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(A) Fabric softening compositions based on pentaerythritol compound and dispersant for such a compound.

A fabric softening composition or article that is effective for its fabric softening purpose but preferably excludes ecotoxic quaternary ammonium salt, includes, as a fabric softening component, a PEC, which is an ester of pentaerythritol, an ester of an oligomer of pentaerythritol, an ester of a lower alkoxylated pentaerythritol or an ester of a lower alkoxylated pentaerythritol oligomer, with a suitable dispersing agent, which increases its fabric softening effect remarkably. The fabric softening component is preferably a partial higher fatty acid ester of pentaerythritol or a partial higher fatty acid ester of a pentaerythritol oligomer, the fabric softening composition is an aqueous emulsion or a particulate or powder composition (preferably with the dispersing carrier of the powder composition being a fabric softening bentonite), or is a softergent, and the fabric softening article is an absorbent material with PEC deposited on it or absorbed by it. Also within the invention are processes for softening fibrous materials, in washed laundry, by employing such compositions and articles, and processes for manufacturing described compositions.

This invention relates to fabric softening compositions and/or articles for applications to laundry during washing, rinsing and/or drying cycles, to apply to the fibers of the fabrics of such laundry fabric softening amounts of fabric softening components of the compositions and/or articles. More particularly, it relates to such compositions and articles that include as fabric softening components higher fatty acid esters of pentaerythritol, of pentaerythritol oligomers, or of ethoxylated derivatives thereof, all of which may be designated PEC (for pentaerythritol compound), together with a dispersing agent for such PEC, such as a clay or an emulsifier, and which do not contain quaternary ammonium salts.

Fabric softening compositions and articles have long been employed to make washed laundry items softer to the touch and more comfortable to the wearer. Such compositions include solutions, emulsions, and particulate and powder products and such articles include paper strips that have been impregnated with fabric softener. The fabric softeners of choice for most commercial products have usually been quaternary ammonium salts, such as dimethyl ditallowyl ammonium chloride, and emulsions of such softener have been added to the rinse water in the washing machine to effectively soften laundry. Alternatively, such emulsions or powder products including such fabric softener can be added to the wash water, with a detergent composition, or the detergent composition can include a fabric softening component, to make a so-called "softergent". Articles that contain a fabric softening component, such as a quaternary ammonium salt, may be added to the automatic laundry dryer, wherein during tumbling of the laundry in a heated environment, the fabric softener is applied to the laundry by repeated contact, and softens it.

Although various fabric softening (and antistatic) compositions, including softergents, have been marketed over the years, with varying degrees of commercial success, and although different fabric softening compounds have been included in them,the most successful of such compounds have been the quaternary ammonium salts. Such compounds are often of the formula

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wherein R, R', R" and R" are all alkyl groups, with at least one of such alkyls being a higher alkyl and with the others being lower alkyl(s) of 1 or 2 carbon atoms, and with X<sup>-</sup> being a salt-forming anion. Preferably, such quaternary ammonium salt is a di-lower alkyl, di-higher alkyl ammonium halide but mono-lower alkyl tri-higher alkyl ammonium halides have also found use in some instances.

While such quaternary ammonium salts have been effective fabric softeners in the described applications they are characterized by disadvantageous properties too, which have led to attempts to find replacements for them. For example, being cationic, they tend to react with anionic materials, such as anionic synthetic organic detergent and builders for synthetic detergents, sometimes to the detriment of their intended fabric softening function. Moreover, they are not as readily biodegradable as is desirable and they have been found to be toxic to aquatic organisms, which could lead to harmful effects on aquatic life in lakes, rivers and other waters into which waste waters carrying such compounds could be emptied.

In efforts to find replacements for quaternary ammonium salts as fabric softeners, neoalkanamides, glyceryl esters, glycol esters, silicones, cationic-anionic complexes, bentonite and various lubricants have been suggested for use alone or in conjunction with reduced amounts of the quaternary ammonium salts but frequently the softening effects thereof were insufficient or the replacement softeners possessed other characteristics which made them less desirable than the quaternary ammonium salts, despite the disadvantages thereof. Now, however, applicants have discovered that the PEC's described herein, including the oligomers and lower alkoxylated derivatives, can satisfactorily soften laundry essentially to the same extent as the quaternary ammonium salts, and they don't exhibit the adverse effects of the quaternary ammonium salts on aquatic organisms. This is an especially important discovery at this time, when the seriousness of the problem is being recognized and when several countries are passing laws and promulgating regulations prohibiting the incorporation of quaternary ammonium compounds (hereafter "quats") in products that may be discharged into sewage and drainage systems.

In accordance with the present invention a fabric softening composition or article from which a PEC is depositable onto fibrous materials, to soften them, comprises a PEC fabric softening component which is a higher fatty acid ester of pentaerythritol, of an oligomer of pentaerythritol, of a lower alkylene oxide derivative of pentaerythritol or of a lower alkylene oxide derivative of an oligomer of pentaerythritol, or a mixture thereof, and a dispersing agent for the PEC. Of the PEC's those which are preferred are the

pentaerythritol distearates and dipentaerythritol dilaurates, and of the dispersing agents those preferred are ethoxylated amines or alkanolamines which are positively charged at acidic pH's, such as 2.5-4, or montmorillonites, such as sodium calcium and potassium bentonites. The invention also includes processes for softening laundry with the invented compositions and articles, and processes for manufacturing such compositions.

A search of prior art relevant to the invention resulted in the finding of the following:

U.S. Patents 3,928,212; 4,126,562; 4,142,978; 4,162,984; and 4,214,038;

European Patent Application 276999-A;

German Patent Application 3612479-A; and

Japanese Patent 90 47,370.

U.S. patent 3,928,212 describes various softening agents which are polyhydric alcohol esters but none of them is a pentaerythritol ester or an ester of an oligomer or ethoxylated derivative of pentaerythritol. U.S. patent 4,126,562 mentions erythritol and pentaerythritol in a list of alcohols which may be reacted with higher fatty acids to produce fabric conditioning agents but no such compound is actually described and none is shown in a fabric softening composition or article. Also, U.S. 4,126,562 is for a combination of a quaternary ammonium salt fabric softener and a nonionic ester of an alcohol with a higher fatty acid, and there is no teaching that the ester would be useful alone as a fabric softener. U.S. patent 4,142,978 describes sorbitan esters with phase modifying components, such as alkyl sulfates, on a dryer sheet for softening laundry while it is being tumble dried in an automatic laundry dryer. The patent does not mention any pentaerythritol esters. U.S. patent 4,162,984 relates to a textile treatment emulsion of a water insoluble cationic fabric softener, which is preferably a quaternary ammonium salt or an alkylimidazolinium salt, with a water insoluble nonionic fabric softener, which is preferably a fatty acid ester of a mono- or polyhydric alcohol or an anhydride thereof, and an aromatic mono- or dicarboxylic acid. Among the polyhydric alcohols that may be esterified, according to the patent, is pentaerythritol, but no pentaerythritol ester is described specifically nor is any oligomer of pentaerythritol suggested, and none is shown to be a useful fabric softening agent in the absence of quaternary ammonium salt and aromatic carboxylic acid. It is clear that the patentees did not know of the present invention because they were aware of the disadvantages of the quaternary ammonium salt component (reaction with anionic detergent from the wash cycle) and found that its content could be reduced if the pentaerythritol ester and aromatic carboxylic acid were present, but they never recognized and apparently never made a fabric softening composition which did not contain quaternary ammonium halide or equivalent cationic fabric softener. U.S. patent 4,214,038 relates to polyglycerol esters as softening agents suitable for deposition on drying laundry from paper substrates charged to the laundry dryer with the laundry being dried. Although polyglycerol is a polyhydric alcohol, as is pentaerythritol, it is not the same as pentaerythritol and the patent does not suggest the use of applicants' pentaerythritol esters as fabric softeners. European patent specification 276999-A mentions fabric conditioning compositions that contain a non-cationic fabric softener and a nonionic cellulose ether. Although esters of polyhydric alcohols are mentioned as suitable conditioning agents, pentaerythritol esters are not disclosed. German patent specification 3612479-A describes textile softening compositions that contain quaternary ammonium compounds with carboxylic esters, and among the carboxylic acid esters are mentioned esters of various alcohols and polyols, including pentaerythritol. However, no such specific ester is described or even named, and no softening composition which does not contain quaternary ammonium compound as the fabric softener is disclosed. Japanese patent 90 47,370 discloses fabric softening compositions that are based on quaternary ammonium salts but may contain higher fatty acid ester of pentaerythritol. No specific such ester is described in the abstract.

In none of the disclosures mentioned above is it taught that any pentaerythritol ester could be employed with a suitable dispersing agent as a fabric softener in place of a quaternary ammonium compound or quat softener and would have essentially as good a softening action, and none of the disclosures mentions any specific pentaerythritol ester nor does any mention any ester of an oligomer of pentaerythritol, of lower alkoxylated pentaerythritol or of an oligomer thereof as a fabric softening agent in a fabric softening composition. Thus, none of the references, either alone or in combination with any of the others, anticipates the present invention or makes it obvious.

The main component of the invented compositions and articles of the present invention, which is usually the only fabric softening compound in such products, other than a fabric softening clay, such as bentonite, which may also be present in them, is preferably a higher fatty acid ester of a pentaerythritol compound, which term is used in this specification to describe higher fatty acid esters of pentaerythritol, higher fatty acid esters of pentaerythritol oligomers, higher fatty acid esters of lower alkylene oxide derivatives of pentaerythritol and higher fatty acid esters of lower alkylene oxide derivatives of pentaerythritol oligomers. Pentaerythritol compound may be abbreviated as PEC herein, which description and

abbreviation may apply to any or all of pentaerythritol, oligomers, thereof and alkoxylated derivatives thereof, as such or as the esters, as will be indicated by the context.

The oligomers of pentaerythritol are preferably those of two to five pentaerythritol moieties, more preferably 2 or 3, with such moieties being joined together through single etheric bonds. The lower alkylene oxide derivatives thereof are preferably of ethylene oxide or propylene oxide monomers, dimers or polymers, which terminate in hydroxyls and are joined to the pentaerythritol or oligomer of pentaerythritol through etheric linkages. Preferably there will be one to ten alkylene oxide moieties in each such alkylene oxide chain, more preferably 2 to 6, and there will be one to ten such groups on a PEC, depending on the oligomer. At least one of the PEC OH groups and preferably at least two thereof will be esterified by a higher fatty acid or other higher aliphatic acid, which can be of an odd number of carbon atoms.

The higher fatty acid esters of the pentaerythritol compounds are preferably partial esters and more preferably there will be at least two free hydroxyls thereon after esterification (on the pentaerythritol, oligomer or alkoxyalkane groups). Usually the number of such free hydroxyls is two or about two but sometimes it may be one, as in pentaerythritol tristearate, or as many as eight, as in pentaerythritol tetrapalmitate.

The higher aliphatic or fatty acids that may be employed as esterifying acids are those of carbon atom contents in the range of 8 to 24, preferably 12 to 22 and more preferably 12 to 18, e.g., lauric, myristic, palmitic, oleic, stearic and behenic acids. Such may be mixtures of such fatty acids, obtained from natural sources, such as coco fatty acid, commercial stearic acid, tallow acid or hydrogenated tallow acid. Intermediate synthetic acids of odd or even numbers of carbon atoms may also be employed. O the fatty acids lauric and stearic acids are often preferred, sometimes depending on the pentaerythritol moiety esterified.

Examples of some esters within the present invention follow:

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## MONOPENTAERYTHRITOL ESTERS

 $R_1 - CH_2 - CH_2 - R_2$   $CH_2 - R_3$   $CH_2 - R_4$ 

# MONOPENTAERYTHRITOL DILAURATE

 $R_1 = CH_3 - (CH_2)_{10} - COO R_2 = CH_3 - (CH_2)_{10} - COO R_3 = OH$   $R_4 = OH$ 

# MONOPENTAERYTRITOL MONOSTEARATE

 $R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = OH$  $R_3 = OH$   $R_4 = OH$ 

# DIPENTAERYTHRITOL ESTERS

# DIPENTAERYTHRITOL TETRALAURATE

 $R_1 = CH_3 - (CH_2)_{10} - CO$   $R_2 = CH_3 - (CH_2)_{10} - CO$   $R_4 = CH_3 - (CH_2)_{10} - CO$ 

# DIPENTAERYTHRITOL TETRASTEARATE

 $R_1 = CH_3 - (CH_2)_{16} - CO$   $R_2 = CH_3 - (CH_2)_{16} - CO$   $R_3 = CH_3 - (CH_2)_{16} - CO$   $R_4 = CH_3 - (CH_2)_{16} - CO$ 

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MONOPENTAERYTHRITOL DISTEARATE

$$R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = CH_3 - (CH_2)_{16} - COO - R_3 = OH$$

MONOPENTAERYTHRITOL TRISTEARATE

$$R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = CH_3 - (CH_2)_{16} - COO -$$

$$R_3 = CH_3 - (CH_2)_{16} - COO - R_4 = OH$$

MONOPENTAERYTHRITOL MONOBEHENATE

$$R_1 = CH_3 - (CH_2)_{20} - COO - R_2 = OH$$
  
 $R_3 = OH$   $R_4 = OH$ 

MONOPENTAERYTHRITOL DIBEHENATE

$$R_1 = CH_3 - (CH_2)_{20} - COO - R_2 = CH_3 - (CH_2)_{20} - COO - R_3 = OH$$

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# PENTAERYTHRITOL 10 ETHYLENE OXIDE ESTER

$$\begin{array}{c} {\rm CH_2-O-(CH_2-CH_2O)}_{n}{\rm H} \\ {\rm R_1-CH_2-C-CH_2-R_2} \\ {\rm CH_2-O-(CH_2-CH_2O)}_{n}{\rm ,H} \end{array}$$

with n+n'=10

MONOPENTAERYTHRITOL 10 ETHYLENE OXIDE DISTEARATE

$$R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = CH_3 - (CH_2)_{16} - COO -$$

# PENTAERYTHRITOL 4 PROPYLENE OXIDE ESTERS

$$\begin{array}{c} \text{CH}_2\text{-O-(CH}_2\text{-CH-CH}_2\text{O)}_2\text{H} \\ \text{R}_1\text{-CH}_2\text{-C}_2\text{-CH}_2\text{-R}_2 \\ \text{CH}_2\text{-O-(CH}_2\text{-CH-CH}_2\text{O)}_2\text{H} \end{array}$$

MONOPENTAERYTHRITOL 4 PROPYLENE OXIDE MONOSTEARATE

$$R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = OH$$

MONOPENTAERYTHRITOL 4 PROPYLENE OXIDE MONOSTEARATE

$$R_1 = CH_3 - (CH_2)_{16} - COO - R_2 = CH_3 - (CH_2)_{16} - COO - R_2 = CH_3 - (CH_2)_{16} - COO - C$$

MONOPENTAERYTHRITOL 4 PROPYLENE OXIDE MONOBEHENATE

$$R_1 = CH_3 - (CH_2)_{20} - COO - R_2 = OH$$

MONOPENTAERYTHRITOL 4 PROPYLENE OXIDE DIBEHENATE

$$R_1 = CH_3 - (CH_2)_{20} - COO - R_2 = CH_3 - (CH_2)_{20} - COO -$$

Although in the formulas given herein some preferred pentaerythritol compounds that are useful in the practice of this invention are illustrated will be understood that various other such pentaerythritol compounds within the description thereof herein may be employed too, including such as pentaerythritol di-hydrogenated tallowate, pentaerythritol ditallowate, pentaerythritol dipalmitate, and dipentaerythritol tetratallowate. Also, in this specification when reference is to a compound of a class, unless it is indicated otherwise therein it is to be considered that the employment of mixtures of compounds of such class are

intended to be included (commercial compounds are often mixtures).

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The PEC's utilized in this invention have some fabric softening effects but such activities are remarkably increased when a suitable dispersing agent for the PEC is present with it. In the absence of such an agent the PEC may be substantially insoluble and undispersed in wash water or in rinse water, in which, if dispersed, it could be conveniently applied to laundry to be softened. When undispersed the PEC could be in solid agglomerate form when cold or in molten form when hot, in neither of which states does it act effectively to soften fabrics (and in both of which cases it can deposit objectionably on treated materials to produce greasy spotting thereof).

Suitable dispersing agents include emulsifiers, usually employed to "solubilize" or disperse the PEC in aqueous liquid compositions that are intended to be employed as rinse cycle softeners (although they may also be added to the wash water), and solids of small (often micron size) ultimate particle sizes, such as clays, which may be present in particulate and other solid products, and in liquid products, too.

The emulsions (which term herein is also intended to refer to dispersions and suspensions in liquid media, as well as to microemulsions [and sometimes solutions may be present, too, in which solvents are the "dispersing agents"]) of this invention will normally be aqueous emulsions in which the aqueous phase is the continuous phase, with the pentaerythritol compound being in the dispersed phase. However, solvents and cosolvents, such as ethanol, isopropanol, propylene glycol and various mono- and di- lower alkyl esters of diethylene glycol (Carbitols®) may also be present in such emulsions and microemulsions to promote formations of stable products, and may also be in the continuous media or solutions.

Various emulsifiers can be employed, and many such are described in the various Detergents and Emulsifiers publications of John W. McCutcheon, issued annually, particularly those for 1969, 1973, 1980 and 1981. Preferred such emulsifiers are those which are alkyl ethers or amines which contain one or more hydroxyalkyl substituents too. Of these the more preferred are the alkyl dialkanolamines or alkyl trialkanol-propylenediamines wherein the alkanol moieties are of 2 to 4 carbon atoms, preferably being 2 or 3 and more preferably being 2, and the alkyl poly(ethylene oxide) ethers are of 2 to 24 ethylene oxide units, preferably of 8 to 12 ethylene oxide units, in which emulsifiers the alkyl is of 8 to 24, preferably 12 to 18 carbon atoms. More preferred such emulsifiers are: stearyl diethanolamine, available from Hoechst A.G. as Genamin® S-020; tallow triethanol propylenediamine, available from CECA, S.A. as Dinoramox® S3; and R-O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>10</sub>H, wherein R is a mixture of C<sub>12-15</sub> alkyls, available from Hoechst A.G. as Genapol® OH-100.

When instead of emulsion form for the invented compositions it is desired that they be in particulate or powder form the dispersing agent for the active pentaerythritol compound softening agent may be any suitable such particulate or powder material that is compatible with the mentioned softening agent, but it may often be preferred to employ such a material that can contribute some fabric softening action to the composition. Such a material is bentonite but other fabric softening clays and clay-like materials may be substituted for it, at least in part. Also, other non-functional substantially water insoluble dispersing agents may be utilized and such, like calcium carbonate and silica, may be carriers for the PEC. Even water soluble carriers, such as sodium sulfate and other "filler salts" may be used, at least in part with the dispersing agent, and sometimes can act as dispersing agents, too. The bentonite employed should preferably be of a type which is gel forming in water and capable of softening fibrous materials, and should be of micron range ultimate particle size, although it may be agglomerated to larger sizes, usually in the range of 8 to 140 sieves, U.S. Sieve Series. If desired, an emulsifier may be utilized in the particulate or solid compositions, and bentonite or other dispersing clay may be present in the emulsions or dispersions, or other swelling clays may be used.

When the pentaerythritol compound softening agent is to be applied to laundry being dried in a laundry dryer, such as an automatic dryer, the PEC or mixture thereof may be applied to a substrate material, from which it may be transferred to the drying laundry under the influence of the heat in the drying air and the rubbing action of the substrate against the moving laundry. The substrate used may be paper or other fibrous material, sponge, preferably cellulose or polyurethane, or other suitable base material, with the pentaerythritol compound being such that it is solid at room temperature and liquefiable and/or softenable at dryer temperatures. The PEC may be blended with other suitable waxy type material, plasticizer or hardener to control the softening point thereof, when such is desirable.

Normally, in the various applications mentioned, the PEC will be employed without the presence of any other fabric softening material (except clay, such as bentonite, montmorillonite or other smectite) but it is possible to utilize such other materials with it if in the proportions and quantities employed they are not ecologically unacceptable and if they do not interfere with the fiber softening action of the PEC. In fact, sometimes, when antistatic action is desirable in the product, such additions may be important because although PEC's have some antistatic properties sometimes those are insufficient for the intended purposes.

Thus, it is possible to formulate fabric softening compositions and articles with the PEC supplemented by other antistatic agents and also by fabric softeners. The foremost of such antistatic materials are the quaternary ammonium salts but when they are present there can be ecological problems, due to their toxicities to aquatic organisms. For example, in standard toxicity tests against daphnia the concentration for 50% effect is less than 1 mg./l. for quaternary ammonium compounds or quats, such as ditallowalkyl dimethyl ammonium chloride, and that is often unacceptable, environmentally. Other antistats and fabric softeners include: higher alkyl neoalkanamides, e.g., N-stearyl neodecanamide; isostearamides; amines, such as N,N-ditallowalkyl N-methyl amine; esterified quaternary salts or esterquats; amidoamines; amidoquats; imidazolines; imidazolinium salts; di-higher fatty acid esters of di-lower alkanolamines, such as dicoco acid ester of diethanolamine; silicones; alkoxylated silicones; and clays, e.g., bentonites and other montmorillonites; and representative examples of some of such classes of such compounds are given below.

## **QUAT**

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H tallow CH<sub>3</sub>
CH<sub>3</sub>
CH<sub>3</sub>

## **ESTERQUAT**

# AMIDO AMINE

# AMIDO QUAT

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**IMIDAZOLINE** 

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tallow - C 
$$N \longrightarrow CH_2$$
  $N \longrightarrow CH_2$   $CH_2 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow C$   $CH_2 \longrightarrow C$   $CH_2 \longrightarrow C$   $CH_2 \longrightarrow C$ 

## **IMIDAZOLINIUM SALT**

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# CLAY

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## = Bentonite

It should be kept in mind then employing supplementary antistats and fabric softeners that they shouldn't make the compositions in which they are incorporated of greater ecotoxicity than is allowable by law and by regulatory authorities in the area of intended use. Thus, quaternary ammonium compounds will usually be avoided, as will be compounds that have similar adverse effects on aquatic organisms, or the amounts

thereof present will be limited so as to avoid such undesirable effects.

Other materials that may be incorporated in the invented compositions include the usual adjuvants that normally are present in other fabric softening compositions (including softergents), such as perfumes, fixatives, solvents, cosolvents, hydrotropes, antioxidants, stabilizers, pH adjusters, buffers, biodegradable antimicrobials, builders, fillers, enzymes, thickeners and fluorescent brighteners, all of which are known classes of materials in the fabric softening compositions field, with examples of several of these being given in the art mentioned in this specification, all of which is hereby incorporated herein by reference.

The last component of the present compositions, which is required in the aqueous emulsions, is water. Normally any clean water can be employed, such as any of a hardness in the range of 0 to 500 p.p.m., as CaCO<sub>3</sub>, but it will be preferred to use water of a hardness of no more than 150 p.p.m., more preferably less than 50 p.p.m., and most preferably the water will be deionized water that has been irradiated.

Although the previous description is primarily directed to fabric softening compositions for addition to wash or rinse waters, especially during automatic washing processes, the invention also includes detergent compositions (softergents) that contain the described PEC and suitable dispersing agent. Such detergent compositions will contain at least one synthetic organic detergent, preferably of the anionic or nonionic type (or a mixture thereof), which may act as a dispersing agent for the PEC.

The anionic detergents are normally of the water soluble sulfated and/or sulfonated lipophile type, which may be designated "sulf(on)ated", and which include lipophilic and sulf(on)ate moieties, but analogous phosph(on)ates may also be utilized. Of the synthetic anionic organic sulf(on)ated detergents those preferred are higher alkyl (preferably linear alkyl) benzene sulfonates, higher fatty alcohol sulfates, higher fatty alcohol ethoxylate sulfates, olefin sulfonates and paraffin sulfonates. Usually such compounds are water soluble alkali metal salts, such as sodium salts, and include higher fatty alkyl or other aliphatic moieties, which serve as lipophilic moieties, and which increase detergency, especially against greasy soils. Such higher alkyl or higher aliphatic moieties will normally be of 8 to 22 carbon atoms, preferably 10 or 12 to 16 or 18 carbon atoms and more preferably, especially for the alkyl sulfates and alkylbenzene sulfonates, the alkyl moieties will be of 12 to 14 carbon atoms. The higher fatty alcohol ethoxylate sulfates that are useful will normally be of 1 to 20 ethoxy groups per mol, preferably 3 to 10 or 15, e.g., 3 or 7. As respresentatives of such detergents there may be mentioned sodium linear dodecylbenzene sulfonate, sodium linear tridecylbenzene sulfonate, sodium lauryl alcohol sulfate, sodium coco alcohol triethoxylate sulfate, sodium C<sub>16</sub> paraffin sulfonate and sodium olefin sulfonate derived from C<sub>14</sub> olefin.

Among the nonionic detergents those which are most preferred are ethylene oxide condensates with higher fatty alcohols or with alkyl phenols, such as condensation products of 3 to 20, 5 to 15, 6 to 12 or 7 to 11 mols of ethylene oxide with higher fatty alcohols of 10 or 12 to 18 or 13 to 17 carbon atoms or with alkyl phenols of 7 to 10 carbon atoms in the alkyl groups, e.g., Dobanol® 25-7, Synperonic® A7, Neodol® 25-3, Neodol 25-7, Neodol 45-11, and  $C_{13-17}$  alcohols condensed with 7 or 11 mols of ethylene oxide per mol. Although the improved softening obtained when a dispersing agent, such as bentonite, is employed with a PEC is noticeable in anionic detergent compositions, such softening action is increased even more when the detergent composition contains a nonionic detergent with the anionic detergent or in replacement of it because the nonionic detergent/PEC is inactive.

In addition to the above examples of suitable anionic and nonionic detergents, extensive listings of such detergents that are useful may be found in standard textbooks relating to synthetic organic detergents, such as the McCutcheon texts, previously cited.

Of the water soluble builders for such detergents it is preferred to employ water soluble salts, such as sodium or potassium salts, more preferably sodium salts, and of these the carbonates, silicates, borates, bicarbonates and phosphates, more preferably polyphosphates, are preferred, such as sodium carbonate, sodium bicarbonate, sodium silicate of Na<sub>2</sub>O:SiO<sub>2</sub> ratio in the range of 1:1.6 to 1:3, preferably 1:2 to 1:3, e.g., about 1:2, 1:2.35 or 1:2.4, sodium tripolyphosphate and tetrasodium pyrophosphate, but sodium sesquicarbonate and sodium sesquisilicate may also be used, as may be the corresponding potassium and other soluble salts, when suitable. Of the water insoluble builders, which builders also have water softening properties, the most preferred are the zeolites, especially the hydrated zeolites. Such zeolites include crystalline, amorphous and mixed crystalline and amorphous zeolites of both synthetic and natural origins, which are of satisfactorily quick and sufficiently effective activities in counteracting calcium hardness ions in wash waters. Preferably, the zeolites employed are characterized as having high exchange capacities for calcium ions, which exchange capacity is normally from about 200 to 400 milligram equivalents of calcium carbonate per gram of the zeolite. Although other ion exchanging zeolites may also be utilized, often the zeolite will be of the formula

 $(Na_2O)x \cdot (Al_2O_3)_y \cdot (SiO_2) \cdot w H_2O$ ,

wherein x is 1, y is from 0.8 to 1.2, z is from 1.3 to 3.5 and w is from 0 to 9, and preferably is 2.5 to 6. Of the crystalline zeolites that are useful those preferred include Zeolites A, X and Y, with A being more preferable, and the most preferred of these is Zeolite 4A. These zeolites are preferably in finely divided state when added to the crutcher with the synthetic detergent prior to drying, and are of ultimate particle diameters in the micron range, e.g., 0.01 to 20 microns, and actual particle sizes in the range of No's. 100 to 400 sieves, preferably 140 to 325 sieves, U.S. Sieve Series. Other builders that may be utilized include organic compounds, which are often sequestrants for hardness ions. Such compounds include organic acids, especially hydroxy acids and amino acids, such as citric and gluconic acids, usually as their water soluble sodium salts, and ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), also usually as their water soluble salts, e.g., sodium salts. Although sodium salts are preferred other acceptable water soluble salts of the organic builder acids may also be utilized. Additional useful builders are the organo-phosphorus chelating agents, such as the Dequests®, e.g., Dequest 2046, which are manufactured by Monsanto Co.

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The proportions of components of the invented compositions and articles will be those which result in stable and effective products for fabric softening applications. For the PEC's the concentration in such compositions and articles will normally be in the range of about 1 to 25%, preferably 1 to 10%, more preferably 2 to 8% and most preferably 3 to 7%, e.g., about 5%, especially for the rinse cycle and wash cycle additive emulsions, although for the articles percentages in the 10 to 20% rang may often be preferred, depending on the type and density of the substrate material (and sometimes for the softergents such a range may be feasible, too.) For the emulsions the content(s) of emulsifier(s) will normally be in the range of 0.2 to 10%, preferably 0.4 or 0.5 to 5% and more preferably 0.7 or 1 to 3%, e.g., about 1.25 or 2%. When the emulsifier is made from an alkyl alkanolamine and an alkyl poly(ethylene oxide) ether, the proportion of the alkanolamine will desirably be equal to or greater than that of the alkyl poly(ethylene oxide) ether, preferably being of 2 to 5 times as much, e.g., about 4 times as much. Thus, such percentages can be of 0.2 to 5% of the amine compound and 0 to 5% of the ether compound, preferably 0.3 to 3% and 0.1 to 2% and more preferably 0.5 to 2% and 0.2 to 1%. For example, as in the composition of the working example, the percentages of such emulsifiers may be 1% of the amine compound and 0.25% of the ether compound. The aqueous medium or water contents of such compositions may be the balances thereof, which will usually be in the range of 65 to 98.8%, preferably 85 to 98.5%, more preferably 87 to 97.5% and most preferably 90 to 96%, e.g., about 93%. It is to be understood that the presences of any adjuvants or supplemental components of the emulsions will be compensated for by corresponding decreases in the water contents of the compositions. Usually the total adjuvants content will be no more than 25%, preferably will be no more than 15% and in many instances will be held to a limit of 5%. None of the adjuvants, in the amounts employed, will be such as to cause unacceptable levels of toxicity which could adversely affect aquatic organisms, including fish, that inhabit lakes and streams into which there are fed washing machine rinses that included the present compositions. Thus, the invented compositions may be considered to consist essentially of the named components, in additive or softergent form, with only environmentally acceptable proportions of adjuvants being allowed to be present therein. As was previously mentioned, the present compositions and articles are preferably essentially free of quaternary ammonium compounds. Most preferably 0% of such are present but when the resulting compositions and articles are not ecotoxic increasing limits of 0.1%, 0.3% and 0.5% may be imposed, which are more preferred, preferred and acceptable limits respectively, under such circumstances, and can be within the invention.

One suitable adjuvant is an acidifying agent, such as hydrochloric acid, which is useful to adjust the pH of the emulsion or other aqueous composition to 2.5 to 5.5, preferably 2.5 to 4, e.g. 3.5. To do that the percentage of HCl (concentrated basis) or equivalent other acidifying agent present will usually be in the range of 0.01 to 0.4%, preferably 0.05 to 0.2%.

When particulate or powder compositions or dryer articles are made the percentages of PEC's may be in the same ranges as given in the preceding paragraph or at least within the wider of such ranges but the powder carrier/dispersing agent or the substrate for the articles may be the balance of the composition or product. If desired, emulsifier(s) may also be present in such compositions and articles, preferably in about the proportions previously given for the emulsions, and of course, suitable adjuvants may be present, too. Thus, the fabric softening powders or particulate compositions may comprise 1 to 25% of PEC and 75 to 99% of carrier clay, such as bentonite, preferably comprise 1 to 10% of the PEC and 90 to 99% of the carrier, and more preferably comprise 3 to 7% of PEC and 93 to 97% of bentonite, e.g., 5% of tripentaerythritol tetralaurate and 95% of bentonite. The fabric softening article may comprise about 1 to 25% of PEC, with the balance being substrate material, or the percentage of PEC may be in the 5 to 20% or 10 to 20% range.

In softergents the percentages of PEC and dispersing agent may be like those previously mentioned above for the corresponding liquid and particulate or solid products, with the proportions of water and carrier being adjusted respectively to compensate for the detergent(s), builder(s) and adjuvant(s) present. Normally, such proportions comprise 3 to 35% detergent, 10 to 80% builder, and 0.5 to 25% adjuvants for the particulate or solid softergents, preferably 3 to 25%, 10 to 60% and 2 to 15%, respectively, and 2 to 20%, 0 to 35% and 0.2 to 20%, respectively, for the liquid softergents (with the balance being water or most water), preferably 3 to 15%, 5 to 25% and 0.5 to 15%, respectively. The percentages of PEC and dispersant are normally in the ranges of 1 to 25% and 0.2 to 90%, preferably being 2 to 15% and 5 to 30% for the solids and 3 to 15% and 3 to 30% for the liquids, respectively.

To manufacture the invented compositions and articles is comparatively simple but to produce applicants' desired stable emulsions (and microemulsions) a particular process is desirably followed. In such cases it is preferable that the PEC be melted before addition to the aqueous medium and the temperature to which the PEC is raised will desirably be within 10°C. of the melting point thereof. It is preferred that the PEC be mixed with any meltable emulsifier, especially one of lipophilic character (or more lipophilic character than another emulsifier present), such as the amine, when a mixed amine-monoether or ethoxylated alcohol emulsifier is employed, and melted together with it, but alternatively the two meltable materials, PEC and amine, may be separately melted and added together or simultaneously to the aqueous medium (usually water), which should also be at about the same elevated temperature, about 60°C., for example. The water employed is often desirably acidified, as by addition to it of HCl or other suitable acid, to generate a final pH in the range of 2.5 to 5.5, preferably 2.5 to 4.0, e.g., about 3.5. After emulsification the emulsion produced may be cooled to room temperature, with the balance of emulsifier (the monoether or ethoxylated alcohol emulsifier, in many cases) being added before or after such cooling, preferably before. The result is a stable emulsion, which resists separation under normal elevated temperature conditions for periods of six months or more.

To manufacture the particulate or powdered product it is only required for the PEC to be mixed with the dispersing material. Preferably, the melted PEC, at elevated temperature, will be sprayed onto a tumbling mass of the particulate agglomerated smectite or montmorillonite powder (such as bentonite) or other disperser/carrier, and will thereby be distributed throughout it evenly. Sometimes the mixer employed will include size reduction means to make sure that the PEC is in small enough particles so as to promote even deposition on the laundry being treated. The bentonite or other disperser particles may be at room temperature when the PEC is being applied to them and the PEC will be solidified on contact with the particulate mass, usually with little agglomeration taking place, but by controlling the PEC application, the temperature and mixer speed, some agglomeration may be obtainable, when desired.

To make the softening article it is usually desirable for the substrate material, in a continuous strip, to be passed through a melt, emulsion or other bath of PEC (w/wo disperser), with any excess being removed by a doctor blade or squeeze rolls. After cooling or drying, the strip, containing the PEC, may be cut into individual pieces and is ready for use.

The softergents may be made in usual manners, with the PEC and disperser being post-added or being added at a suitable stage of the manufacturing process, taking into account that they will not be subjected to destabilizing or destructive temperatures.

In use, the various invented compositions and articles are employed in the same manners as other emulsions, powders, articles and softergents that apply fabric softener to laundry. The emulsion may be added to rinse water and so may the powder and particulate compositions, with the concentations of PEC being in the range of about 0.01 to 0.05% of the rinse water Alternatively, such compositions may be added to the wash water but in such cases the concentrations may be increased, often about 1 to 3 times. Dryer treatment articles may be used in the same manner as products currently being marketed for that purpose, with paper strips (or towels) or equivalent sponges being added to the dryer, usually with a sheet or strip of 300 to 800 sq. cm. being employed. Softergents may be charged to the washing machine as if they were detergents, with the desired concentrations being in the range of 0.1 to 1%, preferably 0.1 to 0.5%, e.g., about 0.15% in the U.S.A. and about 0.5% in Europe, to compensate for different washing conditions employed.

The following examples illustrate but do not limit the invention. Unless otherwise indicated all parts and percentages in this specification and the appended claims are by weight and all temperatures are in °C.

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## **EXAMPLE 1**

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	Component	Percent (by weight)
(1) (2)	Pentaerythritol distearate Genamin® S-020 Genapol® OX-100 Hydrochloric acid (concentrated) Water, deionized	5.00 1.00 0.25 0.087 93.663 100.000

(1) N-stearyl diethanolamine (which can be replaced by N-tallow triethanol propylenediamine)

(2) Alkyl poly(ethylene oxide) ether ethanol wherein the alkyl is a mixture of  $C_{12-15}$  alkyl chains, and which contains about 10 EtO groups

A stable emulsion is made of the above formula by heating together the pentaerythritol distearate and the Genamin S-020 to 60°C. and then admixing such melted mixture with the 60°C. acidified water, after which the Genapol OX-100, also at 60°C., is admixed with the water emulsion of pentaerythritol distearate and Genamin S-020. The resulting stable acidic emulsion, which is at a pH of about 3.5, is a good fabric softening composition, better in fabric softening action than a 5% aqueous emulsion or suspension of distearyl dimethyl ammonium chloride (DSDMAC), when tested against such quat, using hardened cotton terrycloth as the test fabric to be softened. DSDMAC has long been considered to be one of the most effective fabric softeners known in the art.

In the described tests the terrycloth employed is hardened by six treatments with an aqueous hardening composition that includes sodium silicate, sodium sulfate and sodium tripolyphosphate. Such hardening is effected to simulate hardening effects on laundry that

When comparing two fabric softening compositions for softening action nine tests are run on each of such compositions, using 40 cm. X 40 cm. hardened terrycloth swatches and washing each of them and rinsing them in rinse waters containing either of the fabric softening compositions. Evaluations of softening actions (or softnesses of the treated swatches) are made after 1, 5 and 10 washing/rinsing cycles, by six judges in blind comparison tests. The washings effected are normal washing machine washings and the rinsings are in rinse waters containing 110 ml. of softening composition per 25 liters of water (0.44%, by weight), which are employed to treat 3 kg. of fabric or laundry, containing the test swatches. In some instances a mini-test may be carried out, using specially designed reduced scale washing and rinsing apparatuses, and it has been found that such test results are consistent with those from the full size tests. After rinsing, the swatches are air dried in a temperature-and humidity-controlled room, while being maintained horizontal to prevent loss of the fabric softener from the fabric due to dripping. After drying the swatches are ready for softness evaluation by the jury.

The judges rate the swatches for softness by comparing them to a standard, which in the present case is a swatch that was treated with a softening composition that contained the same amount of DSDMAC as the amount of pentaerythritol distearate in the test composition. The judges' ratings are evaluated, using statistical techniques, and final results show whether the softening compositions are equal in softening actions or whether one or the other is significantly better. By the described testing the experimental composition of this example is rated as better in fabric softening effect than a control composition that contained the quat (DSDMAC), whether one, five or ten cycles of washings and rinsings are used.

In similar separate testings, employing pentaerythritol dilaurate and pentaerythritol dibehenate, it was found that although such compositions were useful fabric softeners, they were not as effective as pentaerythritol distearate. Also, pentaerythritol monostearate and pentaerythritol tristearate compositions, while also possessing useful fabric softening properties, were not as effective in that respect as the pentaerythritol distearate.

In the above experiments instead of pure pentaerythritol distearate the pentaerythritol ester may be the di-tallowate or di-hydrogenated tallowate, in which the esterifying acid is tallow acid(s) or hydrogenated tallow acid(s), and the results obtained will be similar. Also, when other dispersing agents, such as those described earlier in this specification, are employed with any of the mentioned PEC's, effective softening is also obtained.

### **EXAMPLE 2**

The procedure of Example 1 is followed, with the exception that in the formula thereof the pentaerythritol distearate is replaced by tripentaerythritol tetralaurate, and it is found that the softening action of such acidic compositions, which are at pH's in the range of 2.5 to 5.5, is comparable to that of the pentaerythritol distearate composition of Example 1. The tetralaurate is superior in softening action to analogues thereof wherein the ester is the tetrastearate and/or tetrapalmitate and/or tetraoleate, and it appears that such differences are related to the maintenance of a more desirable hydrophilic/lipophilic; balance (HLB), inasmuch as the tripentaerythritol tetraester has fewer free hydroxyls per carbon atom than the pentaerythritol diester.

Instead of the tripentaerythritol tetralaurate there may be substituted tripentaerythritol tetramyristate, tripentaerythritol tristearate, tripentaerythritol tritallowate, tripentaerythritol trihydrogenated tritallowate, dipentaerythritol tetrastearate, dipentaerythritol trilaurate, tetrapentaaerythritol tetralaurate, pentapentaerythritol tetrastearate and pentapentaerythritol tetratallowate and various others of the pentaerythritol esters described herein, and fabric softening similar to that of the tripentaerythritol tetralaurate will be obtainable, without the need for the presence of quat fabric softener. In addition, the described emulsions are stable, the fabric softening component is satisfactorily rewettable and may aid perfume to adhere to the treated fabric, and the presence of the dispersed PEC in a softergent and in wash water prevents excessive foaming.

### **EXAMPLE 3**

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	Component	Percent (by weight)
(3)	Bentonite Tripentaerythritol tetralaurate	95.0 5.0 100.0
(3) Gel-forming and swelling sodium bentonite		

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A powdered product is made by blending together the indicated pentaerythritol oligomer ester and the bentonite, and such may be agglomerated to particle size in the 10 to 100 sieve range, U.S. Sieve Series, or the powder may be used as is or suspended in water, with or without the presence of emulsifying agent-(s). The product is employed in the rinse water, with the concentration of the PEC being the same as in Examples 1 and 2, and it is found that the composition described has fabric softening properties like those of DSDMAC compositions containing the same amount of quat as the ester content of such invented composition. Similar results are obtainable when the other named satisfactory esters are substituted for the tripentaerythritol tetralaurate. In all such cases the ester improves the fabric softening action of the bentonite significantly. Additionally, when, in this example and in Examples 1 and 2, a silicone fabric softener, such as a dimethyl polysilicone or an aminosilicone, is also present, its softening action is improved by the presences of the pentaerythritol ester and dispersing agent.

In a variation of the formula of this example a dispersion of the tripentaerythritol tetralaurate in water may be made by mixing together 20 parts of clay, 2 parts of the pentaerythritol ester and 76 parts of water, with 2% of mixed emulsifier (the mixture of Example 1) being optional (preferred).

The powder, agglomerate or emulsions of this example may be added to the rinse water, as is often preferable, or to the wash water, or they may be used with or incorporated into any suitable particulate detergent composition to make a softergent for use in the wash water, or the liquid may be mixed with liquid detergent composition to make a liquid softergent for use in washing. One may also employ the preparations in both the rinsing and washing operations, which is often highly desirable.

When other monomeric pentaerythritol esters of the types described in this specification are employed in the described compositions they usefully soften fabrics too, but it is considered that the pentaerythritol distearate and pentaerythritol dipalmitate are PEC's that best represent the most effective, most readily available and most practicable (from a commercial viewpoint) of these fabric softeners in the described compositions.

The fabric softening effects described can also be obtained when the emulsifiers employed are changed and when the proportions of fabric softening compound(s) and emulsifier(s) are changed, within the ranges mentioned in this specification. Thus, various other emulsifiers mentioned herein and in the

McCutcheon publications, referred to previously, may be substituted for those of the present examples and the favorable results reported will be obtained. Similarly, aesthetic and functional adjuvants may be present, such as perfumes, brighteners and others of the various adjuvants that were mentioned previously, and the desired softening results are still obtainable.

What is surprising about these results is that the present compositions, which are devoid of quaternary ammonium compound fabric softener, the acknowledged most effective fabric softener presently known and in use, are fabric softening compositions of essentially equal softening effectiveness (or nearly equal effectiveness in some cases) and do not possess the undesirable properties of the quats (especially persistent toxicity vs. aquatic organisms and an objectionable reactivity with anionic compounds), so they can be used when and where quats are unacceptable. This is considered to be a significant discovery and represents a substantial advance in the art. However, when the disadvantages of the quats are not controlling, and when such may be tolerated or even desired as components of the fabric softening compositions, they and other previously mentioned cationic and other fabric softeners, antistatic agents and conditioners can be present in the described compositions in tolerable (environmentally acceptable) proportions, so their good effects can be obtained, in addition to those of the combination of pentaerythritol ester and dispersing agent.

### **EXAMPLE 4**

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Component	Percent (by weight)
Pentaerythritol distearate	5.0
Dispersing agent (1 part Ethomeen T12 and 1 part of Synperonic A2)	2.0
Paper (toweling)	93.0
	100.0

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The pentaerythritol distearate and the emulsifier mixture are melted at 60° C. and the paper toweling is drawn through a bath of the melt under such conditions that the final withdrawn sheet includes 5% of the fabric softening pentaerythritol ester. The sheet resulting is then cut to desired size and the strips resulting, often about 10 X 25 cm., are internally and longitudinally cut or sliced to increase contact of the coated paper with tumbling laundry in a laundry dryer. When a sheet of this softening article is added to a laundry dryer that contains 3 to 4 kg. of laundry to be dried (dry weight) it satisfactorily softens such laundry.

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In modifications of the invention the article made may contain emulsifier(s), such as those described in the other working examples and elsewhere in this specification and may also contain other aesthetic and functional adjuvants. Also, other pentaerythritol esters, oligomeric pentaerythritol esters and lower alkoxylated pentaerythritol or oligomeric pentaerythritol esters mentioned in this specification may be substituted for the pentaerythritol distearate in the same proportion or the proportion may be changed, as in other examples and elsewhere in the specification, and similar results will be obtained. In some instances, as when the combination of dispersing agent and pentaerythritol ester or derivative thereof, does not produce sufficient fabric softening action, additional fabric softening, and sometimes additional antistatic action, may be obtained by incorporating in the melt or otherwise applying to the paper additional fabric softeners, such as higher alkyl neoalkanamides, isostearamides, silicones and, when permissible, cationic fabric softeners, e.g., quats (usually in relatively small proportion).

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In other variations of the invention of this example the substrate paper may be replaced with other absorbent fibrous or cellular materials, such as cotton toweling, cloth, synthetic and blends of cotton and synthetic fabric, e.g., cotton/polyester blends. In some instances cellulosic sponges may be used for the substrate and sometimes polyurethane and other synthetic sponges may be employed instead. Alternatively, the invented pentaerythritol ester compositions may be dispensed from dispensing articles and other applicators into the laundry dryer or into the rinse water in the washing machine to soften laundry therein.

### **EXAMPLE 5**

5	Component	% (by weight)
	Sodium linear dodecylbenzene sulfonate	2.00
	Nonionic detergent (condensation product of one mol of	3.90
	C <sub>13-17</sub> mixed fatty type alcohols and 7 mols of EtO)	
	Stearyl hydroxyethyl imidazoline	1.00
10	Sodium silicate ( $Na_2O:SiO_2 = 1:2$ )	4.00
	Sodium tripolyphosphate	23.00
	Sodium carbonate (anhydrous)	5.00
	Ethylenediamine tetra(methylene phosphonic acid), sodium salt	0.38
15	Stilbene type optical brightener	0.21
	Methyl silicone (Dow-Corning X2-3302)	0.18
	Sodium hydroxide	1.00
	Sodium perborate tetrahydrate	12.00
	Proteolytic enzyme (Alcalase® 2T)	0.30
20	Calcium montmorillonite (swellable in presence of sodium)	16.00
	Potassium methyl siliconate	0.50
	Hydroxylamine sulfate	0.30
	Tetraacetyl ethylenediamine	0.89
25	Sodium aluminosilicate	0.25
	Pentaerythritol distearate	6.00
	Sodium sulfate, anhydrous	13.59
	Perfume	0.50
	Water	9.00
30		100.00

or zeolite-built types.

The particulate detergent composition described is made by roll drying (although spray drying can also be used) a crutcher mix of various heat stable components, followed by mixing the particulate product resulting with other powdered or particulate materials, which can be those that are less heat resistant, and then perfuming the product. To make the crutcher mix the components will usually be admixed with the water and any sodium hydroxide that might be present, after which the other components will be admixed in known manner so as to obtain the best mixing, following known mixing procedures. After the crutcher mix is dried the base beads made by the drying process are then blended with other components, such as perborate, clay (montmorillonite), preferably bentonite, which may be in the calcium, sodium or other swellable form, enzyme(s), hydroxylamine sulfate, sodium aluminosilicate and tetraacetyl ethylenediamine, and then the mix may be perfumed.

The finished particulate softergent may then be packaged and marketed. When tested, it shows a surprising improvement over softergents that are based on either clay fabric softener alone or on PEC alone as the fabric softening component thereof and in comparative softening tests the invented Composition scores higher than the best commercial softergent on the market. Similar desirable improvements in fabric softening are noted when the heavy duty fabric softening detergent composition is based on carbonate/zeolite built nonionic detergent formulations and when liquid built detergents are those tested, of either the phosphate-built

## **EXAMPLE 6**

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In this example cotton terrycloth swatches are washed in an automatic washing machine in a 60 °C. wash water containing 0.5% of a softergent composition of the formula of Example 5, rinsed and dried. Other such swatches are washed in conventional detergent compositions, which may be of the same formula except for the omission of the bentonite and PEC, which are replaced by inert filler (sodium sulfate), and are then rinsed (in the last rinse), with rinse water to which any quaternary ammonium or amine salt rinse cycle fabric softening composition has been added, such as dimethyl distearyl ammonium

chloride, so that the rinse water contains about 0.05% (or more) of the fabric softening quat or amine, and such swatches are dried.

Strips are cut of swatches subjected to these different treatments and are tested for water absorption, by dipping lower ends of such vertical strips into an aqueous solution of water soluble dye (red Iragon) and measuring the heights to which the water rises, after 30 seconds, 1 minute, 3 minutes and 5 minutes. The strips washed with the invented softergent absorb water to heights that are about twice those for the strips from the swatches that are washed, as described, and then treated with the rinse cycle softener.

Similar results are obtainable by utilizing rinse cycle fabric softeners of this invention, in which PEC and bentonite are present, when they are compared to rinse cycle fabric softening compositions that are based on quat and/or amine fabric softeners. Nevertheless, the invented softergents and rinse cycle compositions soften the cotton (and other fabrics) about as well as the other rinse cycle softening compositions, which is an exceptional result.

The results of these tests and similar absorption tests on towelling and clothing are important because they show that fabrics treated with the invented compositions, instead of commercial quat-based products, are more capable than such products of absorbing water (which is important for towels) and body sweat (which is important for clothing items, such as underwear, T-shirts and sport apparel).

When the PEC is employed in fabric softening compositions and applications it has been found that the presence with it of the suitable dispersing agent for it is of great importance and greatly improves the fabric softening action of the PEC. In some cases, such as with the Zeolite/carbonate built nonionic synthetic organic detergent compositions, the fabric softening can be increased from essentially nothing to excellent when such a dispersing agent is present with the PEC. In other cases, such as with the phosphate-built anionic detergent compositions the softening action may be increased from fair to excellent, due to the presence of the dispersant. Such increase is significantly more than any expected increase due to any fabric softening properties the dispersant might possess. Thus, although PEC may be of fabric softening activity without the presence of the dispersing agent, such action is significantly and unexpectedly increased by the presence of such dispersant, which thereby increases the importance of the invention. Still, in some circumstances the PEC's may be used in such described fabric softening compositions without dispersing agents, for fabric softening and for other properties thereof, such as foam control, etc.

The invention has been described with respect to various working examples and embodiments thereof hut it is not to be considered to be limited to those because one of skill in the art, with the present specification before him or her, will be able to utilize substitutes and equivalents without departing from the invention.

The invention also extends to the products, compositions, articles and processes set out below.

A fabric softening product, which is a composition or an article for application to fibrous materials, so that a fabric softening component thereof is deposited on the fibrous materials and softens them, which comprises a PEC, which is a fabric softening component which is a higher aliphatic acid ester of pentaerythritol, of an oligomer of pentaerythritol, of a lower alkylene oxide derivative of pentaerythritol or of a lower alkylene oxide derivative of an oligomer of pentaerythritol, or a mixture thereof, and a dispersing agent for it.

A fabric softening composition or article which is essentially free of quaternary ammonium compound fabric softener.

A fabric softening product which is a wash cycle or rinse cycle composition, a dryer article or a softergent, in which the dispersing agent is an emulsifier or a clay.

A fabric softening rinse cycle or wash cycle additive composition which is in aqueous emulsion form and comprises about 1 to 25% of the PEC component, about 0.2 to 10% of an emulsifying agent and about 65 to 98.8% of aqueous medium.

A fabric softening emulsion which comprises 1 to 10% of a higher aliphatic acid ester of pentaerythritol or a higher aliphatic acid ester of an oligomer of pentaerythritol or a mixture thereof, 0.5 to 5% of an emulsifying agent selected from the group consisting of ethoxylated amines, ethoxylated alcohols, and mixtures thereof, and 85 to 98.5% of water.

A fabric softening emulsion which contains no quaternary ammonium compound and which comprises 2 to 8% of a higher fatty acid partial ester of pentaerythritol or a higher fatty acid partial ester of an oligomer of pentaerythritol or a mixture thereof.

A fabric softening emulsion which comprises 3 to 7% of a higher fatty acid diester of pentaerythritol wherein the higher fatty acid is stearic acid, 1 to 3% of the emulsifying agent, which is a mixture of fatty alkyl diethanolamine and fatty alkyl poly(ethylene oxide) ether, wherein the alkyls are of 12 to 18 carbon atoms, and 90 to 96% of water, which emulsion is at a pH in the range of 2.5 to 5.5.

A fabric softening emulsion which comprises about 5% of pentaerythritol distearate, about 1.0% of stearyl diethanolamine, about 0.25% of alkyl poly(ethylene oxide) ether wherein alkyl is a mixture of  $C_{12-18}$  alkyl chains, about 93% of water and about 0.09% of hydrochloric acid, which emulsion is at a pH of about 3.5.

A fabric softening rinse cycle or wash cycle additive product which is in particulate or powder form and comprises about 1 to 25% of the PEC and about 75 to 99% of a particulate or powder carrier for the PEC, in which said PEC is dispersed.

A fabric softening product in particulate or powder composition form, which comprises 1 to 10% of a higher acid ester of pentaerythritol or a higher acid ester of an oligomer of pentaerythritol, or a mixture thereof, and 90 to 99% of a particulate or powder dispersing carrier for it.

A fabric softening composition wherein the particulate or powder dispersing carrier is a fabric softening clay and no quaternary ammonium compound is present.

A composition wherein the fabric softening clay is bentonite and the fabric softening component is an oligomer of pentaerythritol which is incompletely esterified with a higher batty acid of 8 to 24 carbon atoms.

A composition which comprises 3 to 7% of higher fatty  $C_{12-18}$  partial ester of an oligomer of pentaerythritol and 93 to 97% of sodium bentonite or calcium bentonite.

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A composition which comprises about 5% of tripentaerythritol tetralaurate and about 95% of calcium bentonite.

A fabric softening dryer article which comprises an absorbent fibrous or cellular material which has deposited on it or absorbed thereby about 1 to 25% of the fabric softening component, on a fabric softening article basis.

A fabric softening article which comprises a sheet of paper which has been impregnated with 5 to 20% of a partial higher fatty ester of pentaerythritol, a partial ester of an oligomer of pentaerythritol or a mixture thereof, and a dispersing agent for such PEC.

A process for softening washed laundry which comprises applying to such laundry a fabric softening product of the invention in such manner and under such conditions that a fabric softening component thereof is deposited on the laundry and softens it.

A process wherein the fabric softening composition is applied to the laundry and is an aqueous emulsion comprising about 1 to 25% of fabric softening component, about 0.2 to 10% of emulsifying agent and about 65 to 98.8% of aqueous medium, which is applied to the laundry in rinse water in a washing machine after machine washing of the laundry.

A process wherein the fabric softening composition is applied to the laundry in the wash water or in the rinse, is in particulate or powder form and comprises about 1 to 25% of PEC and about 75 to 99% of clay, which is dispersed in the wash or rinse water in a washing machine and at least partially deposits therefrom onto the laundry, thereby softening it.

A process wherein the fabric softening product is a dryer article that is applied to the laundry and is an absorbent fibrous or cellular material which has had deposited on it or absorbed by it about 1 to 25% of PEC, on a fabric softening article basis, which is added to washed and rinsed laundry in an automatic laundry dryer, wherein the fabric softening component is transferred, at least in part, to the laundry being dried, and softens it.

A softergent composition which comprises a synthetic organic detergent composition comprising a synthetic organic detergent of the anionic and/or nonionic type(s), PEC and dispersing agent for the PEC.

A softergent composition wherein the synthetic organic detergent is 3 to 35% thereof, the PEC is 1 to 25% thereof and the dispersing agent is 0.2 to 90% thereof.

A softergent composition wherein the synthetic organic detergent is a mixture of anionic and nonionic detergents, and the proportion thereof is in the range of 3 to 25%, the composition is built with 10 to 60% of builder, and the proportions of PEC and dispersant are in the ranges of 2 to 15% and 5 to 30%.

A process for manufacturing a stable aqueous fabric softening emulsion which comprises melting at elevated temperature 1 to 25 parts of a higher fatty acid ester of pentaerythritol, melting at least a portion of 0.2 to 10 parts of emulsifying agent and mixing both melted materials simultaneously with 65 to 98.8 parts of water at an elevated temperature to form an emulsion, after which any remaining emulsifier is admixed with the emulsion at such elevated temperature, and the emulsion is cooled to room temperature.

A process wherein the pentaerythritol compound is a higher fatty acid diester of pentaerythritol the emulsifying agent includes an alkyl diethanolamine and an alkyl poly(ethylene oxide) ether, such alkyl diethanolamine content is greater than such ether content and the water is acidified to result in a final pH in the range of about 2.5 to 5.5, the proportions of pentaerythritol compound, emulsifier and water are in the ranges of about 3 to 7%, 1 to 3%, and 90 to 96%, respectively, the pentaerythritol compound is heated to a temperature of about 60°C. to melt it, the alkyl diethanolamine is heated to a temperature of about 60°C.

the pentaerythritol compound and the alkyl diethanolamine are admixed with heated acidified water, the alkyl poly(ethylene oxide) ether is admixed with the emulsion resulting, at about 60 ° C., and the resulting emulsion is cooled to room temperature.

### 5 Claims

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- 1. A fabric softening product, which is a composition or an article for application to fibrous materials, so that a fabric softening component thereof is deposited on the fibrous materials and softens them, which comprises a PEC, which is a fabric softening component which is a higher aliphatic acid ester of pentaerythritol, of an oligomer of pentaerythritol, of a lower alkylene oxide derivative of pentaerythritol or of a lower alkylene oxide derivative of an oligomer of pentaerythritol, or a mixture thereof, and a dispersing agent for the PEC which is one or more synthetic organic detergents.
- **2.** A fabric softening composition or article according to claim 1 which is essentially free of quaternary ammonium compound fabric softener.
  - 3. A fabric softening product according to claim 2 which is a wash cycle Composition or a softergent.
- 4. A fabric softening composition as claimed in any one of claims 1 to 3 characterised in that the synthetic organic detergent is of the anionic and/or nonionic type(s), and functions as a dispersing agent for the PEC.
  - **5.** A fabric softening composition as claimed in claim 4 characterised in that the synthetic organic detergent is 3 to 35% thereof, and the PEC is 1 to 25% thereof.

**6.** A fabric softening composition as claimed in claim 5 characterised in that the synthetic organic detergent is a mixture of anionic and nonionic detergents.

- 7. A fabric softening composition as claimed in any one of claims 1 to 6 characterised in that in addition to the synthetic organic detergent it also contains a dispersing agent for the PEC.
  - 8. A composition as claimed in claim 7 characterised in that it comprises 0.2 to 90% of the dispersing agent.
- 9. A composition as claimed in any one of claims 1 to 8 characterised in that it comprises a builder for the said synthetic organic detergent.
  - **10.** A composition as claimed in claim 9 characterised in that the composition contains 10 to 60% of the builder.
  - **11.** A fabric softening composition as claimed in any one of claims 8 to 10 characterised in that the amount of detergent is in the range of 3 to 25%, the composition is built with 10 to 60% of builder, and the proportions of PEC and dispersant are in the ranges of 2 to 15% and 5 to 30%.
- 45 12. A fabric softening product, which is a composition or an article for application to fibrous materials, so that a fabric softening component thereof is deposited on the fibrous materials and softens them, which comprises a PEC, which is a fabric softening component which is a higher aliphatic acid ester of pentaerythritol, of an oligomer of pentaerythritol, of a lower alkylene oxide derivative of pentaerythritol or of a lower alkylene oxide derivative of an oligomer of pentaerythritol, or a mixture thereof, and a detergent builder.
  - 13. A composition as claimed in any one of claims 1 to 12 characterised in that it comprises a filler.
  - 14. A process for manufacturing a stable aqueous fabric softening emulsion which comprises melting at elevated temperature 1 to 25 parts of a higher fatty acid ester of pentaerythritol, melting at least a portion of 0.2 to 10 parts of emulsifying agent and mixing both melted materials simultaneously with 65 to 98.8 parts of water at an elevated temperature to form an emulsion, after which any remaining emulsifier is admixed with the emulsion at such elevated temperature, and the emulsion is cooled to

	room temperature characterised in that the emulsifying agent includes an alkyl diethanolamine and an alkyl poly(ethylene oxide) ether, and the said alkyl diethanolamine content is greater than the said ether content.
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# **EUROPEAN SEARCH REPORT**

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