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[54] **TEXTILE SOFTENER COMPOSITION**
 5 Claims, No Drawings

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 260/567.6

[51] Int. Cl..... **D06m 13/46**

[50] Field of Search..... **252/8.6,**
 8.8; 117/139.5 O, 66; 260/567.6

[56] **References Cited**
 UNITED STATES PATENTS

3,081,265	3/1963	Burr	252/105
3,230,225	1/1966	Arrigo	260/567.6 X
3,296,144	1/1967	White	252/152 X

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ABSTRACT: This disclosure relates to a method and composition for imparting softness to textiles without yellowing by utilizing a borohydride-containing composition either in the form of a fabric-softening quaternary ammonium salt and an alkali metal borohydride or the corresponding quaternary borohydride.

$$\left[\begin{array}{c} R_1 \\ | \\ R_2 - N - R_4 \\ | \\ R_3 \end{array} \right]^+ Y^-$$
$$\text{---}(\text{CH}_2\text{CH}_2\text{O})\text{---H},$$
$$\left[\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{C} \text{---} \text{N} \\ | \quad \quad || \\ \text{R}-\text{C} \quad \quad \text{C}-\text{R}_1 \\ | \quad \quad \quad | \\ \text{R} \quad \quad \quad \text{N}^+ \\ \quad \quad \quad | \quad | \\ \quad \quad \text{R}_2 \quad \text{R}_3 \end{array} \right] \text{Y}^-$$
$$-\left(\text{C}_n\text{H}_{2n}\text{X}\right)_m-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}_4$$
$$\left[\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{C}-\text{N} \\ | \quad \quad | \\ \text{R}-\text{C} \quad \quad \text{C}-\text{R}_1 \\ | \quad \quad || \\ \text{R} \quad \quad \text{N}^+ \\ \quad \quad | \\ \quad \quad \text{R}_3 \end{array} \right] \text{Y}^-$$

Specific examples of suitable quaternary compounds capable of softening textiles are: distearyl dimethyl quaternary ammonium chloride; distearyl dimethyl quaternary ammonium bromide; distearyl dimethyl quaternary ammonium methosulfate; dicoco dimethyl quaternary ammonium chloride; dimethyl arachidyl, behenyl quaternary ammonium chloride; dialkyl dimethyl quaternary ammonium chloride the alkyl groups of which comprise a mixture consisting essentially of 24 parts of hexadecyl, 75 parts of octadecyl and one part of octadecenyl; the latter quaternary compound is also known as dihydrogenated ditallow dimethyl ammonium chloride; hexadecyl trimethyl ammonium chloride; heptadecyl trimethyl ammonium chloride; cetyl trimethyl ammonium chloride; stearyl trimethyl ammonium chloride, etc.

Illustrative imidazolium compounds include 1-(2-stearoxyethyl)-DQ2-heptadecyl-1-benzyl imidazolium chloride; 1-(2-stearoylaminoethyl)-2-heptadecyl-1-benzyl imidazolium chloride; 2-heptadecyl-1-decanoyl-1-octadecyl imidazolium chloride; 1-(2-hydroxyethyl)-2-heptadecyl-1-octadecyl imidazolium bromide; 1-(2-stearoyloxyethyl)-2-ethyl-1-hexadecyl imidazolium chloride; 1-(N-stearoylaminoethylaminoethyl)-2-heptadecyl-1-ethyl imidazolium bromide; 1-(N-stearoylaminoethyl)-1-methyl-2-stearyl imidazolium methosulfate; and others as fully described in U.S. Pat. No. 2,874,074 and British Pat. No. 1,089,010, the compounds of which are incorporated herein by reference.

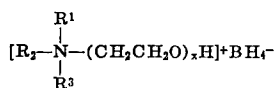
The term "coco" refers to fatty acid groups formed in coconut oil fatty acids. Such acids contain from about eight to 18 carbon atoms per molecule, predominating in C12 to C14 acids.

The alkali metal borohydride may be mixed with the above quaternary fabric softener in the solid state or in a solvent affording mutual solubility and stability, and used in that state. This mixture must be capable of yielding the borohydride anion in solution. A simple borohydride salt such as the alkali metal borohydride, and specifically sodium borohydride, has been found particularly effective when utilizing at least a 1:1 mole ratio of borohydride to quaternary compound. However, the borohydride content may be varied in excess of the 1:1 mole ratio (i.e. borohydride to quaternary). The quaternary salt plus sodium borohydride mixed in situ, inhibits yellowness buildup and retains the soft, fluffy characteristics of the fabric.

The use of a quaternary borohydride in lieu of the mixture of quaternary compound and alkali metal borohydride has been found to be even more effective in the prevention of yellowness buildup, while causing no decrease in softener deposition onto the fabric.

The quaternary borohydrides of the present invention may be illustrated by the following formulas:

1. Long chain monoalkyltriloweralkyl ammonium borohydrides where the long chain alkyl group is C_{16} to C_{24} and the lower alkyl is C_1 to C_6 ;
2. Di(long chain alkyl)di(loweralkyl) ammonium borohydrides where the long chain alkyl group is C_{12} to C_{24} and the lower alkyl is C_1 to C_6 ;
3. Ethoxylated derivatives of quaternary ammonium compounds, generally of the formula:

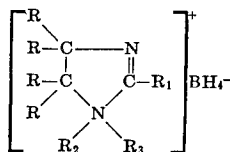


wherein each of the R groups is, independently, an aliphatic, and preferably and alkyl, chain of from one to 24 carbon atoms, and at least one of the R groups is such a chain at least 12 carbon atoms, and preferably, 16 carbon atoms; and X has a value from one to seven;

4. Hydrazinium borohydries, generally of the formula: $[R^1 R^2 R^3 N-NH_2]^{7E} BH_4^+$

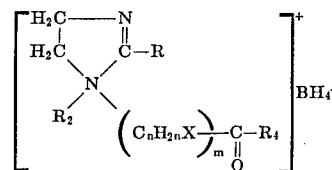
wherein each of the R groups is, independently, an aliphatic, and preferably, an alkyl, chain of from one to 24 carbon atoms, and at least one thereof is C₁₆;

5. Imidazolinium borohydrides:



wherein R, R₁, R₂, and R₃ are as defined above in the description of the imidazolinium salts (i.e. halides, etc);

The preferred imidazolinium borohydries have the formula:



wherein at least two of the radicals R, R₂, and R₄ are C₁₅ to C₂₃ alkyl, and *n, m*, and X are as defined above for the imidazolinium salts.

Illustrative quaternary borohydrides include: distearyl dimethyl ammonium borohydride; dicoco dimethyl ammonium borohydride; dimethyl arachidyl behenyl ammonium borohydride; dihydrogenated ditallow dimethyl ammonium borohydride; hexadecyl trimethyl ammonium borohydride; heptadecyl trimethyl ammonium borohydride; octadecyl trimethyl ammonium borohydride; nonadecyl trimethyl ammonium borohydride; eicosyl trimethyl ammonium borohydride; heneicosyl trimethyl ammonium borohydride; docosyl trimethyl ammonium borohydride; tricosyl trimethyl ammonium borohydride; tetracosyl trimethyl ammonium borohydride; didodecyl dimethyl ammonium borohydride; ditridecyl diCH₃ ammonium borohydride; ditetradecyl dimethyl ammonium borohydride; N-(2-hydroxyethyl)-stearyl dimethyl ammonium borohydride; N-(omega-hydroxyethoxyethyl)-dilauryl ethyl ammonium borohydride; 2-heptadecyl-1-decanoyl-1-octadecyl imidazolium borohydride; 1-(2-stearoxyethyl)-(2-1-methyl imidazolium borohydride; 1-(N-stearoylaminoethylaminoethyl)-2-heptadecyl-1-ethyl imidazolium borohydride; 1-(2-hydroxyethyl)-2-heptadecyl-1-octadecyl imidazolium borohydride; 1-(2-palmitoylaminoethyl)-2-ethyl-1-hexadecyl imidazolium borohydride; 1-(2-stearoylaminoethyl)-2-heptadecyl-1-propyl imidazolium borohydride; 1-(2-stearoylaminoethyl)-2-heptadecyl-1-benzyl imidazolium borohydride.

The quaternary borohydrides are valuable softening agents for textiles and fabrics manufactured from synthetic and natural fibers and blends thereof, inclusive of cellulose, Dacron-cotton blends, nylon, wool, cotton, Orlon, Orlon blends and the like. These borohydrides are stable, water-soluble and/or water-dispersible compounds, capable of imparting the desired degree of softness with a minimal, if any, yellowing, when utilized in amounts of from about 0.05 percent to about 1 percent, and preferably, in amounts from 0.1 percent to 0.5 percent by weight of the fabric. The fabric treated with the softening agent is impregnated and coated therewith, the higher dosages being retained on the treated fabrics even after several subsequent washings without treatment to yield a soft, fluffy fabric. Laboratory tests have shown that fabrics treated in accordance with this invention will not yellow with age or with repeated treatment.

These fabric-softening quaternary borohydrides are prepared in any suitable manner. A preferred method constitutes reacting the corresponding quaternary ammonium salt such as the halide with the alkali metal borohydride in the presence of a polar solvent. This reaction proceeds metathetically at low or moderate temperatures in the presence of the solvent. Suitable solvents include; water; liquid organic amines such as triethylamine, trimethylamine, triisopropylamine; aliphatic alcohols such as methyl, ethyl, n-propyl, isopropyl, and the butyl alcohols; amides such as formamide, etc. Nonreactive solvents are preferred, and consequently, when using particularly water, methyl and ethyl alcohols, the reaction medium should be highly alkaline, i.e. pH above 10, to avoid loss of borohydride due to decomposition.

To exemplify a borohydride preparation, dimethyl distearyl ammonium borohydride is prepared by reacting dimethyl distearyl ammonium chloride with sodium borohydride in isopropyl alcohol. The resultant product is a white solid and analyzed as 90 percent of the theoretical borohydride content by acid hydrolysis. Further evidence for the presence of borohydride was afforded by infrared analysis.

The present invention is more fully described and exemplified in the following examples, wherein parts and percentages are by weight unless otherwise indicated

Examples I and II

Terry cloth swatches were rinsed in a tergotometer bucket rotating at 100 r.p.m. and containing 950 ml. of water, 50 ml. of pH 10 buffer and an amount of softening agent to provide $1 \times 10^{-7}E$ moles. All rinses were conducted at 100° F. for 5 minutes. A high yellow color water supply from Jersey City and a low one from New Brunswick were employed. The results obtained after one and three cycle treatments are shown in table 1, each number in the table being the average of all swatches exposed to that particular treatment. The swatches were line dried at room temperature and evaluated for softness and yellowness. Whiteness values are determined with a Gardner Color Difference Meter, using the $+b$ scale as a measure of the yellow chromaticity. However, higher $+b$ values or whiteness numbers indicate a high amount of yellowness and poor results; whereas low $+b$ values or whiteness numbers denote less yellowness or greater whiteness and excellent results. A difference of 0.05 $+b$ units in the test represents a difference which is visible to the eye.

Results of the tests, illustrating the use of the new additive compositions in a rinse cycle, are set forth in table I.

TABLE I

Water supply	Percent softener on fabric	Treatment cycles	Example I-Example II, increase in yellowness*			
			A	B	C	D
New Brunswick	1.6	1	0.27	2.25	1.67	1.57
		3	0.29	4.51	3.69	2.67
	0.4	1	0.02	0.98	0.95	0.76
		3	0.04	3.11	2.74	2.09
Jersey City	0.4	1	0.09	1.92	1.83	1.66
		3	0.12	6.05	5.48	5.10
	0.1	1				
		3	0.22	1.72	1.61	1.33

*In " b " units.

A-Water blank

B-Dimethyl distearyl ammonium chloride ($1 \times 10^{-7}E^4M$)

C-Dimethyl distearyl ammonium chloride plus sodium borohydride (each $1 \times 10^{-7}E^4M$)

D-Dimethyl distearyl ammonium borohydride ($1 \times 10^{-7}E^4M$)

Swatches treated with compositions B, C, and D felt equally soft after treatment.

The above table clearly shows the superior results obtained with compositions C and D regarding fabric softening with a decrease in fabric yellowing normally associated with softener formulations.

EXAMPLES III - V

Terry cloth swatches were treated as in example I, with the dimethyl distearyl ammonium chloride held at a constant 0.4 percent by weight based on the treated fabric, but the concentration of the sodium borohydride being increased. The results are summarized in table II.

TABLE II

	Conc. of NaBH ₄	Yellowness Increase (bunits)
	none	1.66
Ex. III	$1 \times 10^{-7}E^4M$	1.39
Ex. IV	$1 \times 10^{-7}E^3M$	0.99
Ex. V	$1 \times 10^{-7}E^2M$	0.59

The above table clearly shows a decrease in yellowness with an increase in the sodium borohydride concentration.

The swatches remained equally soft, regardless of the borohydride concentration.

The new compositions can be packaged in paper, plastic or any other suitable packaging medium or material. For example, the textile softener composition can be packaged in a water soluble plastic material such as polyvinyl alcohol, isotactic polyvinyl methyl ether, etc. for use in a rinse cycle (e.g. of a laundering operation). The present compositions can be in solid form in the character of a free-flowing powder, chips, flakes, granules, tablets and the like or in the form of a solution or dispersion.

The new compositions can be used to treat a variety of fabrics, which can be made from natural animal and vegetable fibers and blends of natural and synthetic fibers as well as entirely from synthetic fibers. These include wool, silk, cotton, linen, glass, acetate, rayon, Dacron, Orlon, blends of Dacron e.g. with cotton, Orlon-wool blends, and the like.

This treatment is especially advantageous where it is desired to overcome harshness of feel or to enhance softness to touch and decrease fabric yellowing. Advantages realized herewith are softer, fluffier towels, smoother, silkier sheets and pillowcases, longer garment life and a whiter and/or brighter fabric.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

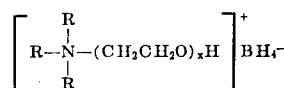
What is claimed is:

I. A method of softening textiles without yellowing which comprises contacting textile materials in the aqueous rinse cycle of a laundering operation with from about 0.05 percent to about 1 percent by weight of a borohydride containing composition consisting essentially of a quaternary borohydride selected from the group consisting of:

A. long chain monoalkyltriloweralkyl ammonium borohydride wherein said long chain alkyl group has from 16 to 24 carbon atoms and said lower alkyl groups have from one to six carbon atoms;

B. dilongchain alkyl dilower alkyl ammonium borohydrides said long chain alkyls have from 12 to 24 carbon atoms and said lower alkyls have from one to six carbon atoms;

C. ethoxylated derivatives of quaternary compounds represented by the formula

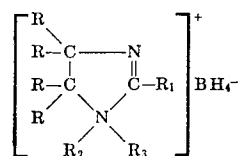


wherein x represents an integer of from one to seven and R is an alkyl group having from one to 24 carbon atoms with the proviso that at least one R has at least 12 carbon atoms;

D. hydrazinium borohydrides represented by the formula $[R^1 R^2 R^3 N-NH_2]^+ BH_4^-$

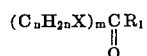
wherein R^1 is an alkyl chain having from 16 to 24 carbon atoms and R^2 and R^3 represent alkyl groups having from one to twenty-four carbon atoms; and

E. imidazolinium borohydrides represented by the formula



wherein R is selected from the group consisting of hydrogen and alkyl groups having from one to six carbon atoms, R_1

represents an alkyl group having from 15 to 23 carbon atoms, R_2 is

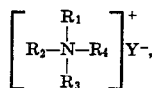


wherein n is an integer of from two to six, m is an integer of from one to seven and X is selected from the group consisting of $-O-$ and $-NH-$ and R_3 is selected from the consisting of alkyl and aralkyl substituents.

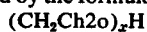
Claim 2. The method of claim 1 wherein said quaternary borohydride is dimethyl-distearyl ammonium borohydride.

3. A method of softening textiles without yellowing which comprises treating materials in the aqueous rinse cycle of a laundering operation with from about 0.05 percent to about 1 percent by weight of a borohydride containing composition consisting essentially of a quaternary compound and an alkali metal borohydride in a mole ratio of from 1:1 to 1:100 and wherein said quaternary compound is selected from the group consisting of

A. quaternary ammonium compounds represented by the formula

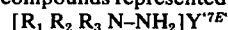


wherein R_1 and R_2 are lower alkyl groups having from one to six carbon atoms, R_3 an alkyl group containing from 12 to 24 carbon atoms, and R_4 is selected from the group consisting of alkyl groups containing 12 to 24 carbon atoms and an ethoxylated group represented by the formula



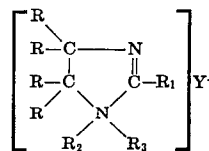
wherein x is an integer of from one to seven, Y is selected from the group consisting of halogen, sulfate, nitrate, phosphate, acetate and methosulfate

B. hydrazinium compounds represented by the formula

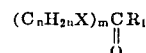


wherein R_1 is an aliphatic group containing 16 to 24 carbon atoms, R_2 and R_3 are alkyl groups containing one to 24 carbon atoms and Y is an anion as defined above:

C. imidazolinium compounds represented by the formula



wherein R is selected from the group consisting of hydrogen and alkyl groups having from one to six carbon atoms, R_1 represents an alkyl group having from 15 to 23 carbon atoms, R_2 is



wherein n is an integer of from two to six, m is an integer of from one to seven and X is selected from the group consisting of $-O-$ and $-NH-$, and R_3 is selected from the group consisting of alkyl and aralkyl substituents.

4. The method according to claim 3 wherein said borohydride composition comprises sodium borohydride and dimethyl distearyl ammonium chloride.

5. The method of claim 3 wherein said borohydride is present relative to the quaternary compound in a 1:1 mol ratio.

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