

[54] **FABRIC SOFTENING COMPOSITIONS
CONTAINING WATER-INSOLUBLE
PARTICULATE MATERIAL AND METHOD**

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[56]

References Cited

UNITED STATES PATENTS

3,696,034	10/1972	Hewitt et al.	252/8.6 X
3,756,950	9/1973	Gluck	252/8.8 X

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[57]

ABSTRACT

Fabric softening compositions with improved conditioning properties comprising a cation-active fabric softener and certain substantially water-insoluble particulate materials are described. The compositions permit the simultaneous attainment of softening, ease of ironing, anti-wrinkling and appearance benefits of fabrics treated therewith.

17 Claims, No Drawings

FABRIC SOFTENING COMPOSITIONS CONTAINING WATER-INSOLUBLE PARTICULATE MATERIAL AND METHOD

BACKGROUND OF THE INVENTION

This invention relates to fabric softening compositions which comprise in addition to conventional fabric softening agents a substantially water-insoluble particulate material. These compositions impart to fabrics treated therewith in a conventional manner a series of fabric-care benefits including anti-wrinkling, ease of ironing, softening, folding ease, enhanced fabric drapability and appearance improvement, which cannot be achieved simultaneously from the use of softening and fabric conditioning compositions known in the art.

Modern fabric-softening and conditioning compositions, washing machines and dryers are subject to continuous improvement with a view to achieve a series of fabric benefits such as, for example, softening, body, anti-wrinkling, ease of ironing, and improvement in appearance. As of yet, however, no single fabric conditioning composition is available capable of providing textiles treated therewith in the conventional matter with a broad spectrum of fabric-care benefits as, for example, referred to hereinbefore.

For example, present day fabric softeners impart a softness to the fabric (actually this softness is best likened to a tactile sensation of lubricity, which is distinguishable from fabric softness occasioned by enhanced fabric bulkiness) and control of electrostatic charge. Modern day washing machines and dryers by means of elaborate cycles and temperature control are able to markedly improve the extent of fabric wrinkling. Other products such as well-known laundry starches, if desired in combination with particulate organic constituents having a melting point below ironing temperatures, impart when applied after the washing cycle, crease permanence and ease of ironing benefits and also impart a body to the fabric, i.e., a sizing effect.

The softening compositions of this invention, however, impart all of these and other benefits simultaneously when applied in a conventional manner. That is, the softening compositions of this invention, by some imperfectly understood physical-chemical interaction at the fiber or yarn level, impart, through the rinse cycle or in general through the conditioning operation, the benefits enumerated, by way of example, hereinbefore. These benefits are solely attributable to the presence of a substantially water-insoluble particulate material as hereinafter defined in combination with cation-active fabric softener compounds.

Fabric softening compositions on the basis of quaternary ammonium compounds such as ditallowdimethylammonium chloride are known in the art and have been commercialized for a decade as rinse softening compositions. Other approaches to fabric softening involve the use of various clay particles. For example, U.S. Pat. No. 3,033,699, pertains to compositions and processes for improving the anti-static properties of synthetic fiber yarns through the application of an aqueous suspension of magnesium montmorillonite clay and an alkali stabilized colloidal silica salt. U.S. Pat. No. 3,594,212 teaches that cellulosic fibrous materials can be softened by treatment thereof with montmorillonite clays and polyamines or polyquaternary ammonium compounds. U.S. Pat. No. 3,063,128 dis-

closes a process for controlling static properties of synthetic textile fibers and exhibiting moisture regain not exceeding 5% through the application of an aqueous suspension of montmorillonite to the fibers followed by drying such as to insure that at least about 0.5% of the montmorillonite clays have been deposited on the fibers. The co-pending applications; Gloss, U.S. Ser. No. 333,104, filed Feb. 16, 1973, and Bernardino, Ser. No. 337,331, filed Mar. 2, 1973; relate to the use of smectite-type clays in fabric softening compositions.

Other known fabric conditioning compositions containing various particulate materials for the purpose of a specific function are known in the art. Examples thereof are detergent scouring compositions containing water-insoluble particulate materials, which mostly have a particle diameter in the range from about 50 to 100 micrometers and a hardness of about 7 on the Moh scale. Thermoplastic particulate materials are also known in the art and have been used in connection with laundering and conditioning operations, mainly for the purpose of textile finishing, ease of ironing, and sizing. These thermoplastic materials are softened or fused during, e.g., ironing thereby providing a sizing to the fabric.

The prior art teachings, however, aim at achieving specific functions and objectives which, as regards the properties of the particulate materials, i.e., water-insolubility, shape, integrity, particle size diameter, hardness, presence of exchangeable alkaline earth metal ions and melting (softening) temperatures, are essentially different from the physical properties of the water-insoluble particulate materials which qualify for use in the compositions of the instant invention.

In any event, prior art fabric conditioning compositions containing the particulate materials referred to hereinbefore do not produce the fabric conditioning benefits of the instant compositions, and in many cases, tend to impart harshness or stiffness to the fabric.

Accordingly, it is an object of the present invention to provide fabric softening compositions comprising cation-active fabric softener compounds and water-insoluble particulate materials which impart anti-wrinkling, ease of ironing, softening, anti-static, folding ease, enhanced fabric drapability and appearance benefits to fabrics treated therewith.

It is an additional object of the present invention to provide fabric softening compositions capable of conditioning fabrics treated therewith with a view to obtaining a degree of enhanced tactile and appearance properties by reference to what results from the use of fabric softening compositions applied in a conventional manner, i.e., during the rinsing operation.

By utilization of certain particulate materials capable of conferring desirable fabric benefits when present in combination with cation-active fabric softener compounds, these above-described objectives can now be attained and fabric softening compositions formulated which are capable of imparting to fabrics treated therewith a series of desirable properties including anti-wrinkling, ease of ironing, fabric softening, anti-static, folding ease, enhanced fabric drapability, and appearance benefits.

SUMMARY OF THE INVENTION

The instant invention provides softening compositions which are capable of imparting a broad range of desirable properties to fabrics treated therewith. Such compositions comprise:

- a. from about 0.5% to about 95% by weight of a cation-active fabric softener compound having from one to two straight-chain organic groups of from 8 to 22 carbon atoms; and
- b. from about 95% to about 0.01% by weight of a substantially water-insoluble particulate material having:
 - i. an average particle size in the range from about 1 to about 50 micrometers;
 - ii. a shape having an anisotropy of about 5:1 to 1:1;
 - iii. a hardness of less than about 5.5 on the Mohr scale;
 - iv. a melting point above about 150° C; and
 - v. substantial freedom from exchangeable calcium and magnesium ions.

In its method embodiment, the present invention provides a process capable of simultaneously imparting a series of desirable fabric-care benefits to textiles treated therewith. Such method comprises treating textiles in a liquor comprising:

- a. from about 0.2 ppm (part per million) to 5,000 ppm of a cation-active fabric softener compound having from one to two straight-chain organic groups of from 8 to 22 carbon atoms; and
- b. from about 0.2 ppm to 1000 ppm of a substantially water-insoluble particulate material having:
 - i. an average particle size in the range from about 1 to about 50 micrometers;
 - ii. a shape having an anisotropy of about 5:1 to 1:1;
 - iii. a hardness of less than about 5.5 on the Mohr scale;
 - iv. a melting point above about 150°C; and
 - v. substantial freedom from exchangeable calcium and magnesium ions.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to fabric softening compositions capable of imparting a series of fabric-care benefits to fabrics treated therewith.

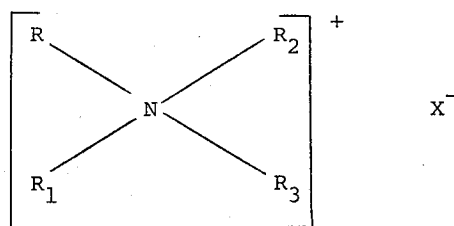
These compositions comprise (1) a cation-active fabric softener compound; and (2) a substantially water-insoluble particulate material.

Unless indicated to the contrary, the "percent" indications stand for "percent by weight."

The essential cation-active fabric softener compound will normally be employed in the compositions of this invention in an amount from about 0.5% to about 95%. Obviously, depending upon physical state and intended use of a particular composition, the amount of cationic fabric softener can vary. For example, a liquid softening composition preferably comprises from about 1% to about 30%, especially from about 2% to about 25% of said cationic softener. If, in liquid compositions, more than about 30% is used, product stability problems may occur, such as, for example, thickening and the possible formation of undesired gel. If less than 0.5% is used, excessive amounts of softener composition are required to achieve acceptable softening, i.e., this creates uneconomical conditions as regards storage and handling of low-active formulae. Solid, granular or powdered, softening compositions of this invention preferably comprise from about 1% to about 60%, especially from about 5% to about 40% of cation-active

ingredient; the upper limit being dependent upon the physical state of the softening ingredient and, if applicable, upon the amount of drying and/or granulating carrier material to be added for obtaining a solid softening composition. The lower cation-active limit, as for the liquid softening composition, is based on economical and performance considerations, i.e., handling cost versus overall fabric benefits desirable from a given amount of solid softening composition.

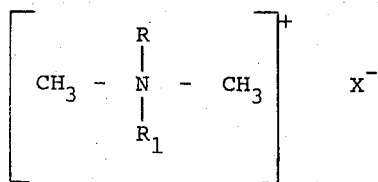
- 10 The cation-active organic fabric softener compounds, for use in the compositions of this invention, are known fabric-softening compounds. Generally, these comprise cationic nitrogen-containing compounds such as quaternary ammonium compounds and amines and have one or two straight-chain organic groups of at least eight carbon atoms. Preferably, they have one or two such groups of from 12 to 22 carbon atoms. Preferred cation-active softener compounds include the quaternary ammonium softener compounds corresponding to the formula



wherein R is hydrogen or an aliphatic group of from 1 to 22 carbon atoms; R₁ is an aliphatic group having from 12 to 22 carbon atoms; R₂ and R₃ are each alkyl groups of from 1 to 3 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and methyl sulfate radicals.

- Because of their excellent softening efficacy and ready availability, preferred cationic softener compounds of the invention are the dialkyl dimethyl ammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow. As employed herein, alkyl is intended as including unsaturated compounds such as are present in alkyl groups derived from naturally occurring fatty oils. The term "tallow" refers to fatty alkyl groups derived from tallow fatty acids. Such fatty acids give rise to quaternary softener compounds wherein R and R₁ have predominantly from 16 to 18 carbon atoms. The term "coconut" refers to fatty acid groups from coconut oil fatty acids. The coconut-alkyl R and R₁ groups have from about 8 to about 18 carbon atoms and predominate in C₁₂ to C₁₄ alkyl groups. Representative examples of quaternary softeners of the invention include tallow trimethyl ammonium chloride; ditallow dimethyl ammonium chloride; ditallow dimethyl ammonium methyl sulfate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; dieicosyl dimethyl ammonium chloride; didocosyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methyl sulfate; dihexadecyl diethyl ammonium chloride; dihexadecyl dimethyl ammonium acetate; ditallow dipropyl ammonium phosphate; ditallow dimethyl ammonium nitrate; di(coconut-alkyl) dimethyl ammonium chloride.

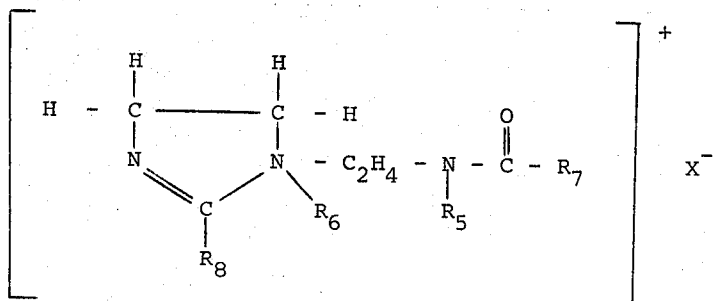
An especially preferred class of quaternary ammonium softeners of the invention correspond to the formula



wherein R and R₁ are each straight chain aliphatic groups of from 12 to 22 carbon atoms and X is halogen, e.g., chloride. Especially preferred are ditallow dimethyl ammonium chloride and di(hydrogenated tallow-alkyl) dimethyl ammonium chloride and di(-coconut-alkyl) dimethyl ammonium chloride, these compounds being preferred from the standpoint of excellent softening properties and ready availability.

Suitable cation-active amine softener compounds are the primary, secondary and tertiary amine compounds having at least one straight-chain organic group of from 12 to 22 carbon atoms and 1,3-propylene diamine compounds having a straight-chain organic group of from 12 to 22 carbon atoms. Examples of such softener actives include primary tallow amine; primary hydrogenated-tallow amine; tallow 1,3-propylene diamine; oleyl 1,3-propylene diamine; coconut 1,3-propylene diamine; soya 1,3-propylene diamine and the like.

Other suitable cation-active softener compounds herein are the quaternary imidazolinium salts. Preferred salts are those conforming to the formula



wherein R_6 is an alkyl containing from 1 to 4, preferably from 1 to 2, carbon atoms, R_5 is an alkyl containing from 1 to 4 carbon atoms or a hydrogen radical, R_8 is an alkyl containing from 1 to 22, preferably at least 15, carbon atoms, R_7 , an alkyl containing from 8 to 22, 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 quaternary ammonium fabric softeners described hereinbefore. Particularly preferred are those imidazolium compounds in which both R_7 and R_8 are alkyls of from 12 to 22 carbon atoms, e.g., 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4,5-dihydroimidazolium methyl sulfate; 1-methyl-1-[palmitoylamide)ethyl]-2-octadecyl-4,5-dihydroimidazolium chloride.

Other cationic quaternary ammonium fabric softeners, which are useful herein include, for example, alkyl (C_{12} to C_{22})-pyridinium chlorides, alkyl (C_{12} to C_{22})-alkyl (C_1 to C_3)-morpholinium chlorides, and quaternary derivatives of amino acids and amino esters.

The cationic fabric softeners mentioned above can be used singly or in combination in the practice of the present invention.

Operability of the essential substantially waterinsoluble particulate component for use in the compositions of the instant invention is dependent on a series of characteristics; namely, (1) an average particle size from about 1.0 to about 50, preferably from about 5 to about 30 micrometers; (2) a shape having an anisotropy of about 5:1 to 1:1; (3) a hardness of less than about 5.5 on the Moh scale; (4) a melting (softening) temperature above about 150°C; and (5) substantial freedom from exchangeable calcium and magnesium ions. Said particulate component is used in the instant compositions in an amount from about 0.01% to about 95%. As with the cationic component, the level of particulate material can vary widely, depending upon physical state and intended use of a particular composition. For example, liquid softener formulations normally have a level of particulate material from about 0.01% to about 10%, preferably from 0.1% to 6%, more preferably from 0.2% to 4 %. The upper limit is normally dictated by the material possibility for incorporating a given amount of particulate component without disturbing the liquid state of the composition, i.e., to avoid, for example, gelatinization, phase separation and precipitation. As with the cation-active softener, the lower limit is based on economical and performance considerations, i.e., a further reduction of softener compound entails that excessive amounts of softening composition are needed to achieve the inventive advantages. The solid softening compositions of this invention preferably contain from about 0.1% to

about 50%, more preferably from about 0.2% to about 25% of the essential particulate component. Increasing the level of particulate ingredient above the upper limit (95%) does not procure additional performance advantages.

The average particle size of the substantially water-insoluble particulate component is within the range from about 1 to about 50, preferably from about 5 to about 30 micrometers. The particle diameter limitation appears to relate to the diameters of (commercially) available textile fibers which fall mostly within the range of about 10 to about 30 micrometers. Accordingly, the use of particulate water-insoluble materials having an average diameter of more than about 50 micrometers will not provide the fabric benefits enumerated hereinbefore. On the other hand, the use of particulate water-insoluble materials having an average particle size diameter of less than about 1 micrometer will not provide the overall fabric benefits obtainable through the practice of this invention.

The substantially water-insoluble particulate component is further characterized by an anisotropy (axial ratio) of about 5:1 to 1:1. The determination of particle

size can be based on the measurement of the projection area of the water-insoluble particle or on the linear measures of this projection area. Or, in other words, the loose particle resting on its surface of maximum stability, the long and intermediate axis are normally horizontal and the short axis vertical. In that context, the term "long axis" represents the maximum overall length of the particle; "intermediate axis" stands for the maximum dimension of a particle in a direction perpendicular to the long axis; whereas "short axis" represents the maximum dimension in a direction perpendicular to the plane containing the long and intermediate axis. The meaning of anisotropy represents the ratio of long axis to short axis for a specific particulate material. Preferred for use in the compositions of this invention are particulate materials having an anisotropy within the range from about 3:1 to about 1.1:1.

See also: *Advances in OPTICAL and ELECTRON MICROSCOPY*, Vol. 3, R. Barer and V. E. Cosslett, ACADEMIC PRESS 1969, London and New York.

The essential particulate component for use herein has a hardness of less than about 5.5 on the Moh scale. The hardness as so measured is a criterion of the resistance of a particular material to crushing. It is known as being a fairly good indication of the abrasive character of a particulate ingredient. Examples of materials arranged in increased order of hardness according to the Moh scale are as follows: h(hardness)-1: talc; dried filter-press cakes, soap-stone, waxes, aggregated salt crystals; h-2: gypsum, rock salt, crystalline salt in general; h-3: barytes, chalk, brimstone, calcite; h-4: fluoride, soft phosphate, magnesite, limestone; h-5: apatite, hard phosphate, hard limestone, chromite, bauxite; h-6: feldspar, ilmenite, hornblendes; h-7: quartz, granite; h-8: topaz; h-9: corundum, emery; and h-10: diamond.

Suitable particulate materials have a hardness of less than about 5.5 on the Moh scale. Although some fabric-care benefits can be obtained from particulate materials having a Moh hardness of, for example 7, it is submitted that as regards overall benefits said particulate materials do not qualify for use in the instant compositions. The reason for this being unknown, it is assumed, without being bound to this theory and limited as a result thereof, that as a result of excessive particle hardness, fiber and yarn damage occur which adversely affect the fabric, particularly through cumulative ac-

tion resulting from multicycle textile-treating operations.

The substantially water-insoluble particulate material has a melting point about 150°C. Particulate materials having a melting point below that temperature do not provide the fabric benefits because of their tendency to melt and accordingly spread through the fabric thereby giving body to the fabric which is commonly known as sizing. This is undesirable in the context of this invention and the particulate materials must be such as to maintain under ironing conditions, i.e., above around 150°C, their integrity and shape as said characteristics are essential for the attainment of the fabric-care benefits derivable from the uses of the compositions of the instant invention.

In addition, the particulate material must be substantially water-soluble as its function depends upon its integrity, shape, firmness, etc. as described in detail hereinbefore. It should be recognized, however, that minor parts of the particulate ingredient, preferably not more than 20%, can be water-soluble without markedly decreasing the performance advantages.

The water-insoluble particulate materials are substantially free of exchangeable calcium and magnesium ions. The presence of exchangeable alkaline earth metal ions such as calcium and magnesium in the particulate materials appears to increase their hydrophilic properties. This results in enhanced swellability characteristics, which, in turn, constitute an obstacle to the uniform and stable enmeshing of particulate material within the fiber structure. As a result, particulate materials having exchangeable calcium and magnesium ions in their structure detract from attaining overall fabric benefits as described hereinabove.

Preferred for use in the instant compositions are surface-treated starch derivatives such as "DRY-FLO" starch manufactured by NATIONAL STARCH PRODUCTS, New York. DRY-FLO starches are surface-modified starches bearing hydrophobic moieties which have been reacted with the starch molecule through the formation of ester and ether linkages. As a result of its chemical modification, these starch derivatives are water-repellant and accordingly substantially water-insoluble. Dry-Flo starches have an average particle size diameter of about 9-11 micrometers.

Additional substantially water-insoluble particulate materials suitable for use in the compositions of the instant invention include:

Ingredient	Melting Point	Average Particle Size μm	Range Particle Size μm
-poly(methylmethacrylate) $\text{H}(\text{CH}_2\text{CH}(\text{C}(=\text{O})\text{OCH}_3))_n$	160°C (isotactic form) 200°C (syndiotactic form)	18 18	-- --
-poly(tetrafluorethylene) $\text{F}(-\text{CF}_2\text{CF}_2-)_n$ (1) (2)	327 - 330°C --	10 10	-- --
-polystyrene $\text{H}(-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))_n$	240-250°C	--	14-16
-poly(styrenedivinylbenzene) (3) $\text{H}(-\text{CH}_2\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5))_n$	-- --	6 40	5-14 25-50
-poly(vinyltoluene) (3) $\text{H}(-\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}_3))_n$	meta = 215°C ortho = 360°C	-- --	5
-poly(melamineformaldehyde-ureaformaldehyde)	thermo-setting	5	--
-poly(ureaformaldehyde) $\text{H}(-\text{OCH}_2\text{NH}-\text{C}(=\text{O})-\text{HNCH}_2)_n$	thermo-setting	6	--

(1) Teflon[®] DuPont de Nemours, (2) Molykote 522 (Dow-Corning), (3) Dow-Corning

Ingredient	Average Particle Size μm	Range Particle Size μm
-fine glass micro-balloons (ECCO-SPHERES) ⁽⁴⁾	8	5-15
-glass beads PF 12-R (coated) ⁽⁵⁾	17	5-45
-glass beads PF-11 ⁽⁵⁾	30	10-50
-glass beads (unispheres) ⁽⁵⁾	22	15-37
-glass microballons (ECCOSPHERES IG) ⁽⁴⁾	30	—
-glass beads PF-12 ⁽⁵⁾	17	5-44
-glass beads PF-12S ⁽⁵⁾	17	—

⁽⁴⁾ Emerson & Cuming; Canton, Mass.
⁽⁵⁾ Cataphote Corp.; Jackson, Miss.

See also: (1) Technical Data Sheet for "Teflon" 7A; and brochure re "Typical Properties Common to All Granular Teflon FFE-Fluorocarbon Resins," No. A-43044; both being issued by DuPont de Nemours; (2) Catalog of Small Glass Beads, issued by Microbeads Division, Cataphote Corporation, Jackson, Mississippi; particularly documents MB-111-DS-5/72; MB-IV-DS-5/72; MB-V-LP-5/72; and MB-VII-LP-5/72; and (3) Technical Information Brochure concerning ECCOSPHERES, hollow glass and ceramic microspheres, MICROBALLOONS, issued by Emerson and Cuming, Inc., Canton, Mass.; the above documents being hereby incorporated by reference.

Another substantially water-insoluble particulate component for use in the instant compositions is a starch granule having, in addition to the essential parameters as defined in the claims, a swelling power of less than about 15 at a temperature of 65°C. Modification of the starch granules in a manner such as to render it more soluble by gelatinizing, derivatizing, or degrading is to be avoided to the extent it leads to starches which can lose their firm shape and also do not qualify for use in the present invention. Soluble or gelatinizable starches having a swelling power of more than about 15 to 65°C are less suitable as they tend to lose their individual shape and consequently run into the fiber which, in turn, leads to undesirable stiffness of fabrics.

The swelling power is determined according to the method set forth in *Cereal Chem.*, 36, pp. 534-544 (1959) Harry W. Leach, et al. Ten grams of starch are suspended in 180 ml. of distilled water in a tared 250-ml. centrifuge bottle. The suspension is mechanically stirred with a small stainless-steel paddle (0.75-in. wide, 1.5-in. high) at a rate just sufficient to keep the starch completely suspended (i.e., 200 r.p.m.) This low speed avoids shearing the fragile swollen granules and consequent solubilization of the starch. The bottle is lowered into a thermostatted water bath maintained at a temperature of 65°C ($\pm 0.1^\circ\text{C}$) and held for 30 minutes, slow stirring being continued during this period. The bottle is then removed, wiped dry, and placed on the torsion balance. The stirrer is removed and rinsed into the bottle with sufficient distilled water to bring the total weight of water present to 200.0 g. (including the moisture in the original starch). The bottle is stoppered, mixed by gentle shaking, and then centrifuged for 15 minutes at 2,200 r.p.m. (i.e., 700 times gravity). The clear supernate is carefully drawn off by suction to within $\frac{1}{4}$ in. of the precipitated paste. An aliquot of this supernate is evaporated to dryness on the steam bath

and then dried for 4 hours in the vacuum oven at 120°C. The percentage of solubles extracted from the starch is calculated to dry basis. The remaining aqueous layer above the sedimented starch paste is then siphoned off as quantitatively as possible. The bottle and paste are reweighed on the torsion balance, and the swelling power calculated as the weight of sedimented paste per g. of dry-basis starch.

Starches having a swelling power of more than 15 at 65°C are not suitable for use in the instant composition. Although the final choice of starch which will meet requirements of this invention depends upon the origin of the material and also upon process conditions such as bleaching, degradation, and isolation applied to a given species, suitable starches can, for example, be obtained, from corn, wheat, and rice. Current potato and tapioca starches have a swelling power exceeding 15 at a temperature of 65°C and, therefore, are not suitable for being used in the compositions of this invention. More complete information concerning water-insoluble starches, the processes for their preparation and isolation from a variety of raw materials are well known [see, for example: *THE STARCH INDUSTRY*, Knight, J. W., Pergamon Press, London (1969)].

As explained hereinafter, however, without being limited as a result thereof, it is thought that the parameters of the particulate material for use in the instant compositions are essential to the extent that said characteristics directly contribute to the beneficial fabric properties.

These critical limitations as to the nature of the particulate material were determined initially by actual experimentation. While applicants will not be held by any theoretical interpretation of these critical limitations, it appears that the particulate material interacts with the textile material at the fiber level to impart the above enumerated benefits to the textile fabric as a whole. In this respect it is to be noted that textile materials consist essentially of assemblies of fine flexible fibers arranged in more or less orderly geometrical arrays. Individual fibers within the assembly are usually in a bent or twisted configuration and are in various states of contact with neighboring fibers. When the assembly is deformed the fibers move relative to each other and this relative motion accounts to a large extent for the characteristic flexibility of textile materials. To what extent a given textile material will recover when a deforming force is removed is largely determined by the nature of the interaction of the individual fibers making up the textile material. Textile fibers are viscoelastic and hence will exhibit delayed recovery from strain. However, the large number of interfiber contact points provide frictional restraints which further hinder the recovery process. In most textile structures the area of interfiber contact is probably less than 1% of the total fiber area. The force per contact point is generally estimated to be within the range of 1 to 10 dynes.

It is with this view of textile materials that applicants hypothesize going to explain the efficacy of particulate materials in imparting the related effects of anti-wrinkling, ease of ironing, softness, anti-static benefits and appearance improvements can be appreciated. For purpose of conceptualization, this hypothesis will hereinafter be referred to as the "ball bearing effect." The conceptualization is useful in interpreting the interaction of the particulate material and the textile matrix under imposed forces of deformation.

By means of microscopic analysis and staining techniques, it has been determined that textile fabrics treated in accordance with the present invention are characterized by having discrete particulate materials intimately dispersed, in a substantive fashion, in the interstices of the fiber matrix. It is believed that these particulate materials, so interfiberly positioned, act in the manner of ball bearings to reduce interfiber forces during deformation of the textile fabric as a whole. The gross effect is the enhancement of visco-elastic recovery (anti-wrinkling effect) and diminution of the forces operable at interfiber contact points (ease of ironing effect). Under this conceptualization, and as already referred to hereinbefore, the particle diameter limitation is appreciated since most commercially available textile fibers have diameters which fall within the range of about 10 to about 30 micrometers. Therefore, to be effective, the particulate material of the invention must preferably be comparable to the textile fiber diameters. The above-mentioned benefits are similarly related to the presence of the particulate material at points within interstices of individual fiber yarns. Microscopic examination of textile yarns in cross section reveals that textiles treated in accordance with the present invention have greater yarn diameters than similar textile yarns which are distinguishable by the absence of particulate materials. Apparently, the particulate materials positioned in the interfiber spaces effectively open up the yarn (apparent increase in bulk) resulting in a softer, fluffier textile fabric. The anti-static benefit appears to be related to a change in the resistivity of the fabric matrix containing the particulate materials; for example, the copresence of chemically modified starch granules such as DRY-FLO starch, in the textile fabric, increases the equilibrium moisture content of the matrix, thereby decreasing its resistivity and diminishing static build-up.

A particular embodiment of the present invention provides a method for treating fabrics for simultaneously imparting fabric-care benefits to textiles treated therewith. To that effect, the fabrics are treated in an aqueous liquor comprising from about 0.2 ppm (part per million) to about 5,000 ppm, preferably from about 2.5 ppm to about 1,000 ppm of a cation-active fabric softener. Suitable and preferred cationic softening agents for use in the instant method are the same as those which fit the composition aspect of this invention; these species have been described in great detail hereinbefore.

Another essential component for use in the aqueous liquor is represented by substantially water-insoluble particulate materials having: (1) an average particle size in the range from about 1 to about 50 micrometers; (2) a shape having an anisotropy of about 5:1 to 1:1; (3) a hardness of less than about 5.5 on the Moh scale; (4) a melting point above about 150°C; and (5) substantial freedom from exchangeable calcium and magnesium ions. The particulate material is used in an amount from about 0.2 ppm to about 1,000 ppm, preferably from about 0.5 ppm to about 500 ppm. Suitable and preferred species are those which fit the composition requirements of this invention; said species are described in greater detail hereinbefore.

The aqueous liquor needed for carrying out the method of this invention can, for example, be prepared by adding to a substantially aqueous medium softening compositions corresponding to the fabric softening

compositions in this invention. Similar results can also be obtained, however, by adding the individual ingredients to an aqueous medium. As an example thereof, one may consider adding to the aqueous medium a softening composition containing all ingredients except the particulate material which is to be added separately. It is also possible to prepare a softening composition containing the cation-active agents and other usual ingredients whereas the particulate material can be added in combination with inerts like urea or with other minor ingredients.

The particulate material can be admixed with a conventional previously prepared fabric softening composition, or can be incorporated together with the individual ingredients of the composition prior to the mixing and uniformizing process. Whatever route is selected for incorporating the essential particulate component, care has to be taken to avoid processing steps which might alter the native granular integrity of the particulate material. As an example, excessive heating and grinding operations must be avoided as these steps may contribute to a disruption of the particulate material structure and accordingly render the softening composition less effective for fabric conditioning operations. As is well known to the skilled artisan, the preparation of homogenous and storage stable liquid softening compositions in accordance with this invention may require the incorporation of phase stabilizers, suspending agents, thickeners, and the like in the usual amounts.

The compositions of the instant invention can also contain additional ingredients to make them more attractive or more effective and also inert fillers. For example, the composition of this invention can contain thickeners, solubilizing agents, and also minor amounts of detergent ingredients for the purpose of rendering, for example, the liquid compositions hereof, more storage stable and also in order to facilitate incorporation therein of higher amounts of the essential ingredients. Dyes, perfumes and anti-bacterial agents can be incorporated for improving the aesthetics and for performance reasons. In the solid softening compositions of this invention there can be present major amounts of inerts such as urea, sodium sulfate and sodium chloride.

The conditioning compositions of the present invention are evaluated by certain tests upon textile fabrics treated therewith as set forth below.

Anti-Static Test

A bundle of mixed fabrics (ca. 53% all-cotton; 12% 65/35 polyester/cotton blend; 17% nylon; 18% Dacron) is treated for 10 minutes in a miniature agitator washer containing two gallons of aqueous liquor containing the test softening compositions (as set forth below). The temperature is 100°F; water hardness 7 grains/gallon artificial hardness. The bundle comprises 5% by weight of the softening liquor. The bundle is spin extracted prior to being dried in a commercial dryer.

The static charge on each fabric is then measured by a standard electrostatic technique within a Faraday cage. The sum of the absolute values of the charges on all fabrics in the bundle, divided by the sum of the area (yards²) of the total fabric surface (2 sides of the fabric) is then computed. This so-called "static value" (volts/yard²) correlates with gross observations of the effects of static charges on fabric surfaces, i.e., electrical shocks, sparks, fabric clinging, etc. Depending on the fabric bundle tested, no static clinging is exhibited

by fabrics having a static value less than about 1.5 volt-s/yards²; substantial static clinging is noted in fabrics having a static value above 4.5 volts/yard².

Anti-Wrinkling Test

A bundle of mixed fabrics (ca. 53% all-cotton; 12% 65/35 polyester/cotton blends; 17% nylon; 18% Dacron) is treated for ten minutes in a miniature agitator washer containing two gallons of aqueous liquor containing the test softening compositions (as set forth below). The temperature is 100°F; water hardness 7 grains/gallon artificial hardness. The bundle is spin extracted prior to being dried in a commercial dryer.

The extent of wrinkling on a given piece of fabric is then measured by mounting the fabric on a flat, movable surface within a light-tight box. A fine beam of light from a source above the fabric impinges upon the fabric at an angle of 90°. As the mounted fabric is moved through a predetermined distance, a miniature photocell affixed adjacent to the stationary light source responds to scattered light at an angle of 45° to the fabric surface. A plot of the light intensity measured by the photocell versus the length of the fabric path traversed gives a profile (curve) which is in all practical respects a facsimile of the surface of the test fabric. That is, a smooth, unwrinkled fabric gives essentially a straight line of constant light intensity whereas a wrinkled fabric gives a series of peaks and minima. The ratio of the absolute distance through which the fabric was moved to the length of the plotted curve is quantitatively related to the extent of wrinkling.

Ease of Ironing Test

A bundle of mixed fabrics (ca. 53% all-cotton; 12% 65/35 polyester/cotton blends; 17% nylon; 18% Da-

(measured). These tests are performed against untreated controls.

Other tests such as, for example, softness (related to bulkiness), ease of folding, fabric drapability and fragrance are assessed subjectively by expert panelists against unmarked controls.

The following examples are illustrative of this invention.

BASE COMPOSITION

A liquid base fabric softening composition was prepared having the following formula:

Ingredient	Parts by Weight
Ditalowdimethylammonium chloride	5.25
Particulate material	See below
Emulsifier, isopropanol, ethanol, dye, perfume, miscellaneous	1.5
Water	Balance to 100

A substantially water-insoluble particulate material was added to the base composition prior to testing. The softening composition so prepared was used at a concentration of 0.1% in the rinse water. The fabric-care benefits represent reduced wrinkling and reduced ironing efforts measured as previously described. In all cases, the performance of the inventive formulations tested was compared to the performance of an identical formulation which did not contain particulate materials. Each of the particulate materials listed in the table below provided a statistically significant ($\alpha = 0.05$, one-tailed test) reduction in both wrinkling and ironing efforts. The fabrics treated were polyester/cotton 65/35 and cotton.

Example	Particulate Material	Average Particle Size μm	PPM in Rinse-Solution	Particulate Material % in Softener Formulation
I	Glass micro balloons (ECCOSPHERES IG)	30	30	3
II	Poly(tetrafluorethylene) (MOLYKOTE 522)	10	30	3
III	Poly(ureaformaldehyde)	6	3	0.3
IV	Poly(methylmethacrylate) (syndiotactic)	18	3	0.3
V	Glass beads PF-12S	17	3	0.3
VI	Glass beads PF-12T	17	3	0.3
VII	"DRY-FLO" Starch	10	30	3
VIII	Poly(melamine formaldehyde/ureaformaldehyde)	5	3	0.3
IX	Glass beads (Unispheres)	22	3	0.3
X	Glass beads PF-12R	17	3	0.3
XI	Poly(styrene-divinylbenzene)	6	3	0.3
XII	Glass beads PF-11	30	3	0.3

cron) is treated for 10 minutes in a miniature agitator washer containing 2 gallons of aqueous liquor containing the test softening compositions (as set forth below). The temperature is 100°F; water hardness 7 grains/gallon artificial hardness. The bundle is spin extracted prior to being dried in a commercial dryer.

The ease of ironing of each fabric is then measured by using an instrumented, but otherwise conventional, iron. In essence, the iron by means of sensors fitted in its interior measures the amount of effort required by an operator to smooth the surface of the test fabric to a subjectively smooth appearance. The total amount of work required to achieve this appearance is a function of the force exerted on the iron (measured) and the distance traversed by the iron in the plane of the fabric

EXAMPLE XIII

A fabric softening composition having the formula given hereinafter simultaneously imparts softening, ease of ironing, anti-wrinkling and appearance improvements to fabrics treated therewith.

Ingredient	Parts by Weight
Distearyl dimethyl ammonium chloride	9.0
DRY-FLO starch; average particle size diameter: 10 μm	1.5
Minor ingredients including emulsifier, isopropanol, dye, perfume	2.0
Water	Balance to 100

Substantially identical results are obtained when the distearyl dimethyl ammonium chloride is replaced with an equivalent amount of: tallow trimethyl ammonium chloride; ditallow dimethyl ammonium methyl sulfate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; dieicosyl dimethyl ammonium chloride; didocosyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methyl sulfate; dihexadecyl diethyl ammonium chloride; dihexadecyl dimethyl ammonium acetate; ditallow dipropyl ammoniumphosphate; ditallow dimethyl ammoniumnitrate; di(coconut alkyl) dimethyl ammonium chloride; primary tallow amine; primary hydrogenated-tallow amine; tallow-1,3-propylene diamine; oleyl 1,3-propylene diamine; coconut-1,3-propylene diamine; and soya 1,3 propylene diamine.

Substantially identical results are also obtained when the distearyl dimethyl ammonium chloride is substituted by an equivalent quantity of: 1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4,5-dihydroimidazolinium methyl sulfate; and 1-methyl-1-[(palmitoylamide)ethyl]-2-octadecyl-4,5-dihydroimidazolinium chloride.

Substantially identical results are also obtained by substituting DRY-FLO starch by an equivalent amount of poly(methylmethacrylate) isotactic or syndiotactic form; poly(tetrafluoroethylene); polystyrene; poly(styrenedivinylbenzene); polyvinyltoluene; poly(melamineformaldehyde-ureaformaldehyde); poly(ureaformaldehyde); fine glass micro-balloons; glass beads, coated if desirable; and starch.

A broad range of fabric-care benefits are as well obtained when distearyl dimethyl ammonium chloride is incorporated at a level of: 2.5%; 4.5%; 7%; 11%; 14.5%; 18%; 20.5%; and 25%, respectively.

A broad range of fabric-care benefits are also obtained when the DRY-FLO starch is used (in the formulation) at a level of: 0.2%; 0.8%; 1.2%; 2%; 3%; 4.5%; 6%; 7.2%; and 9%, respectively.

Solid fabric-conditioning compositions, which provide a broad range of benefits to fabrics treated therewith, are prepared having the following formulas:

Ingredients	PARTS BY WEIGHT						
	XIV	XV	XVI	XVII	XVIII	XIX	XX
Dioctadecyldimethyl ammonium chloride	55			20			30
Ditallow dimethyl ammonium chloride			5		60	30	
1-methyl-1-[(stearoylamide)ethyl]-2-heptadecyl-4,5-dihydroimidazolinium methyl sulfate		30			40		
Urea	25	15	71	69.2	15	40	45
DRY-FLO starch: average particle diameter 10 μ m	13	50	20	0.8	20	18	20
Minors, including dye, perfume, emulsifying agent, hydrotropes and moisture	7	5	4	10	5	2	5

Substantially identical results are obtained when DRY-FLO starch is replaced with an equivalent amount of: poly(methylmethacrylate) isotactic or syndiotactic form; poly(tetrafluoroethylene); polystyrene; poly(styrenedivinylbenzene); polyvinyltoluene; poly(melamineformaldehyde-ureaformaldehyde); poly(ureaformaldehyde); fine glass micro-balloons;

glass beads, coated if desirable; and starch. Substantially identical results are also obtained when urea is replaced with an equivalent amount of sodium sulfate, sodium chloride and the like fillers.

We claim:

1. A fabric softening composition comprising

a. from about 0.5% to about 95% by weight of a cation-active fabric softener compound having from one to two straight-chain organic groups of from 8 to 22 carbon atoms; and

b. from about 95% to about 0.01% by weight of a substantially water-insoluble particulate material having

i. an average particle size in the range from about 1 to about 50 micrometers;

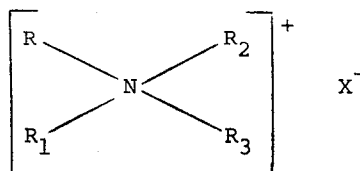
ii. a shape having an anisotropy of about 5:1 to 1:1;

iii. a hardness of less than about 5.5 on the Moh scale;

iv. a melting point above about 150°C; and

v. substantial freedom from exchangeable calcium and magnesium ions.

2. A composition in accordance with claim 1 wherein the cation-active softener compound has the formula



wherein R is hydrogen or an aliphatic group of from 1 to 22 carbon atoms; R₁ is an aliphatic group having from 12 to 22 carbon atoms; R₂ and R₃ are each alkyl groups of from 1 to 3 carbon atoms; and x is an anion selected from halogen, acetate, phosphate, nitrate and methyl sulfate radicals.

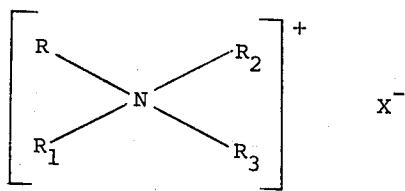
3. A composition in accordance with claim 2 wherein the substantially water-insoluble particulate material is selected from the group consisting of surface-modified starch, poly(methylmethacrylate), poly(tetrafluoroethylene), polystyrene, poly(styrenedivinylbenzene),

poly(vinyltoluene), poly(melamineformaldehyde-ureaformaldehyde), poly(ureaformaldehyde), glass beads, glass microballoons, starch, and mixtures thereof.

4. A liquid fabric softening composition comprising

a. from about 1% to about 30% by weight of a cation-active fabric softener compound having from 1 to

- 2 straight-chain organic groups of from 8 to 22 carbon atoms; and
- b. from about 0.01% to about 10% by weight of a substantially water-insoluble particulate material having:
- i. an average particle size in the range from about 1 to about 50 micrometers;
 - ii. a shape having an anisotropy of about 5:1 to 1:1;
 - iii. a hardness of less than about 5.5 on the Moh scale;
 - iv. a melting point above about 150°C; and
 - v. substantial freedom from exchangeable calcium and magnesium ions.
5. A composition in accordance with claim 4 wherein the cation-active fabric softener compound is present in an amount from about 2% to about 25% by weight.
6. A composition in accordance with claim 5 wherein the substantially water-insoluble particulate material is present in an amount from about 0.1% to about 6% by weight.
7. A composition in accordance with claim 6 wherein the cation-active softener compound has the formula



wherein R is hydrogen or an aliphatic group of from 1 to 22 carbon atoms; R₁ is an aliphatic group having from 12 to 22 carbon atoms; R₂ and R₃ are each alkyl groups of from 1 to 3 carbon atoms; and x is an anion selected from halogen, acetate, phosphate, nitrate and methyl sulfate radicals.

8. A composition in accordance with claim 7 wherein the substantially water-insoluble particulate material is selected from the group consisting of surface-modified starch, poly(methylmethacrylate), poly(tetrafluoroethylene), polystyrene, poly(styrenedivinylbenzene), poly(vinyltoluene), poly(melamineformaldehyde-ureaformaldehyde), poly(ureaformaldehyde), glass beads, glass microballoons, starch, and mixtures thereof.

9. A solid fabric softening composition comprising

- a. from about 1% to about 60% by weight of a cation-active fabric softener compound having from 1 to 2 straight-chain organic groups of from 8 to 22 carbon atoms; and

- b. from about 0.1% to about 50% by weight of a substantially water-insoluble particulate material having:

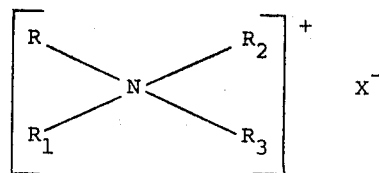
- i. an average particle size in the range from about 1 to about 50 micrometers;
- ii. a shape having an anisotropy of about 5:1 to 1:1;
- iii. a hardness of less than about 5.5 on the Moh scale;
- iv. a melting point above about 150°C; and
- v. substantial freedom from exchangeable calcium and magnesium ions.

10. A composition in accordance with claim 9 wherein the cation-active fabric softener is used in an amount from about 5% to about 40% by weight.

11. A composition in accordance with claim 10 wherein the substantially water-insoluble particulate material is present in an amount from about 0.2% to about 25% by weight.

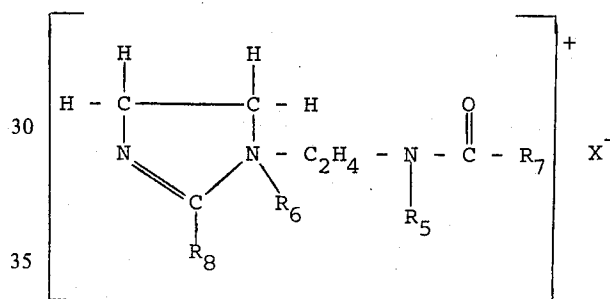
12. A composition in accordance with claim 11 wherein the cation-active fabric softener is selected from the group consisting of

- i. quaternary ammonium compounds of the formula



wherein R is hydrogen or an aliphatic group of from 1 to 22 carbon atoms; R₁ is an aliphatic group having from 12 to 22 carbon atoms; R₂ and R₃ are each alkyl groups of from 1 to 3 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate, and methyl sulfate radicals; and

ii. imidazolinium salts of the formula



wherein R₆ is an alkyl containing from 1 to 4 carbon atoms, R₅ is an alkyl containing from 1 to 4 carbon atoms or a hydrogen radical, R₈ is an alkyl containing from 1 to 22 carbon atoms, R₇ is an alkyl containing from 8 to 22 carbon atoms, and X is an anion.

13. A composition in accordance with claim 12 wherein the substantially water-insoluble particulate material is selected from the group consisting of surface-modified starch, poly(methylmethacrylate), poly(tetrafluoroethylene), polystyrene, poly(styrenedivinylbenzene), poly(vinyltoluene), poly(melamineformaldehyde-ureaformaldehyde), poly(ureaformaldehyde), glass beads, glass microballoons, starch, and mixtures thereof.

14. A composition in accordance with claim 13 wherein the quaternary ammonium fabric softener is selected from the group consisting of tallow trimethyl ammonium chloride; ditallow dimethyl ammonium chloride; ditallow dimethyl ammonium methyl sulfate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; dieicosyl dimethyl ammonium chloride; didocosyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methyl sulfate; dihexadecyl diethyl ammonium chloride; dihexadecyl dimethyl ammonium acetate; ditallow dipropyl ammonium phosphate; ditallow dimethyl ammonium nitrate; di(coconut-alkyl) dimethyl ammonium chloride.

15. A method for treating fabrics to impart desirable fabric-care benefits, said method comprising treating fabrics in an aqueous liquor comprising:

- a. from about 0.2 ppm (part per million) to 5,000 ppm of a cation-active fabric softener compound having from 1 to 2 straight-chain organic groups of from 8 to 22 carbon atoms; and
- b. from about 0.2 ppm to 1,000 ppm of a substantially water-insoluble particulate material having:
 - i. an average particle size in the range from about 1 to about 50 micrometers;
 - ii. a shape having an anisotropy of about 5:1 to 1:1;
 - iii. a hardness of less than about 5.5 on the Moh scale;
 - iv. a melting point above about 150°C; and

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v. substantial freedom from exchangeable calcium and magnesium ions.

16. A method in accordance with claim 15 wherein the cation-active fabric softener compound is used in a amount from about 2.5 ppm to about 1,000 ppm.

17. A method in accordance with claim 16 wherein the substantially water-insoluble particulate material is selected from the group consisting of surface-modified starch, poly(methylmethacrylate), poly(tetrafluoroethylene), polystyrene, poly(styrene-divinylbenzene), poly(vinyltoluene), poly(melamine-formaldehyde-urea-formaldehyde), poly(urea-formaldehyde), glass beads, glass microballoons, starch, and mixtures thereof.

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