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METHOD OF TREATING SHAPED ARTICLES WITH BETAIN- TYPE POLYMERS AND THE ARTICLES THEREBY OBTAINED

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10 Claims

ABSTRACT OF THE DISCLOSURE

Shaped articles, more particularly fabrics of various fibers, especially cotton and/or hydrophobic synthetic fibers, e.g., of linear polyesters (such as of polyethyleneglycol terephthalate) are treated with polymers of betaines or sulfobetaines or copolymers thereof with or without acrylic acid and/or an acrylic ester, such as methyl acrylate—preferably the treating composition also contains an aminoplast condensate capable of imparting creaseproofing, wrinkleproofing, and durable press characteristics on curing with an acidic catalyst. The process and treated fabrics are claimed.

DESCRIPTION OF THE INVENTION

This invention concerns the treatment of shaped articles, such as films, sheets, plates and filamentary materials of a hydrophobic nature so as to give them a durable, hydrophilic, antistatic, antisoiling and soil-releasing finish.

Hydrophobic materials, when formed into shaped articles of various types, tend to accumulate static charges. These charges are particularly evident in the preparation of fibers and the subsequent manufacture into textile articles. As a result of formation of these static charges, the materials have been found unsuited for certain purposes and somewhat unsatisfactory for garments. Therefore, it has been desirable to provide a treatment for hydrophobic materials which would dissipate the static charges, but which would not subsequently impair such critical properties of the garment as tensile strength, flexibility, elongation, resistance to chemical, bacterial, and fungal agencies, and dyeability. It is also important to give the textiles a hydrophilic surface particularly in fabrics used in the manufacture of undergarments, for instance, where rapid transmission of perspiration is an asset.

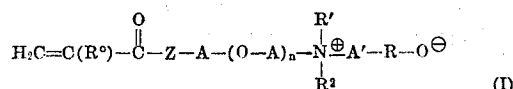
One object of this invention is to provide a finish for hydrophobic shaped articles which does not alter the basic physical properties but gives them an antistatic hydrophilic surface. Another object is to provide a durable antistatic finish for textile and other shaped products. A further object of the invention is to bond an amphoteric polymer to the surface of a shaped article while at the same time causing partial chemical reaction to occur which insolubilizes the polymeric coating without destroying its hydrophilic characteristics. A still further object of the invention is to provide wettable finishes for textile products, which finishes are further characterized by possessing antisoiling and soil-releasing properties. Additional objects would be apparent from the disclosure contained herein.

Fabrics treated in accordance with the present invention demonstrate the ability of reducing or preventing pick-up of oily dirt during laundering, and also providing release of soil during cleaning, especially laundering. These are desirable properties, particularly in regard to the soiling properties such as are encountered with fabrics comprising polyester-type materials. While we do not desire to be bound by any theory concerning the mechanism of the

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coatings of this invention, this antisoiling property which is imparted to hydrophobic materials such as polyesters is probably associated with a certain degree of substantivity of these fibers for oils. The hydrophilic layer of our polymeric betaine coating prevents the deposition of oily dirt either by charge effect or degree of polarity.

In accordance with the present invention it has been found that these improved properties are obtained by the application to the shaped articles, such as textile fabrics, of a polymer containing units of a polymerized betaine of the formula



wherein

n is zero or an integer having a value of 1 to 10,

R° is H or methyl,

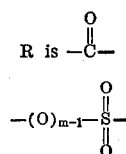
Z is $-\text{O}-$ or $-\text{NH}-$,

A is an alkylene group having 2 to 6 carbon atoms, at least two of which extend in a chain between the quaternary nitrogen atom and the adjoined Z radical when n is 0, but when n is 1 to 10, A is a (C_2-C_3) alkylene group having at least 2 carbon atoms extending in a chain between O atoms or between an O atom and the adjoined N atom or Z radical,

R' is (C_1-C_4) alkyl,

R^2 is (C_1-C_4) alkyl, or

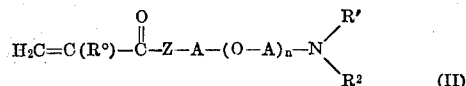
R' and R^2 may together form with the N atom a 5- to 6-atom ring, in which the atoms are C, N, or O, such as the morpholino, piperidino, and piperazino groups, A' is a divalent saturated aliphatic hydrocarbon radical, such as alkylene, having 1 to 4 carbon atoms, and



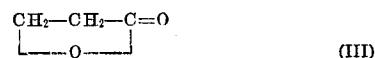
wherein m is 1 or 2.

While the monomers just defined do not all fall within the strict definition of betaines, they can be referred to as of betaine-type by virtue of the quaternary ammonium nitrogen atom which is substituted by a carboxyl-containing radical and the fact that they form an inner salt as is indicated in Formula I hereinabove. For convenience, these compounds may sometimes be referred to as a betaine, a betaine-type compound or as an "inner salt of the N-(2-carboxyethyl) quaternary" of the tertiary amine from which the compound is derived; for example, the expression "N-(2-carboxyethyl) inner salt of dimethyl-aminoethyl acrylate (DMAEA)" may be applied to the product obtained by reaction of acrylic acid with DMAEA. Similarly, the polymers used herein may be referred to as a betaine polymer, a betaine-type polymer, or a polymer of a betaine, a betaine-type monomer of "an inner salt of the N-(2-carboxyethyl) quaternary" of the tertiary amine monomer from which the monomer is derived.

The monomeric betaines may be made by the reaction of tertiary amines of the formula



wherein the symbols are the same as designated above, with a lactone of the formula



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or derivatives of the lactone, having 3 to 7 carbon atoms in which one to four of the hydrogen atoms are replaced by alkyl groups having one to four carbon atoms. Examples of compounds of Formula II include:

(β -acryloxyethyl)dimethylamine
 dimethyl(β -methacryloxyethyl)amine
 (acryloxyethoxyethyl)diethylamine
 (acryloxyethoxyethoxyethyl)dibutylamine
 dimethyl[methacryloxyethyl(oxyethyl)₂]amine
 (β -methacryloxypropyl)dimethylamine
 [β -(β -methacryloxypropyloxy)propyl]dimethylamine
 N-(dimethylaminoethyl)-acrylamide,
 N-(dimethylaminoethyl)-methacrylamide,
 N-(dimethylaminopropyl)-acrylamide,
 N-(dimethylaminopropyl)-methacrylamide.

Examples of β -lactone compounds of Formula III include:

β -propiolactone,
 β -butyrolactone,
 β -valerolactone,
 β -iso-valerolactone,
 α -methyl- β -propiolactone,
 α -ethyl- β -propiolactone,
 β -isopropyl- β -propiolactone,
 β -isopropyl- β -propiolactone,
 β -methyl- β -valerolactone.

The reaction may be carried out in aqueous solution (in which case the quaternary ammonium hydroxide is formed by hydrolysis of the betaine) in the presence of an inert organic solvent, or simply by admixing the two reactants in the absence of any solvent or diluent. Preferably, an inert organic solvent is utilized since stirring of the reaction mixture and heat removal is thereby facilitated, and the tendency for the beta-lactone to polymerize is repressed. The specific nature and amount of the solvent used, if any, are not all critical since any polar or non-polar organic solvent may be used so long as it is capable of existing in the liquid state, and is substantially inert to the reactants under the conditions used. It is desirable that the solvent be volatile, preferably that it have a boiling point below 150° C. since it can then be more readily recovered and reused in the process. Specific inert solvents which are effective include benzene, toluene, pentanes, hexanes, and other liquid saturated aliphatic or aromatic hydrocarbons; chlorinated liquid derivatives of such hydrocarbons such as chlorobenzene and ethylene dichloride; liquid ethers such as diethyl ether, dipropyl ether, etc.; liquid esters such as methyl acetate, ethyl acetate, methyl propionate and the like; liquid organic nitriles such as acetonitrile, propionitrile, benzonitrile, etc.; and liquid ketones such as acetone, methyl ethyl ketone, etc. Liquid alcohols are also substantially inert to the reactants under the preferred conditions of the reaction (that is, at temperatures of -30° to 60° C.), despite the fact that alcohols do react with beta-lactones under other conditions. Accordingly, such alcohols may be employed as solvents if desired, examples of suitable alcohol solvents being methanol, ethanol, ethylene cyanohydrin, ethylene chlorohydrin, and especially tertiary alcohols such as tertiary butanol, and the like.

No special reaction conditions are necessary in order to carry out the reaction. The quantities of beta-lactone and tertiary amine employed are not critical but it is generally preferred to use equimolecular proportions of lactone and amine or an excess of the amine, for example, from 1 to 2 moles of amine for each mole of lactone.

The reaction is preferably carried out at atmospheric pressure and at a temperature in the range of -30° C. or lower to 100° C. or even higher, more preferably at 0° C. to 50° C. The reaction is exothermic and liberates heat, hence, it is unnecessary to supply heat externally but it often is desirable to cool the reaction mixture in order to maintain the preferred temperature. However, other temperatures and pressures may be used provided the

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reactants are maintained in the liquid condition during the reaction.

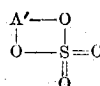
In carrying out the reaction of this invention, it is generally preferable to add the amine to a solution of the beta-lactone in water or one or more of the solvents listed hereinabove at such a rate about 1/2 to 5 hours are required for addition of the entire amount of amine, and with continued agitation of the solution during the addition. However, the beta-lactone may be added to a stirred solution of the amine in an organic solvent, or water, if desired, without affecting the fundamental course of the reaction to give a quaternary amine or any other procedure for bringing the reactants together in an organic medium at -30° C. to 60° C. is also effective. Slow addition of one reactant to the other, and agitation of the solution during reaction are both helpful in maintaining the desired temperature (since the reaction is exothermic and may generate sufficient heat to cause the temperature to rise considerably above 60° C. if heat transfer is not efficient) but are not critical expedients in themselves. The time during which the reactants must be left in contact is likewise not critical and will depend upon the total quantities of reactants being used; in general the reaction is quite rapid and is complete, as evidenced by cessation of heat evolution, within a short time after all of the two reactants have been brought into efficient contact with each other.

As the reaction proceeds, the product usually separates from the reaction mixture in the form of crystals which may be easily separated from unreacted amine and beta-lactone as well as the solvent, if any, simply by filtering. A product of high purity is obtained by recrystallizing the solid product from an organic solvent such as ethanol or methanol. However, other conventional methods of separation may also be used without seriously affecting the yield of the product obtained.

The monomeric sulfobetaines and their preparation are disclosed in Hwa Ser. No. 316,163, filed Oct. 14, 1963, now Pat. 3,497,482. As disclosed therein, they may be prepared by reacting an amine of the Formula II above with either a sultone of Formula IV or a cyclic sulfonate of Formula V:



(IV)



(V)

the symbol A' being as defined hereinbefore.

Examples of the alkane sultones of Formula IV include 1,2-ethane sultone, 1,3-propane sultone, 1,4-butane sultone, and the alkyl-substituted sultones such as 1-methyl-1, 3-propane sultone.

Examples of the cyclic sulfates of Formula V include ethylene sulfate, 1-methyl-ethylene sulfate, and 1,2-dimethylethylene sulfate.

The tertiary amine and the cyclic sulfo compound (of either Formula IV or Formula V) are generally used in equimolar proportions although a wide variation from equimolar proportions is permissible.

However, there is no need, and generally no advantage is obtained by using an excess of either reactant over the equimolar equivalent of the other reactant. The reaction may be effected merely by mixing the two reactants in bulk, the reaction occurring at room temperature or temperatures below or above room temperature. For example, 10° C. up to 80° C. or higher (depending on the boiling point of the solvent used) may be employed. Generally, temperatures from 30 to 70° C. are preferred. At elevated temperatures it is frequently desirable to use a polymerization inhibitor to prevent polymerization of the monomer produced during its preparation. Instead of gradually mixing the two reactants in bulk, they may be

mixed in any suitable solvent of inert character (in regard to the reaction) such as water, or such organic solvents as hydrocarbons (octane, heptane, benzene, toluene, xylene); esters such as ethyl acetate, butyl acetate, amyl acetate, β -hydroxyacetate, the methyl ether of β -hydroxyethyl acetate, 2-hydroxyethoxyethyl acetate; ketones such as acetone and methyl isobutyl ketone; nitriles such as acetonitrile; chlorinated hydrocarbons such as ethylene dichloride, chloroform, and carbon tetrachloride; ethers such as dioxane, ethyl ether, methyl isopropyl ether, and ethyl butyl ether, and alcohols having from 1 to 6 carbon atoms such as ethanol, methanol, isopropanol, tert-butanol, and cyclohexanol.

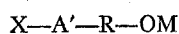
The products are generally crystalline solids which precipitate from the reaction medium except when that medium is water, an alcohol, or a mixture thereof. The product may be recovered from the solution in the latter case by evaporation of solvent.

An advantageous method of producing monomeric betaines is that disclosed and claimed in an application for U.S. Pat. Ser. No. 856,822, filed Sept. 10, 1969, of Norman Shachat, Richard Haggard and Sheldon Lewis entitled "Method of Producing Betaines, Monomers and Polymers Containing Betaine-Type Units and Novel and Useful Copolymers Thereby Obtained." This method involves the reaction of an amine of Formula II above with either acrylic acid or with a (C_1-C_8) alkyl acrylate and water, which reaction when the alkyl acrylate is used, liberates a (C_1-C_8) alcohol and the betaine.

Polymers containing betaine-type groups may then be prepared from the monomeric betaines and sulfobetaines thus obtained in conventional ways, using, for example, a free-radical catalyst. The polymerization may be effected as a solution polymerization, a suspension polymerization, an emulsion polymerization, or a precipitation polymerization. Any suitable free-radical catalyst may be employed, and especially water-soluble types when the polymerization is to be effected in aqueous media. In an aqueous system, whether involving solution or emulsion polymerization, it is desirable to operate at a pH of about 1.5 to 3.5, e.g. by adjustment with an acid, such as sulfuric acid. Examples of catalyst include hydrogen peroxide, ammonium persulfate, or an alkali metal persulfate. A redox system using such a persulfate with a reducing agent such as sodium hydrosulfite is quite useful. In solution systems involving organic solvents for the monomers and polymers, a free-radical initiator soluble in the particular medium may be employed such as benzoyl peroxide, lauroyl peroxide, tert-butyl peroxide, or hydroperoxide. The usual amounts of initiator may be employed such as from 0.1% to 6% on the weight of the monomer, and in the redox systems the persulfate may be employed in amounts of about 0.05 to 1% or so in conjunction with about 0.05 to 1% of sodium hydrosulfite. Chain-transfer agents and other molecular weight regulators may be used.

For imparting antistatic and/or soil-release properties to shaped articles, such as films or textiles respectively, a homopolymer or copolymer of a betaine of Formula I can be applied, and the application may be made in conjunction with a thermosetting aminoplast textile resin for enhancing durability of the antistatic and/or soil-release effects.

Besides direct polymerization of one or more betaines of Formula I with or without one or more other monomers, especially monoethylenically unsaturated monomers having a terminal group $H_2C=C<$, the polymers that are useful in accordance with the invention may be made from homopolymers or copolymers of an amine of Formula II above by reacting it with a suitable reagent, such as a lactone of Formula III above, a sulfone of Formula IV above, a cyclic sulfonate of Formula V above, or an alkali metal salt of a haloalkanoic acid of the following Formula VI:



(VI) 75

wherein

X is chlorine or bromine,

R is the same as defined hereinabove, and

M is an alkali metal, such as sodium, potassium, or lithium.

Examples of compounds of Formula VI are:

sodium α -chloroacetate
potassium α -bromoacetate
sodium β -chloropropionate
lithium 4-chlorobutyrate
sodium α -chloro- α -methyl propionate
sodium α -chloropropionate

This quaternization reaction may be effected in a polar solvent such as water, ethanol, acetonitrile, dimethylformamide, or glycol ethers such as ethoxyethyl hydroxyethyl ether or mixtures of one of these solvents with benzene or toluene at a temperature of 10° to 100° C. for a period of about two to twelve hours. The alkylating agent of Formula VI may be used in a quantity that is molarly equivalent to the total number of amine groups in the polymer to quaternize all of such groups. However, when there is more than 5 percent by weight of the monomeric units containing a quaternizable amine group, it is unnecessary to quaternize all of such amine groups and the amount of quaternizing agent may be less than the amount required to quaternize all of the amine groups in the polymer provided sufficient is used to provide 5 weight percent of quaternized monomeric units having Formula I in the final polymer.

Alternatively, the polymer or copolymer of an amine monomer of Formula II may be reacted with acrylic acid or with a (C_1-C_8) alkyl acrylate, preferably methyl acrylate, and water in the manner described in the aforementioned application Ser. No. 856,822. As in the quaternization reactions described in the preceding paragraph, the reaction with acrylic acid or with an acrylic ester and water may involve sufficient of the latter reagent to convert all of the amine units into betaine-type units in the polymer or only a portion thereof provided the resulting polymer contains at least 5 weight percent of the units of Formula I above.

The molecular weight of the betaine polymers should be at least about 5,000 and is preferably at least 10,000. It may be up to 100,000 or even up to 1,000,000 or several million in some instances, especially in the case of copolymers.

In accordance with the present invention, polymers that produce improvement in durability of soil release, anti-static and/or fungistatic properties when applied in conjunction with a thermosetting textile resin of aminoplast type are copolymers of (a) about 5 to 100% by weight of a betaine of Formula I above, (b) 0 to 95% by weight of an α,β -monoethylenically unsaturated acid and 0 to 95% by weight of other monoethylenically unsaturated monomers having a group of the formula $H_2C=C<$, such as a (C_1-C_8) alkyl acrylate, methyl methacrylate, acrylonitrile, styrene, vinyltoluene, methacrylic acid, itaconic acid, maleic acid, fumaric acid, the mono (C_1-C_4) alkyl esters of itaconic acid, maleic acid, or fumaric acid, acrylamide, methacrylamide, the N-methylol derivatives of the last two monomers, hydroxyethyl acrylate or methacrylate, hydroxypropyl acrylate or methacrylate, hydroxyl vinyl ether or sulfide or mixtures of any two or more of such comonomers. However, when relatively highly hydrophobic monomers, such as styrene, vinyltoluene, and acrylonitrile are used as comonomers, it is preferable that the copolymer contain at least 10% to 20% of the betaine-type monomers or of a mixture of the betaine-type monomer and acid monomer. While soil release is obtained when water-insoluble emulsion copolymers are used, it is preferred that the copolymers have some water-solubility for ease of application and optimum effect on soil release effect. Preferred copolymers with respect to the imparting of soil-release properties on tex-

tile fabrics generally, and especially those containing polyester fibers, are those containing copolymerized therein about 20 to 60% by weight of at least one Formula I betaine, 15 to 50% by weight of acid, such as acrylic acid and/or methacrylic acid, and 10 to 60% by weight of at least one other monomer, such as methyl acrylate.

Application of the betaine-type polymers, with or without an aminoplast, to provide antistatic, fungistatic, soil-release, and/or anti-soiling properties is generally beneficial on all types of fibrous materials, including fibers or fabrics of the natural fibers, such as cotton, silk, linen, and wool, and of the artificial fibers, such as regenerated cellulose (viscose or cuprammonium cellulose), cellulose esters, e.g., cellulose acetate, casein polyamides or nylons of all types, acrylonitrile polymers including its copolymers, (e.g., with vinyl acetate, methyl acrylate, and/or vinylpyridine), vinylidene chloride polymers including its copolymers with vinyl acetate, methyl acrylate, acrylonitrile and/or acrylic acid, methacrylic acid, or itaconic acid, vinyl chloride polymers including its copolymers with vinyl acetate or acrylonitrile.

The present invention is particularly directed to a process for imparting soil release and durable press characteristics to a textile material, especially one comprising linear polyester fibers which comprises applying thereto an aminoplast textile resin, a textile resin catalyst, and a betaine polymer which is stable under the conditions of application, and curing the textile resin. The polymer comprises at least 5 weight percent of betaine-type units, and the proportions of betaine polymer solids deposited on the textile material is from 0.25% to 30% and, preferably, from 0.5 to 15% by weight, based on the dry weight of the textile material.

The amount of soil release polymer in the pad bath may vary from about 2.5 to 40%. Preferably, the polymer solution or dispersion is adjusted to pH 4-5 with a mineral acid, such as H_2SO_4 , or base, such as NaOH, before preparation of the pad-bath solution or dispersion, or alternatively, the final pad bath solution or dispersion containing aminoplast, soil-release polymer, catalyst, and, if desired, softener and other textile modifiers is adjusted to pH 4-5 with mineral acid or base. If the polymer contains a considerable proportion of such highly hydrophobic units as styrene, vinyltoluene, or acrylonitrile, the pH is preferably above 5 such as from about 5.5 to 8.

Soil removal ability is improved on any organic substrate, especially those comprising hydrophobic fibers, such as linear polyester fibers, when the betaine polymer is applied thereto. Suitable substrates comprising polyester fibers, which should not be considered as limiting, may be prepared from paper, synthetic polymers, cotton, wool, mixtures of the above, etc. Products made from these materials include without limitation, wall paper; synthetic wall coverings; textile fabric wall coverings; lamp shades; automobile seat covers; automobile upholstery, e.g., door panels, overhead liners, etc.; upholstery for furniture; clothing; apparel accessories, e.g., ties, fabric belts, scarves, hats, etc.; canvas products, e.g. tents, folding cots, etc.; draperies; throw pillows; hassocks; sporting goods; fabric garment bags and luggage; fabric handbags; fabric shoes or shoes made from synthetic materials; linens; book covers; mattress covers; stuffed toys; hammocks; deck chairs, etc.

The term "textile material" comprising polyester fibers comprises polyester fibers with other fibers within the above definition, e.g., cotton, paper, linen, jute, flax, regenerated cellulose fibers, including viscose rayon, in the form of staple, yarn and fabrics. This invention is directed primarily and preferably to polyester and cellulosic containing textile fabrics either knitted, woven, or nonwoven, but preferably woven. However, the advantages of this invention can be achieved by treating the fibers, yarns, or threads employed to produce these fabrics.

Moreover, and more specifically, the process of the present invention is preferably used for treating textile ma-

terials containing both polyester and cellulosic and non-cellulosic fibers, especially, if the non-cellulosic fibers have minimum-care characteristics of their own. For example, the fabrics treated may be formed from a mixture of polyester, such as poly(ethylene terephthalate) and polyamide, such as poly(hexamethylene adipamide), or acrylic fibers, such as polyacrylonitrile and copolymers containing at least about 85% combined acrylonitrile, cotton or rayon. It should be pointed out, however, that textile material containing only non-cellulosic fibers such as those listed above is also within the scope of the present invention.

The soil-release properties of pure cellulosic fiber fabrics are much better than those of synthetic fiber containing fabrics, e.g. polyester fibers, in that, the synthetic fibers are generally hydrophobic and thus prevent the ingress of water that is necessary for cleaning the fabric and also possess an electrical charge that attracts soil particles. The present invention is therefore primarily directed to fabrics containing a substantial portion of synthetic hydrophobic fibers such as polyester fibers.

An aminoplast textile resin is also applied with the polymer. Very unexpectedly, it has been observed that when the textile resin and the betaine polymer are both applied to the textile material followed by subjecting the material to textile resin curing conditions, improved soil release is realized.

Hence, the present invention is also directed to a process for treating a textile material by applying thereto an aminoplast textile resin, a textile resin catalyst and a film-forming synthetic betaine polymer, said polymer containing at least 5 weight percent betaine and effecting the formation of a film around the fibers that make up the textile material while curing the textile resin.

The term "textile resin" according to the present invention includes both monomers and polymers which when applied to a textile material and reacted under proper conditions undergo polymerization and/or condensation and are transformed to the thermoset state. Textile resins that may be employed when practicing the present invention are the aminoplast resins. These nitrogen containing resins when applied to a textile material in the presence of a catalyst at temperatures of from 130° C. to about 200° C. are transformed into the thermoset state. The aminoplast resin condenses with the cellulose molecules and when vinyl groups are present in the aminoplast resin, it undergoes addition polymerization with itself and also with the cellulose molecule if irradiated. The cured textile resin on the textile material affords the textile material a durable press and/or wrinkle resistant characteristic.

Exemplary of the aminoplast resins that may be employed according to the present invention are the urea formaldehydes, e.g., propylene urea formaldehyde, dimethylol urea formaldehyde, etc.; melamine formaldehydes, e.g., tetramethylol melamines, pentamethylol melamines, etc.; ethylene ureas, e.g., dimethylol ethylene urea, dihydroxy dimethylol ethylene urea, ethylene urea formaldehyde, hydroxy ethylene urea formaldehyde, etc., carbamates, e.g., alkyl carbamate formaldehydes, etc., formaldehyde-acrolein condensation products; formaldehyde-acetone condensation products; alkylol amides, e.g., methylol formamide, methylol acetamide, etc.; acrylamides, e.g., N-methylol acrylamide, N-methylol methacrylamide, N - methylol - N-methacrylamide, N-methylmethacrylamide, N-methylol methylene-bis(acrylamide), methylene-bis(N-methylol acrylamide), etc.; haloethylene acrylamide; diureas, e.g., trimethylol acetylene diurea, tetramethylol - acetylene diurea, etc.; triazines, e.g., dimethylol-N-ethyl triazine, N-N' - ethylene-bis dimethylol triazine, halotriazines, etc.; haloacetamides, e.g., N-methylol-N-methylchloroacetamide, etc.; urons, e.g., dimethylol uron, dihydroxy dimethylol uron, etc.; and the like. Mixtures of aminoplast textile resins are also within the scope of the present invention.

The amount of aminoplast textile resin applied to the fabric is primarily determined by the ultimate use of

garments or articles prepared from the fabric. On durable press fabrics or garments, the amount of resin employed is preferably that which will afford good crease retention and flat dry properties while not adversely affecting the hand. For the purposes of the present invention, the amount of textile resin in the pad bath may vary between about 2 and 30%. Resin applied to the fabric should be in the range of about 2 to 20% based on the dry weight of the fabric and preferably in the range of about 4 to 9%.

Catalysts employed within the scope of the present invention depend upon the specific textile resin that is applied to the textile material. For instance, if the textile resin has a functional group that is reactive under acidic conditions, then an acid catalyst is used. Likewise, when a functional group is present that is reactive under alkaline conditions, then a base catalyst is used. Furthermore, both acid and base catalysts may be used when both type functional groups are present in the textile resin. In this instance, the catalysts may be added separately or together. When they are added together, one must be a latent catalyst, i.e., one that will not initiate its reaction during the opposite type reaction, but may be activated subsequently under proper catalytic conditions.

The catalysts useful in activating the acid or base reactive groups are those conventionally used to activate the reaction of textile resins containing the same group for reaction with hydroxy groups of cellulose. Preferably, latent acid or base acting catalysts are utilized, that is, compounds which are acidic or basic in character under the curing conditions. The most common acid acting catalysts are the metal salts, for example, magnesium chloride, zinc nitrate and zinc fluoborate and the amino-salts, for example, monoethanol-amine hydrochloride and 2-amino-2-methyl-propanol nitrate.

The base acting catalyst preferably is a compound which does not initiate substantial reaction between the base reactive group and hydroxy groups of cellulose under normal acid conditions, but does initiate substantial reaction under prescribed conditions, such as elevated temperature or some other activating means, as through use of another chemical compound. For example, an alkali metal sulfite can be padded onto the fabric and be decomposed into strongly basic alkali metal hydroxide by including small amounts of formaldehyde in the steam used for curing.

The latent base acting catalyst utilized herein preferably comprises alkali-metal salts, such as alkali-metal carbonates like sodium carbonate, which is neutral to mildly alkaline, for example, pH of about 8.5 on the fabric but decomposes at temperatures in excess of about 80° C. to form the stronger base sodium oxide which will initiate substantial reaction at the elevated temperatures utilized during curing. Sodium carbonate may be utilized if desired since the pH in the fabric produced by this compound in normal conditions is generally insufficient to initiate the desired degree of reaction under normal temperature conditions.

If fabrics containing a base reactive group are maintained at pH levels above about 10, however, degradation occurs, so that essentially neutral or mildly alkaline catalysts are preferred when base reactive compounds are utilized.

Additional base acting catalysts include potassium bicarbonate, potassium carbonate, sodium silicate, alkali metal phosphates, barium carbonate, quaternary ammonium hydroxides and carbonates for example, lauryl trimethyl ammonium hydroxides and carbonates and the like.

The amount of catalyst to be utilized is that conventionally used in activating the reaction between textile resins and hydroxy groups of cellulose, for example, up to about 15% by weight of an acid acting catalyst in the application bath with the preferred range being from about 1% to about 7%. A preferred range for the base acting catalyst is again the conventional amount and is generally

between about 0.2% to about 16%, preferably about 2 to 16%. The amount of catalyst to be utilized will further depend in part on the temperature at which the reaction is conducted and the amount of catalyst consumed in the reaction. For example, when base catalysts are utilized and if a highly acidic group is released during the reaction, the amount of base applied to the textile material should be at least sufficient to provide an excess of base in addition to that which is consumed by the highly acidic group.

The term "soil release" in accordance with the present invention refers to the ability of the fabric to be washed or otherwise treated to remove soil and/or oily materials that have come into contact with said material. The present invention does not prevent the attachment of soil or oily materials to the fabric, but hinders such attachment and renders the heretofore uncleanable fabric now susceptible to a successful cleaning operation. While the theory is still somewhat of a mystery, soiled, treated fabric when immersed in the detergent containing wash water experiences as agglomeration of the oil at the fabric surface. This water is basic in nature and it has been determined that soil release is best realized in wash water that is basic in nature. These globules of oil are then removed from the fabric and rise to the surface of the wash water. This phenomenon takes place in the home washer during continued agitation, but the same effect has been observed even under static conditions. In other words, a strip of polyester/cotton fabric treated according to the process of the present invention and soiled with crude oil, when simply immersed in a detergent solution will lose the oil without agitation. The oil just balls up on the fabric, dislodges therefrom, and rises to the surface of the solution.

An added feature of the present invention is the prevention of soil redeposition from the wash water. One of the greatest disadvantages of the synthetic polymers is the feature that even after removing the soil by washing, there is the continued danger that the soil will be redeposited onto the fibers from the wash water before the garment is removed therefrom. It has been observed that the soil release ability of the presently treated fabric diminishes after repeated washings. Even after the ability to remove soil from the fabric has diminished, however, the observation has been made that the prevention of redeposition of soil from wash water remains potent. This phenomenon likewise is unexplainable, but it has been established that the troublesome soil is negatively charged and presumably there remains enough acid on the fabric to repel the negatively charged soil.

Numerous of the substrates that may be treated according to the process of the present invention may not be feasibly removed from their environment and washed in a washing machine. Further, there are also substrates that may be treated which when subjected to the action of a washing machine are adversely affected either in structure or in looks. Articles within these classes may still be easily cleaned in place or otherwise by scrubbing the soiled area lightly with a solution of a commercial detergent and water.

The soil release polymer of the present invention is capable of forming a film around the fibers that constitute the textile material. Softness of the film is important, for if the film is too hard, the hand of the textile material is adversely affected. Further the film must have hydrophilic properties and yet be relatively insoluble in water. The film, if water soluble, would, of course, be easily washed from the fabric. Thus, it is ordinarily necessary that the soil release polymer have a molecular weight of at least about 5000 but may be as low as about 2000 to 3000 in some instances.

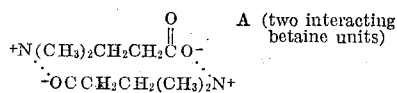
In summary, the shaped article, such as a textile fabric is treated with an aqueous solution containing (a) about 0.25 to 20% (preferably 0.5 to 15%) by weight of the betaine or (sulfobetaine) polymer, (b) about 2 to 20% by weight of an aminoplast, such as a ureaformaldehyde

or melamine formaldehyde or N,N'-ethyleneurea formaldehyde condensate, and (c) about ½ to 4% by weight, based on the weight of the condensate, of a catalyst for setting or curing the condensate. The treatment may be effected by spraying or immersion, such as in a textile pad at room temperature or up to 30° C. The treatment equipment, such as the pad, may be controlled to provide from 70 to 100% wet pick-up. The treated fabric may then be dried such as at room temperatures or at an elevated temperature up to about 120° C. To cure the resin and set the composition, the drying is preferably followed by a heating step, such as to about 130 to 200° C. for a period of ½ to 30 minutes, the longer times being used with lower temperatures.

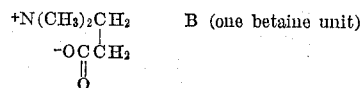
In using the betaine-type copolymers mentioned, the betaine and/or acid units therein cause the film on the treated materials to swell without being substantially dissolved. In the case of the preferred copolymers this swelling is drastic, on the order of 500-1000%. It appears that the swelling action that occurs during washing in aqueous media virtually expels the dirt by mechanical action from the interstitial spaces in the yarns of the fabric.

To some extent, carboxylic acid groups, if any are present in the soil release polymer, contribute to durability of polymer to washing. This may be attributed to anhydride formation or hydrogen bonding between acid groups an adjacent polymer chain segments, or reaction of such groups with aminoplast resin. However, in many cases, it has been found that physical and chemical interaction of carboxylic acid groups alone does not provide satisfactory durability to washing. For example, fabrics (65/35 polyester/cotton blends) treated with synthetic acid emulsion polymers in accordance with U.S. Pat. 3,377,249 can be made which have an excellent (4-5 Deering Milliken Rating) soil releasing effect which, however, endures only 10 to 15 washes. However, the treatment of fabrics of the same type with preferred compositions of the present invention have resulted in excellent soil-releasing effects after as many as 20 to 30 washes, and in many cases, the treated fabrics of the present invention have shown improvement in soil release even after as many as 50 washes. This unusual durability to washing may be attributed to the inclusion of betaine units in the polymers used.

With the understanding that applicants do not intend to be limited to any particular theories of action, the following explanations for excellent soil release and durability to washing of polymers containing betaine monomers are proffered. The betaine units, whether or not an aminoplast textile resin has been applied to the fabric with the polymer, may have some bonding action, either chemical or physical, with the fabric. This may be the result of ionic charges on the polymer chain that may favor such adherence by an ionic linking to a fabric substrate that develops an electric charge in aqueous wash solution. Furthermore, polymer may be insolubilized by intra- or intermolecular ionic crosslinking between betaine units on adjacent polymer chain segments. In those copolymers which contain neutral or non-ionic monomers such as the acrylic esters, in addition to betaine units, with or without acrylic acid units, the neutral and acid units, if any, apparently serve to dilute the concentration of betaine units within a given polymer chain. Such a dilution results in a lower probability of charge interaction between different betaine units and favors neutralization of charge by ion-pair formation within a given betaine unit, i.e.,



or more probably



It appears that the most effective soil release requires controlled swelling and controlled gradual, though slow removal of the soil release agent from the fabric during washing periods.

By selecting the concentration of diluting monomer in the soil release polymer, the extent of swelling and the rate of removal is readily controlled, the ease of removal being gradually increased by increase of the proportion of diluting monomer units, and the extent of swelling being increased by increasing the proportion of betaine units and, if any, of acid units. However, even when the release polymer contains few or no diluting units, repeated washings in alkaline detergent solutions cause the slow and gradual breaking of the ionic bonds between polymer chain segments and the polymer, even though initially having low swelling tendency, acquires the ability to swell satisfactorily, as a result of washing during use. Thus, when fabrics are treated with polymers low in diluting units (such as less than 10%), soil release may initially be of marginal character but gradually improves after the fabrics have been washed a number of times, especially if care is taken to avoid severe soiling or staining during the early period of use; after two to ten washes, depending on the particular soil release polymer, excellent soil release is generally obtained.

Soil release polymers containing betaine and acrylic acid monomers are preferably applied at an optimum pH which can be determined from the titration curves of the polymers. There are two inflection points in the titration curves. The first generally occurs in the pH 4-5 range for polymers containing betaine of Formula I and corresponds to complete neutralization of any strong acid present used for polymerization, as well as complete neutralization of the carboxylic acid groups of betaine units. (The carboxylic acid groups of betaine units are generally stronger acids than acrylic acid.) The second inflection point occurs at higher pH and corresponds to neutralization of acrylic acid in the copolymer backbone. Optimum soil release and durability to washing is generally obtained when the polymer is applied in such a manner that the carboxylic acid groups of the betaine units, but not those of acrylic acid, are neutralized. This generally corresponds to a pH range of 4-5. However, when the soil-release polymer contains relatively large proportions of highly hydrophobic units, as of styrene, acrylonitrile, etc., the use of higher pH values, such as from 6 to 8, may be preferred. Apparently, if betaine units are not neutralized prior to washing, the basicity of wash solutions is consumed first in neutralizing the acid groups of betaine units. These negatively charged groups immediately form ion pairs with positively charged nitrogen resulting in little additional net charge development on the polymer chain, and therefore, minimal electrostatic repulsion necessary for drastic swelling of polymer and effective soil release. In such cases, excellent soil release is sometimes not obtained until the fabric has been washed a number of times before severe soiling or staining. Each subsequent washing results in increased ionization of polymer until satisfactory swelling is obtained. On the other hand, if polymer is applied at too high a pH, too much acrylic acid is ionized before washing. Washing results in unnecessarily excessive swelling of polymer and rapid removal from the fabric substrate; initial soil release ratings are excellent, but poor soil release is obtained after fabrics are washed a few times.

In the illustrative examples which follow, the parts and percentages are by weight and the temperatures are in ° C. unless otherwise noted. The following procedure is the one used to evaluate the soil release properties of a fabric. An air-dry, 7 in. x 6 in., sample is stained with four soils, each in a different location on the sample:

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refined mineral oil (Nujol), used motor oil, spaghetti sauce (Ragu), and pepper sauce (Tabasco). These materials are left on the fabric for 30 min. The excess is then blotted and the fabric air-dried for 10 min. The samples are rinsed for 12 min. in cold water in the automatic washer to remove heavily caked-on soil and then laundered as described in the next paragraph with a 4 lb. ballast of terrycloth bath towels. The samples are then tumble-dried at the "hot" setting of a home laundry dryer and visually rated for soil release appearance using the Deering Milliken photographic standards for comparative purposes (col. 16, lines 13-15, of U.S. 3,377,249). A rating of 1 indicates essentially no removal and 5 complete removal of soil; 4 to 5 is excellent, 3 to 4, good. The average rating given is the average of the individual ratings of the four soiled areas.

The treated fabrics are washed once or repeatedly in an impeller-type automatic home laundry washer, each cycle with 16 gal. of water at 60° C., one cup of anionic detergent (Tide), and a ballast of 10 terrycloth bath towels. After various numbers of washes, samples are removed for the testing or evaluation of soil release performance at those stages, the results being summarized, for example, in Table I. In this fashion, the durability of soil-release properties in the treated fabrics are determined.

Example 1

(a) A mixture (about 23 parts) containing 49% of the betaine which is the N-(2-carboxyethyl) inner salt of dimethylaminoethyl methacrylate (DMAEMA), 31% of acrylic acid (AA) and 20% of methyl acrylate (MA) is added to 80 parts of water containing about 0.25 part of sodium isododecylphenoxypoly (40) ethoxy sulfate and is adjusted to a pH of 2.1 with sulfuric acid. Then 0.047 part of ammonium persulfate and 0.025 part of sodium hydrosulfite are added. The temperature rises and after the batch cools the product is a 21.3% solution of a copolymer of about 49% of the specified betaine, 31% of AA and 20% of MA having a viscosity of 7800 cps. (Brookfield Viscometer, 60 r.p.m.). Sodium hydroxide is added to adjust the pH to 4.5, the viscosity rising to 24,600 cps.

(b) A pad-bath solution containing a durable-press aminoplast resin and the soil-release polymer just described is prepared by mixing reagents at the following concentrations in water: 11% (solids) dimethylol-dihydroxy-N, -N'-ethylene urea (DMDHEU) (using a 45% aqueous solution), 6% $MgCl_2 \cdot 6H_2O$, 2% poly (20) ethylene glycol ester of oleic acid softener, and 5% (solids) of the 49% betaine/31% AA/20% MA copolymer of part (a) hereof. This pad-bath solution is applied to 65% Dacron/35% cotton shirting fabric (No. 7406 Test-fabrics, Inc.) to about 80% fabric wet pickup. The fabric is then dried at 110° C. for 5 min. on a tenter frame and then cured at 160° C. for 3 min.

This procedure is then repeated with conventional carboxylic-type soil release emulsion polymers, Polymers 1(b) and 1(c) in Table I, substituted for the betaine Polymer 1(a).

(c) Average soil release ratings of untreated fabric, fabric treated only with DMDHEU durable press resin, and fabric treated in a one-bath process with DMDHEU and the betaine polymer, Polymer 1(a), are listed in Table I. Also included in Table I are soil release ratings of fabrics treated in a one-bath process with DMDHEU and conventional carboxylic soil release polymers which do not contain betaine.

Soil release ratings of fabric treated with the betaine polymer are substantially better than those of untreated and DMDHEU-treated fabric. Not only is the initial soil release rating of fabric treated with the betaine polymer superior to those of fabrics treated with conventional carboxylic soil-release polymers. After about 10-20 washes, so much of the conventional soil-release polymers has

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been removed in washing that soil release ratings are only slightly better than those of untreated fabric whereas soil release ratings of fabrics treated with betaine polymer are substantially better than untreated fabric up to about 30 washes. It is clear, then, that the betaine polymer is substantially more durable to washing than the conventional carboxylic soil-release polymers.

Table I shows the soil-release ratings of the treated fabrics at various stages of the life of the fabric after treatment, that is, the life as determined by the number of washings to which the fabric is subjected before the stain-test, the rating obtained from which is reported.

TABLE I

Washes before evaluation by stain-test	Average soil release rating				
	Untreated	DMDHEU ¹	Polymer		
			1(a) ²	1(b) ³	1(c) ⁴
0.....	1.9	1.8	4.5	2.8	3.7
1.....	1.9	1.8	-----	2.6	4.1
4.....	1.9	1.8	4.5	3.4	4.2
9.....	2.0	1.9	4.5	3.2	3.4
14.....	2.0	1.9	4.3	-----	-----
19.....	2.0	1.9	4.1	2.9	2.6
24.....	2.0	2.0	3.6	-----	-----
29.....	2.0	2.0	3.1	2.8	2.8
34.....	2.9	2.0	2.7	-----	-----

¹ No polymer.

² Polymer 1(a) = 49% betaine/31% AA/20% MA.

³ Polymer 1(b) = 80% methacrylic acid (MAA)/20% ethyl acrylate (EA).

⁴ Polymer 1(c) = 33% MAA/17% methyl methacrylate (MAA)/50% EA.

(d) Similarly improved soil release properties are obtained when the copolymer used in part (b) above is replaced with each of the following copolymers:

(A) N-(2-carboxyethyl) inner salt of diethylaminoethyl acrylate (45%), methacrylic acid (30%) and butyl acrylate (25%).

(B) 60% N-(2-carboxypropyl) inner salt of 3-dimethylaminopropyl acrylate, 15% itaconic acid, and 25% styrene.

(C) 55% N-(2-carboxyethyl) inner salt of morpholinoethyl methacrylate, 25% monoethyl maleate, 20% acrylonitrile.

(D) 60% N-(2-carboxyethyl) inner salt of piperidinoethyl methacrylate, 25% acrylic acid, and 15% vinyl-toluene.

(E) 50% N-(2-carboxyethyl) inner salt of piperazinoethyl acrylate, 30% acrylic acid, 5% styrene, and 15% methacrylamide.

(F) 45% N-(2-carboxyethyl) inner salt of N-(dimethylaminoethyl)-methacrylamide, 30% acrylic acid, 25% methyl acrylate.

(G) 61% N-(2-carboxyethyl) inner salt of N-(diethylaminoethyl)-acrylamide, 35% monomethylitaconate, 4% N-methylolacrylamide.

(H) 50% N-(4-carboxyethyl) inner salt of N-(diethylaminoethyl)-acrylamide, 30% acrylic acid, and 20% methyl acrylate.

(I) 54% N-(3-sulfonopropyl) inner salt of dimethylaminoethyl methacrylate (see Ex. 1 of Hwa Ser. No. 316,163 filed Oct. 14, 1963, 27% acrylic acid, 19% ethyl acrylate).

(J) 60% N-(3-sulfonopropyl) inner salt of N-(3-dimethylaminopropyl)-methacrylamide (Ex. 2 of Ser. No. 316,163 supra), 20% acrylic acid, 20% styrene.

(K) 48% N-(2-sulfatopropyl) inner salt of N-(2-dimethylaminoethyl)-acrylamide (Ex. 6 of Ser. No. 316,163 supra), 20% acrylic acid, 32% methyl acrylate.

(L) 52% N-(2-sulfatoethyl) inner salt of dimethylaminoethyl methacrylate (Ex. 5 of Ser. No. 316,163 supra), 28% methacrylic acid, 10% methyl methacrylate, 10% ethyl acrylate.

(M) 5% N-(2-carboxyethyl) inner salt of dimethylaminoethyl methacrylate, 15% acrylic acid, 80% methyl acrylate.

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(N) 10% N-(2-sulfatoethyl) inner salt of dimethyl-aminoethyl methacrylate, 5% acrylic acid, 15% acrylamide, 70% ethyl acrylate.

(O) 85% N-(2-carboxyethyl) inner salt of dimethyl-aminoethyl methacrylate, 5% acrylic acid, 10% dimethyl-aminoethyl methacrylate.

Example 2

A series of polymers of varying betaine, acrylic acid, and methyl acrylate content prepared by the procedure described in Example 1(a) using different proportions of the same monomers are substituted for the betaine polymer in the procedure of Example 1(b). The pH of the polymers is adjusted to 4.5 before use. Average soil release ratings are listed in Table II.

TABLE II

Polymer	Average soil release rating			
	2(a)	2(b)	2(c)	2(d)
Washes before stain-test:				
0	2.6	4.2	4.4	4.1
1	2.5	3.6	3.5	3.4
4	3.0	3.7	3.9	3.4
9	4.3	3.7	4.0	3.7
14	3.8	4.3	4.3	4.1
19	3.7	4.0	4.3	3.8
24	3.6		3.6	4.0
29	3.5		4.0	3.5

Polymer 2(a)=61.4% betaine/38.6% AA.
Polymer 2(b)=40% MA/37% betaine/23% AA.
Polymer 2(c)=50% MA/31% betaine/19% AA.
Polymer 2(d)=60% MA/25% betaine/15% AA.

Example 3

(a) A series of copolymers containing betaine, acrylic acid, and methyl methacrylate (MMA) or ethyl acrylate (EA) are prepared as described in Example 1(a) and are substituted in the pad-bath formulation for the betaine polymer used in the procedure of Example 1(b). Average soil release ratings are listed in Table III.

TABLE III

Polymer	Average soil release rating					
	3(a)	3(b)	3(c)	3(d)	3(e)	3(f)
Washes before stain-test:						
0	4.7	5.0	5.0	4.9	5.0	4.9
1	4.4	4.8	4.4	4.3	4.9	4.4
4	3.7	4.1	3.8	3.5	4.0	4.0
9	3.9	4.2	4.1	3.7	4.2	3.7
14	3.7	4.1	3.8	3.6	3.7	3.7
19	3.8	3.1	3.0	3.0	3.6	2.9
24	3.9	2.9	2.9	3.2	4.0	3.1

Polymer 3(a)=20% MMA/58% betaine/20% AA/2% DMAEMA, pH=4.3.
Polymer 3(b)=30% MMA/51% betaine/17.5% AA/1.5% DMAEMA, pH=6.2.
Polymer 3(c)=40% MMA/44% betaine/15% AA/1% DMAEMA, pH=5.6.
Polymer 3(d)=50% MMA/36.5% betaine/12.5% AA/1% DMAEMA, pH=4.3.
Polymer 3(e)=20% EA/58% betaine/20% AA/2% DMAEMA, pH=4.5.
Polymer 3(f)=40% EA/44% betaine/15% AA/1% DMAEMA, pH=4.5.

(b) A homopolymer of the betaine used in Example 1 is substituted for the copolymer in the pad-bath formulation of Ex. 1(b) (5% being used as in Ex. 1(b)) and a Dacron/cotton fabric is treated with the resulting composition in the same manner as in Example 1(b). After 15 washes, the treated fabric showed progressive improvement in soil-release properties on each succeeding wash.

Example 4

The procedure of Example 1(b) is repeated with the exception that 100% cotton fabric (80² cotton fabric from Testfabrics, Inc.) is treated rather than 65% Dacron/35% cotton fabric. Average soil-release ratings are listed in Table IV, together with those of an untreated control fabric and the same cotton fabric treated only with DMDHEU durable-press resin.

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TABLE IV

	Average soil release rating			
	Untreated	DMDHEU ¹	Polymer	
			1(a) ²	2(a) ³
Washes before stain-test:				
0	2.3	2.4	3.4	4.6
1	2.3	2.2	3.1	4.5
4	2.3	2.2	3.7	3.6
9	2.7	2.2	3.6	3.6
14	2.7	2.3	3.7	3.0
19	2.7	2.3	3.7	3.0
24	2.7		3.8	2.7
29	2.7		3.6	2.9

¹ No polymer.

² Polymer 1(a)=49% betaine/31% AA/20% MA, pH=4.5.

³ Polymer 2(a)=61.4% betaine/38.6% AA, pH=6.0.

Example 5

The procedure of Example 1 is repeated with the exception that the pH of the polymer is adjusted with NaOH to pH 3.5 or 6.0 before mixing with the other components of the bath. Average soil release ratings are listed in Table V. If the polymer is adjusted to pH 6.0, initial soil release is excellent but durability is poor. If pH is adjusted to 3.5, durability is excellent but soil release is only moderately good throughout the series of 29 washes. These results may be compared with the excellent results obtained in Example 1 where the pH of the polymer is adjusted to 4.5. The results of this example emphasize the necessity of applying polymer at the proper pH in order to obtain optimum soil release and durability to washing.

TABLE V

	Average soil release rating	
	pH=3.5	pH=6.0
Washes before stain test:		
0	3.2	4.6
1	2.8	4.3
4	3.1	2.8
9	3.9	2.7
14	3.3	3.3
19	3.3	2.7
24	3.7	2.9
29	3.4	2.6

Example 6

A 49% betaine/31% acrylic acid/20% methyl acrylate copolymer is prepared as described in Example 1(a), except that the emulsifier is omitted. The pH of the solution copolymer is adjusted to 5.0 with NaOH before use. Addition of base resulted in an increase in viscosity to 20,000 cps. The appearance and viscosity of this polymer are equivalent to that obtained when the emulsifier is used in preparation.

Polymer is applied with durable press reagent to fabrics as described in Example 1(b). Average soil release ratings are listed in Table VI.

TABLE VI

Washes before stain-test:	Average soil release ratings
0	4.9
1	4.6
4	4.5
9	2.8
14	3.0
19	2.7

EXAMPLE 7

The procedure of Example 1(b) is repeated except that a dimethylol methoxyethyl carbamate durable press reagent is substituted on an equal solids basis for DMDHEU in the pad-bath formulation of Example 1(b). Average soil release ratings are listed in Table VII.

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TABLE VII

Washes before stain-test:	Average soil release rating
0 -----	4.4
1 -----	4.1
4 -----	4.3
9 -----	4.2

EXAMPLE 8

The 37% betaine/23% AA/40% MA and 25% betaine/15% AA/60% MA copolymers used in Example 2 are adjusted to pH 6.0 with NaOH and applied alone to 65% Dacron/35% cotton shirting (i.e., without DMDHEU) fabric using the pad-dry cure procedure described in Example 1(b). Average soil release ratings are listed in Table VIII.

TABLE VIII

Polymer-----	Average soil release rating	
	2(b)	2(d)
Washes before stain test:		
0 -----	3.7	3.1
1 -----	3.4	3.1
4 -----	3.4	3.3
9 -----	3.4	3.6

Polymer 2(b)=37% betaine/23% AA/40% MA, pH=6.0.
Polymer 2(d)=25% betaine/15% AA/60% MA, pH=6.0.

EXAMPLE 9

An 18% betaine/11.6% AA/70% MA copolymer is prepared in aqueous solution adjusted to pH 2.5 with sulfuric acid by a gradual addition redox process with 0.2% ammonium persulfate, 0.1% sodium metabisulfite and 1% emulsifier. The final product contains 19.8% solids and the viscosity is 29.5 cps. The pH of the copolymer is adjusted to 6.2 with NaOH before use. The procedure of Example 1(b) is repeated except this polymer is substituted for the betaine polymer used in Example 1(b). Average soil release ratings are listed in Table IX.

TABLE IX

Washes before stain-test:	Average soil release rating
0 -----	3.9
1 -----	3.9
4 -----	3.3
9 -----	3.6
14 -----	3.0
9 -----	2.8

EXAMPLE 10

65% Dacron/35% cotton shirting fabric is treated with the durable press reagent (DMDHEU) and the 49% betaine/31% AA/21% MA copolymer as in Example 1(a). The surface electrical resistivity is determined by the American Association of Textile Chemists and Colorists Test Method 84-1960 in order to estimate propensity for accumulation of static electricity. The results are shown in Table X. The fabric treated with betaine polymer shows lower resistivity and reduced tendency to develop charges under use conditions than the control.

TABLE X

	Surface resistivity at 76° F. (ohms)	
	9% relative humidity	40% relative humidity
Treated fabric-----	4.8×10^{13}	1.1×10^{10}
Untreated fabric-----	2.9×10^{14}	2.6×10^{13}

EXAMPLE 11

The resistance of fabric treated with betaine polymer in accordance with Example 1(b) to pickup of dry soil is evaluated as follows. Separate 4 in. x 4 in. cuttings of treated and untreated fabric are tumbled 20 min. at 76° F. in glass jars containing 6 rubber balls and 0.1 g. of vacuum cleaner soil which had been filtered through a

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100-mesh screen. After tumbling, excess soil is shaken off the samples, and clean swatches are then tumbled with the soiled samples for 20 min.

Weight changes and reflectance measurements are recorded for all samples. Reflectance measurements are made on a Photovolt (610) meter equipped with a blue filter and set at the late reflectance as a base point. Results in Table XI show that treatment of fabric with betaine polymer substantially reduces pickup of dry soil.

TABLE XI

	Treated fabric	Untreated fabric
Soil pickup, (g.):		
Soiled-----	0.0069	0.0092
Soil transfer-----	0.0022	0.0025
Reflectance (K/S) (0.000=white):		
Initial-----	0.012	0.009
Soiled-----	0.070	0.105
Soil transfer-----	0.021	0.025

EXAMPLE 12

Nylon taffeta fabric (No. 306A, Testfabrics, Inc.) is treated with the 49% betaine/31% acrylic acid/12% methyl acrylate copolymer of Example 1(a) using the pad-dry-cure process described in Example 1(b) except the pad-bath solution contains only the copolymer at 5% concentration. A 2.0% add-on (weight polymer/weight fabric) is obtained. At 76° F., 9% relative humidity, surface resistivity of the treated fabric is 4.4×10^{14} ohms, while that of an untreated control fabric is 1.4×10^{15} ohms.

Average soil release rating of treated fabrics is 5.0 compared with 4.5 for that of an untreated control fabric.

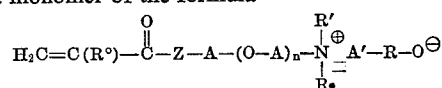
EXAMPLE 13

The process of Example 1(b) is repeated except a fabric of an acrylonitrile polymer (Orlon) (Type 81, No. 801 from Testfabrics, Inc.) is substituted for the polyester/cotton fabric and the reagents other than polymer and water are omitted from the pad-bath formulation. Average soil release rating of treated fabric is 4.8 compared with 3.0 for an untreated control fabric.

We claim:

1. A method for modifying a textile material which comprises applying to the material a liquid medium containing:

(a) an addition polymer of 5% to 100% by weight of a monomer of the formula



wherein

n is zero or an integer having a value of 1 to 10,

R° is H or methyl,

Z is $-\text{O}-$ or $-\text{NH}-$,

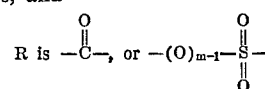
A is an alkylene group having 2 to 6 carbon atoms, at least two of which extend in a chain between the quaternary nitrogen atom and the adjoined Z radical when n is 0, and A , when n is 1 to 10, is a (C_2-C_3) alkylene group having at least 2 carbon atoms extending in a chain between O atoms or between an O atom and the adjoined N atom or Z radical,

R' is (C_1-C_4) alkyl,

R_2 is (C_1-C_4) alkyl, or

R' and R_2 may together form with the N atom a 5- to 6-atom ring, in which the atoms are C, N, or O, such as the morpholino, piperidino, and piperazino groups,

A' is a divalent saturated aliphatic hydrocarbon radical, such as alkylene, having 1 to 4 carbon atoms, and



wherein m is 1 or 2,

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(b) a thermosetting aminoplast condensate, and
(c) an acidic catalyst for setting the condensate, the application being controlled to deposit about 0.25 to 30% by weight of dry polymer on the weight of fibers in the textile, drying the treated textile and heating it to about 130 to 200° C. to set the composition thereon.

2. A method according to claim 1 for imparting soil release and durable press characteristics wherein the textile material comprises linear polyester fibers and the aqueous composition contains: about 2.5 to 40% by weight of the addition polymer, about 2 to 30% by weight of the thermosetting aminoplast condensate, and up to 15%, based on the weight of the condensate, of an acidic curing catalyst for the condensate.

3. A method according to claim 1 in which the addition polymer is a copolymer of 5 to 100% by weight of at least one monomer of Formula I, 0 to 95% by weight of at least one α,β -monoethylenically unsaturated acid, and 0 to 95% by weight at least one other copolymerizable monoethylenically unsaturated monomer.

4. A method according to claim 1 in which the addition polymer is a copolymer of 20 to 60% by weight of at least one monomer of Formula I wherein R is



15 to 50% by weight of at least one α,β -monoethylenically unsaturated acid, and 10 to 60% by weight of at least one other copolymerizable monoethylenically unsaturated monomer having a group of the formula $\text{H}_2\text{C}=\text{O}<$.

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5. A method according to claim 1 in which the textile material is a cellulosic fiber-containing material.

6. A method according to claim 1 in which the textile material is a blend of cotton and polyethylene glycol terephthalate fibers.

7. A textile material prepared according to claim 1.

8. A method according to claim 2 in which the addition polymer is a copolymer of 20-60% by weight of the N-(2-carboxyethyl) inner salt of dimethylaminoethyl methacrylate, 15-50% by weight of acrylic acid, and 10-60% by weight of methyl acrylate.

9. A textile material prepared according to claim 3.

10. A textile material having soil-release and durable press characteristics prepared according to claim 4.

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