherein the tall oil is unsaturated and has mostly C₁₈, some C₁₆ and C₁₄ carbon chain lengths. "Orvus K" is an anionic, liquid formulation comprising (in parts by weight) 37.5 parts modified ammonium dodecylsulfate, 9 parts dodecanolamide, 20 parts denatured ethyl alcohol, and 30.4 parts water.

In all examples, the compositions and softening formulations are expressed as parts or percentages by weight, unless otherwise noted.

Example I

200 grams of a softening formulation consisting of 97% "Adogen 448" and 3% perfume, were placed into a container and melted by immersing the container in a water bath heated to about 150° F. The absorbent paper substrate was an 11" wide roll wrapped about a hollow, tubular cardboard core. A rod was passed through the core and held so as to allow the paper to easily unroll.

A padding machine was used to treat the paper. This machine, an "Atlas Laboratory Wringer" (Model No. LW-391, Type LW-1) made by Atlas Electrical Devices Co., Chicago, Ill., is commercially available and is espe-

cially adaptable to small scale use. The machine basically comprises two hard rubber rollers mounted so that their surfaces touch (fit flush together). Pressure can be exerted onto the rollers and adjusted by means of weights. A trough-like pan under the rollers is so constructed as to provide guiding members along its length for feeding or leading the paper into the rollers.

The liquid softener was then added to the pan, which was heated to about 150° F. in order to keep the softener in a liquid state. The paper was unrolled and passed submerged through the softener liquid in the pan. The paper, traveling at a rate of 5 to 6 feet per minute, was then directed upward and through the turning rollers onto which a 5 pound weight was exerted and which squeezed off excess softener liquids. The turning rollers continuously pulled the paper through the rollers and gave a fabric softener impregnation of about 2.7 to 1 by weight of the dry pre-treated paper. After passing through the rollers, the softener liquid, now impregnated into the paper, rapidly cooled down and hardened upon evaporation of substantially all the isopropanol and water mixture. This resulted in a softening composition (hereinafter designated "Composition A") that was substantially solid, stable to decomposition, not "runny" or dripping, and which, although waxy to the touch, did not cause the paper to stick together when folded. The impregnated and cooled paper had about 9.7 grams of the fabric softener (s.p. about 130° F.) per foot length of paper and was then re-rolled about a hollow tubular cardboard core; prior to re-rolling, the paper can be perforated at desired uniform lengths, or instead of re-rolling, the paper can be cut at desired lengths and packaged as paper sheets.

A 12" x 8½" sheet of this composition was tested for softening performance in an automatic "Kenmore 800," electric clothes dryer and good softening results with no staining of the fabrics was obtained, and the fabrics were left with a pleasant perfume odor.

An equivalent composition was achieved when "Arquad 2HT-75" was substituted for "Adogen 448."

Example II

The following softening compositions were made by substituting the fabric softeners described below for "Adogen 448" and impregnating them into paper using the procedure and substrate of Example I:

Composition B—A softening formulation consisting of 98% "Aliquat-264" and 2% perfume, was impregnated into the paper. A 10 pound weight was used on the rollers. "Aliquat-264" was sufficiently liquid at room temperature; thus, it was not necessary to melt the softener or heat the pan. After the softener had been applied to the paper, the composition was dried and substantially all the isopropanol/water mixture evaporated by laying the treated paper open on aluminum foil for 24 hours to give about 9.9 grams of the fabric softener (s.p. about 120° F.) per foot length of paper.

Composition C—150 grams of tallowdimethyl (3-tallowalkoxypropyl) ammonium chloride was solvent-treated with about 50 grams of 2-propanol. 2 grams of perfume was added to the softener/alcohol formulation and the liquid impregnated into the paper using a 10 pound weight on the rollers. The composition was dried for 24 hours, during which time nearly all of the alcohol evaporated, leaving a substantially solid softening composition having about 10.4 grams of the fabric softener (s.p. about 130° F.) per foot length of the paper.

Composition D—A softening formulation comprising 58% C₂₀-C₂₂ alkyl-dimethyl amine* oxide, about 21% isopropanol, and about 20% water, was heated to about 150° F. on a steam bath. 100 grams of the formulation was solvent-treated with 100 grams of isopropanol. 2 grams of perfume was added to the softener/alcohol and water formulation and the formulation was then impreg-

*Derived from C₂₀ to C₂₂ alkyl-dimethyl amine, available from Humko Chem. Co., Catalog #T-1902D.

nated into the paper substrate with no weight being used on the rollers. After drying the treated paper for 24 hours to evaporate isopropanol and water, about 10.5 grams of the fabric softener (s.p. about 145° F.) had been impregnated into each foot length of the paper.

12" x 8½" sheets of Compositions B, C, and D were tested for softening performance and provided good fabric odor and good softening of treated fabrics without marked fabric staining.

Example III

200 grams eicosyltrimethyl ammonium chloride is mixed with about 60 grams of isopropyl alcohol and 20 grams of water to completely liquify the fabric softener. 2 grams of perfume is then added to the softener/alcohol/water liquid.

A roll of the 11" wide paper is set up in the manner described in Example I. As the paper substrate is unrolled and approaches the rollers, it is sprayed with the softener/isopropanol/perfume formulation. Even distribution of the softening formulation on the absorbent paper substrate is obtained by using controlled spray nozzles which are stationary and perpendicularly directed to cover the entire width of the substrate passing below.

The sprayed substrate is then passed through the rollers. No weight is used on the rollers which squeeze off excess softening formulation. The paper is then dried by laying the treated substrate on a flat surface for 24 hours, during which time much of the isopropyl alcohol evaporates. The treated and dried substrate is a softening composition impregnated only on one side with about 12 grams of the fabric softener (s.p. about 115° F.) per foot length of paper. It can then be cut or perforated and packaged as described in Example I.

Example IV

Prior to forming the multi-ply paper substrate of this and the prior examples, each sheet or ply of the paper substrate can be separately treated with softener, thereby providing a composition able to deliver effective amounts of softener to fabrics over a long time period or with repeated uses when employed in a dryer.

An 8½" wide roll of the paper sheet or ply, from which the above indicated particularly preferred paper structure is made, is mounted so as to easily unroll. The paper ply is unrolled and treated with "Adogen 448" and perfume in the same amounts and by the same process as described in Example I. After treatment, the paper ply is laid out to dry for 24 hours and the process repeated for a second treated ply. Using pressurized rollers singly or in combination with a polyvinyl alcohol resin adhesive, the plies are then joined to obtain a 2-ply, substantially solid, softening composition comprising the particularly preferred paper substrate, each ply of which is impregnated on both sides with about 10 grams of fabric softener (s.p. about 130° F.) per foot length.

By similar procedure, a third ply used to make the particularly preferred paper structure, which ply is not embossed, treated with softener in the same fashion as in Example IV and adhesively joined in between the 2 previously treated plies to give a softening composition comprising a 3-ply preferred paper structure having each ply treated with a fabric softener.

Adhesive joinder is effected by treating (e.g., spraying) the paper plies with the polyvinyl alcohol resin and passing the resin-treated plies through pressurized rollers. By spray-treating one of the paper plies with the softener formulation and using the untreated side of this ply as an externally exposed side, a multi-ply softening composition in which only one externally exposed side is treated and all other plies are treated on both sides, is achieved.

Example V

A 12" x 8½" sheet of the paper substrate was immersed into a pan containing about 7 grams of melted TAE₉₀ to which about 25 grams of acetone had been added to

aid the dispersion and impregnation of the fabric softener into the paper. After drying for 24 hours and weighing, the paper was found to have absorbed about 7 grams of the fabric softener (s.p. about 135° F.) and substantially all of the acetone had evaporated. The softening composition (hereinafter designated "Composition E") was similar to that of Example I.

By repeating the procedure with TAE₂₀ substituted for TAE₃₀, an equivalent softening composition (hereinafter designated "Composition F") was achieved in which a similar amount of the fabric softener (s.p. about 115° F.) was impregnated into the paper.

A third repetition of the procedure herein, wherein about 11 grams of "Adogen 448" was substituted for TAE₃₀, provided an equivalent softening composition (hereinafter designated "Composition G") in which the paper had absorbed about 8.1 grams of the fabric softener (s.p. about 130° F.).

Yet another similar softening composition (hereinafter designated "Composition H") was obtained when about 20 grams of a softening formulation consisting of 55% C₂₀-C₂₂ dimethylamine oxide, 23% isopropyl alcohol, and 22% water was substituted for the TAE₃₀ to provide a paper sheet impregnated with about 10.7 grams of the fabric softener (s.p. about 145° F.); acetone was not used to disperse this formulation.

Example VI

Using the procedure of Example V, about 19 grams of the anionic, liquid "Orvus-K" was substituted for the TAE₃₀ in said example. About 9 grams of the fabric softener (s.p. about 120° F.) was absorbed by the paper after drying. No acetone was used to aid in dispersal of the formulation into the paper.

Example VII

A particularly preferred softening composition (hereinafter designated "Composition I") was made by impregnating the following softening formulation into a roll of 8½" wide paper by the method of Example I.

	Percent
3-(N-eicosyl-N,N-dimethylammonio) - 2 - hydroxypropane - 1 - sulfonate	71.4
Isopropyl alcohol	28.6

A 99:1 softener formulation/perfume mixture was impregnated into the paper; an orifice (about 3 to 4 thousandths of an inch) between the surface of the rollers was created by twice wrapping a piece of plastic tape about the ends of the bottom roller; no weights were used on the rollers. After drying the composition for 24 hours, about 18.9 grams of the fabric softener (s.p. about 145° F.) were impregnated into each foot length of the paper.

By placing various weights on the taped rollers, amounts of 16.1 grams, 13.2 grams, and 9.2 grams of the softener/perfume mixture were similarly impregnated into the paper to achieve equivalent compositions.

This softener is particularly preferred inasmuch as large amount of fabric softener were impregnated into an absorbent substrate and the compositions softened fabrics in a dryer without staining the fabrics.

Example VIII

A softening formulation consisting of 99% "Adogen 448" and 1% perfume, was impregnated into (8½" wide) roll of non-woven Stock A and non-woven Stock B to achieve softening compositions (hereinafter respectively designated "Composition J" and "K") particularly preferred herein. The method of impregnation used was that of Example VII, with no weight on the rollers. About 5.31 grams and 3.34 grams, respectively, of the fabric softener (s.p. about 130° F.) were impregnated into each foot length of Stock A and Stock B.

Sheets of the compositions were tested for softening

performance in a dryer and found to provide good softening of the treated fabrics.

The softening compositions herein provide a pre-measured amount of softener. Preferably, the composition is in the form of a tubular roll of absorbent paper perforated along the width of the roll at uniform lengths; also preferred is the packaging of the compositions herein into individual sheets of desired length and width much like ordinary facial tissues are packaged. When so packaged, the amount of fabric softener on a given length or sheet of the absorbent substrate is pre-measured so as to be sufficient to soften an average washer or dryer load of clothes; fabric softeners impregnated into absorbent substrates in the amounts and ratios disclosed hereinabove have been found sufficient to soften such loads. Further, the user is free to add to, or reduce the amount of softener by cutting the impregnated sheet or length. By using the compositions in pre-measured form, the user suffers little, if any, waste due to over-use or spillage, and the problem of underuse is eliminated.

Most important, however, is the elimination of past restrictions of fabric softener use to the laundry washing process. While the softening compositions of this invention can be used, as other fabric softeners, in the rinse cycle of an automatic washer, these compositions are particularly suitable for effective use as a laundry dryer additive.

The softening compositions of this invention are disposable after use.

The most important aspect of the softening compositions herein relates to the absorbency of the substrate employed. When a softening agent is coated onto a dense substrate (e.g., one-ply kraft or bond paper), the softening agent, when melted by the dryer temperatures, is not sufficiently retained by the nonabsorbent substrate, but, instead, is rapidly released. Thus, when a fabric contacts the coated substrate, too much of the softening agent adheres to the fibers of the fabric at the point of contact. The result is that the fabric appears greatly stained, feels "greasy" or waxy to the touch at points of fabric-substrate contact, and is inadequately softened. Staining is particularly severe on colored, polyester/cotton fabrics, and the staining on any fabric becomes even more pronounced upon ironing. Additionally, a composition containing such a nonabsorbent substrate cannot be utilized more than once.

Thus, by using an absorbent substrate, staining of fabrics is eliminated or substantially reduced. The absorbent substrate acts to retain the fabric softener, yet permits the steady and continuous release of the softener from the substrate; by controlling the absorbency of the substrate, the softening effected by a dryer added composition can be controlled so as to effect the release of sufficient softener to adequately soften the fabric without the accompanying staining of the prior art compositions. Additionally, when the softening composition employs an absorbent substrate, the novel composition can be re-used a number of times before disposal.

The following examples serve to further illustrate the importance of the substrate's absorbent capacity. The examples compare the softening compositions herein with compositions representative of the prior art in regard to staining of duplicate fabric loads. The fabric loads used in the comparisons were the same and, unless otherwise noted, consisted of a variety of common laundry items (e.g., men's T-shirts, bed-sheets, ladies' slips and towels) and a variety of fabric materials (e.g., cotton, nylon, polyester/cotton and terrycloth); these loads weighed about 5½ pounds dry and about 9¾ pounds wet (i.e., average load weights). The fabric loads were all first washed, at least once, with 69 grams of a standard anionic synthetic detergent in a "Kenmore 800" automatic, electric, home washing machine for 10 minutes in 125° F. water having 7 grains of hardness per gallon; where indicated in the Examples, certain loads were also

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given an earlier washing with 77 grams of another anionic synthetic detergent under similar conditions as above. After one or two washings, each fabric load went through the rinse cycle (using 100° F. water with 7 grains of hardness per gallon), the spin-dry cycle, and was then dried in a "Kenmore 800" automatic, electric, home clothes dryer along with a softening composition, after which each load was visually graded and compared by a panel of four judges for staining.

A representative prior art composition, against which the softening compositions herein were compared, consisted essentially of regular one-ply bond paper (absorbent capacity of about 2.5 to 3) coated with about 2.9 grams of the fabric softener from "Adogen 448" per foot length of paper. The composition was 45% by weight softener and 55% by weight paper, and it was packaged as a tubular roll about 8½" wide.

Example IX

Into one dryer containing a twice washed fabric load was placed a 12" by 11" sheet of Composition A herein. The fabric load was dried for 45 minutes, and the fabrics were then checked for staining.

A duplicate fabric load was added to a dryer along with a 12" by 8½" sheet of the prior art composition.

Visual examination of each of the two fabric loads demonstrated that the prior art composition caused marked staining of the fabrics in the load, while the same softener impregnated into an absorbent paper preferred herein, and in larger amounts, caused no staining.

Example X

Five 12" by 12" swatches were cut from a blue 65% polyester/35% cotton tablecloth. Four large terrycloth bath towels were added to each of the swatches to make up 5 fabric loads. After one washing, rinsing, and spin-drying, each fabric load was separately dried for 45 minutes in the dryer, a different softening composition being placed into the dryer with each load. Four of the softening compositions were of the novel type disclosed herein and were 12" by 8½" sheets of Compositions E, F, G, and H. The fifth was a 12" by 8½" sheet of the prior art composition.

At the end of the drying cycle each swatch was removed from the dryer and visually examined for stains; marked grease-like stains appeared only on the swatch dried with the prior art composition.

Example XI

Three twice-washed fabric loads were prepared and dried for 45 minutes. One load was dried with a 12" x 8½" sheet of Composition I, the second with a 12" x 8½" sheet of Composition J, and the third with a foot length of the prior art composition. Staining was observed only with the fabrics dried with the prior art composition.

Example XII

A 9¼ pound wet fabric load was placed into a dryer, and a softening composition, consisting of about 9 grams of the fabric softener (from "Adogen 448") impregnated into a 12" by 8½" sheet of the paper substrate used in Example I, was added. After a 45 minute drying cycle, the load was removed, re-wetted and again placed into the dryer for a 45 minute cycle. This process was repeated two more times for a total of 4 runs, the same sheet of softening composition being used in each run.

Similarly, a fabric load was run 4 times with a foot length of the prior art composition. A comparison of the weights of the respective softening compositions during the process in the table below revealed that the use of an absorbent substrate effects a more steady softener release than the prior art composition and permits the absorbent-substrate softening composition to be re-used if desired,

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whereas the prior art composition cannot be repeatedly used and still provide adequate softening.

	"Adogen 448" plus absorbent substrate, grams	Prior art composition, grams
Initial composition weight.....	11.32	6.54
Weight after run:		
#1.....	8.95	5.35
#2.....	7.95	5.06
#3.....	7.29	4.96
Weight after final run #4.....	6.52	4.93

Example XIII

The softening compositions disclosed herein provide very good softening results, when used in the washing rinse cycle as well as in the dryer.

A fabric load was made up and twice washed as in Example IX. A sheet of a softening composition herein, consisting of a 12" by 8½" sheet of the paper structure used in Example I impregnated with a softening formulation of 99% by weight of "Adogen 448" and 1% by weight perfume, was prepared. Upon drying, about 10 grams of fabric softener (s.p. about 130° F.) were impregnated into the paper sheet. The sheet was added to the final rinse of the second washing process.

At the end of the rinse cycle, the fabric load was removed and examined; the fabrics had a very noticeable perfume odor and were noticeably softer.

Example XIV

Absorbent woven cloth can also be employed as a substrate in the softening compositions herein.

A standard terrycloth wash cloth, 8" by 10½", weighing 22.8 grams and having an absorbent capacity of 6.6, was washed with a standard anionic synthetic laundry detergent and dried. The terrycloth was then placed in a flat tray in which 30 grams of isopropyl alcohol and 20 grams of "Adogen 448" had been admixed. The terrycloth rapidly absorbed about 19.7 grams of the softener/alcohol mixture and was hung up to dry. After 6 hours, the weight of the impregnated terrycloth decreased to about 36.3 grams, due to evaporation of isopropyl alcohol, leaving about 13.5 grams of fabric softener (s.p. about 130° F.) impregnated into the cloth.

The softener-impregnated terrycloth was tested for softening performance in a standard, automatic dryer with an average fabric load and gave good results with no visible staining of the softened fabrics.

Example XV

An absorbent sponge can be used as the substrate in the softening compositions herein.

TAE₂₀ (30.5 grams) was melted and was poured onto a cellulosic sponge (Amsco Super Gel, Medium size #6) piece, ¼" thick, weighing 3.9 grams and having an absorbent capacity of 12. The impregnated sponge, after drying, had absorbed all the fabric softener (s.p. about 115° F.) and was then put into a standard, automatic dryer containing several clothing items; after the drying cycle ended, the clothes were examined and noted to be soft, and there was no visible staining.

The compositions herein can additionally be used in a variety of other ways. For example, the sheet or length of a composition herein can be used to manually wipe off fabrics which are prone to exhibit static electricity (e.g., the polymeric vinyl fabrics used generally in automobile upholstery and cushions and in simulated-leather coats or other wearing apparel); the composition can be used as it is formulated or can first be moistened with ordinary tap water (i.e., from a faucet), before wiping, and this method is generally suitable for other synthetic fabrics, such as is often found on furniture. After wiping with the compositions herein, it is desirable to wipe off the upholstery or other substance treated with a dry, ordinary

wiping cloth, rag, or the like to remove excess or undried fabric softening left on the upholstery.

Moreover, the compositions herein can be used in a dryer for the purpose of imparting anti-static properties to such items as socks, ladies stockings, sweaters and other items made of synthetic fabrics. When so used, it is not necessary that the clothes be first wetted; thus, the garments can be treated without the "tuffing" or "balling-up" of the fabric fibers that often occurs when such fabrics are wetted.

Further, the softeners (especially the cationic quaternary ammonium compounds and the nonionics, anionics, and Zwitterionics of C₁₀ to C₂₀ alkyl range) used in the compositions herein exhibit surfactant properties which make the compositions herein very useful, for example, in cleaning metallic surfaces and leather in wearing-apparel, shoes and other objects. For this purpose the composition is preferably wetted before application and the cleansed surface or leather wiped dry.

All of the above examples are intended to illustrate particular embodiments of the invention herein, and it is understood that they do not limit said invention. Further, other embodiments within the scope of the invention hereing will be obvious to those skilled in the art.

Having particularly described the invention in detail, what I now claim is:

1. A fabric softening composition consisting essentially of a fabric softener impregnated into an absorbent substrate having an absorbent capacity of from 5.5 to 12 and having from about 40% to about 90% free space based on the overall volume of the substrate; said fabric softener having a softening point of from 100° F. to 170° F. and being selected from the group consisting of dialkyl dimethyl ammonium chlorides where the alkyl has from 12 to 20 carbon atoms; tallowdimethyl (3-tallowalkoxypropyl) ammonium chloride; cationic imidazolium salts and Zwitterionic quaternary ammonium compounds; said absorbent substrate being a water-laid or air-laid non-woven cloth consisting essentially of lubricated cellulosic fibers, said fibers having a length of from 3/16" to 2" and a denier of from 1.5 to 5 and being at least partially oriented haphazardly, adhesively bonded together with a binder-resin; and the weight ratio of fabric softener to the dry substrate ranging from 10:1 to 2:1.

2. The composition of claim 1 wherein the fibers and binder-resin, respectively, constitute 70% and 30% by

weight of the non-woven cloth, the cloth having a basis weight of from 20 to 24 grams per square yard.

3. The composition of claim 2 wherein the non-woven cloth is air-laid and the fibers are regenerated cellulose which are 1/4" in length with a denier of 1.5 and are adhesively bonded together with a nonionic self-crosslinking acrylic polymer.

4. The composition of claim 1 wherein the ratio of fabric softener to non-woven absorbent substrate is from 4:1 to 2:1 by weight of the dry substrate.

5. The composition of claim 1 wherein the fabric softener is 3-(N-eicosyl - N,N - dimethylammonio)-2-hydroxypropane-1-sulfonate.

6. The composition of claim 1 wherein the fabric softener is ditallow dimethyl ammonium chloride.

7. The composition of claim 1 wherein the fabric softener is tallowdimethyl (3-tallowalkoxypropyl) ammonium chloride.

8. The composition of claim 1 wherein the fabric softener is dialkyl dimethyl ammonium chloride where the alkyl has from 12 to 20 carbon atoms.

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U.S. Cl. X.R.

117—120 139.5 CQ, 154; 252—8.6, 8.7, 8.75, 8.8, 8.9, 91