

[54] **SOIL-RELEASE CHARACTERISTICS OF TEXTILE MATERIALS**

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[56]

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UNITED STATES PATENTS

2,754,280	7/1956	Brown et al.	8/115.6 X
2,810,624	10/1957	Wardell	8/115.6 X
2,868,748	1/1959	Frazier et al.	8/115.6 X
2,977,665	4/1961	McElrath	8/115.6 X
3,125,405	3/1964	Gardon	8/116.3
3,125,406	3/1964	Herman	8/116.3
3,152,920	10/1964	Caldwell et al.	8/115.6 X
3,236,685	2/1966	Caldwell et al.	8/115.6 X
3,377,249	4/1968	Marco	8/115.6
3,434,161	3/1969	Walsh	8/116.3

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[57]

ABSTRACT

The soil-release properties imparted to textile materials through treatment with a copolymer containing acidic groups are enhanced by utilizing an ethoxylated alkyl phenol in conjunction with the copolymer. Conventional cross-linking agents and modifying resins may also be used.

12 Claims, No Drawings

SOIL-RELEASE CHARACTERISTICS OF TEXTILE MATERIALS

This invention relates to a process for treating a substrate to impart a soil-release characteristic thereto, and to products produced thereby. Preferably, the present invention relates to a process for imparting soil release to a textile substrate.

The genesis of synthetically produced textile fibers has brought about a tremendous effort in the textile industry along numerous avenues. There has been much research effort directed to the improvement of these synthetic fibers per se, and improved blends of synthetically produced fibers with natural fibers, i.e., cellulosic fibers or keratinous fibers. Results of this research have been successful and the direction of research has been diverted from the synthetic polymer per se and/or blends of said polymers with other naturally occurring fibers. Of recent, fiber research has been directed towards improving physical characteristics of fabric produced from synthetic fibers and/or blends of these synthetic fibers with naturally occurring fibers, and, more specifically, to the physical characteristics and/or endurance properties of garments produced from synthetic fabrics and/or fabric produced from blends of synthetic fibers and naturally occurring fibers.

Tremendous effort has ensued towards achievement of a garment containing synthetic and naturally occurring fibers such that creases in the garment are very durable and are not appreciably affected by wear or cleaning processes. In other words, after repeated washings and/or dry cleaning, the creases remain in the garment in a substantially unaltered condition and further treatment of the garment, i.e., pressing, is not required for maintenance of the crease. Likewise, much effort has been expended towards the attainment of good wash-and-wear fabric.

Additionally, further research has been directed to the attainment of a garment having improved soil-release properties. Numerous of the synthetically produced fibers that are presently being incorporated in blends with naturally occurring fibers have a propensity to accept and retain oily grime and dirt. Accordingly, when the garment is being worn the soil and/or oily materials accumulate on the garment and settle in the fabric. Once the garment becomes soiled, it is then subjected to a cleaning process for removal of the dirt and/or oily deposits, and only a drycleaning process will successfully clean the garment.

The cleaning process normally employed, however, is washing in a conventional home washing machine by the housewife. During a wash cycle, it is virtually impossible to remove the soil and/or oily stains from the garment and, secondly, assuming that the undesirable materials are removed from the garment or a fairly clean garment is being washed, soil remaining in the wash water is redeposited onto the garment prior to the end of the wash cycle. Hence, when the garment is removed from the washing machine and subsequently dried, it has not been properly cleaned. Such a condition, heretofore unavoidable, is quite disadvantageous in that the garment after being worn never again assumes a truly clean appearance, but instead tends to gray and/or yellow due to the soil and/or oily materials deposited and remaining thereon. Further use and washing of the garment increases the intensity of the graying to the point that ultimately the garment is unacceptable for further wear due to its discoloration. The process of the present invention solves the soiling problem as hereinafter described.

In attempting to solve the problem of soiling in the synthetic fabrics and blends containing synthetic fabrics, a substantial amount of research has been conducted and numerous patents have issued as a result thereof. None of these patents, however, disclose subject matter as relevant to the problem as is instantly set forth herein. Strong basis of this fact is evidenced by the absence from the market of a product that may be easily cleaned so as to remove soil and alleviate redeposition of soil from the wash water. Antisoiling research has been directed along two general avenues, one of which utilizes inorganic materials and the second employing the utilization of or-

ganic materials. Set forth below is a brief summary of prior efforts.

U.S. Pat. No. 2,999,774 to Schappel features the utilization of silica particles and a salt of a multivalent metal for the purpose of rendering a fabric soil-resistant. U.S. Pat. No. 2,734,835 to Florio et al. employs at least two hydrous table metal oxides selected from aluminum, silica, titanium, beryllium, cerium, cobalt, germanium, manganese, tin, zinc and zirconium. U.S. Pat. No. 3,089,778 to Pierce et al. teaches the utilization of a water-insoluble basic aluminum salt having an ultimate particle size of less than 0.5 microns. U.S. Pat. No. 2,992,943 to Coover et al. while not purely related to inorganic materials is directed to prevention of dry soiling only. In other words, the Coover et al. treatment dictates the use of a water-soluble compound (an alkyl titanate and an organic solvent) and therefore to obtain the desired soil-resistant properties only a drycleaning process may be employed.

The organic approach to the soiling problem of synthetic-fiber-containing fabrics includes the following patents and their teachings. It should be noted, however, that some of the patents incorporated in the following group are not per se directed to reducing the soiling propensity of the synthetic-fiber-containing fabric.

U.S. Pat. No. 3,236,685 to Caldwell et al. renders a fabric antistatic and soil-resistant by coating a fabric with a solution or solutions containing a polymeric acid defined as containing $-\text{COOH}$, $-\text{SO}_3\text{H}$ and/or $-\text{PO}_4\text{H}_2$ groups. Additionally, a compound containing a polyol or a compound having incorporated therein epoxide groups is included which under proper conditions reacts with the acid to form an ester. U.S. Pat. No. 3,152,920 also to Caldwell et al. is a complement of the above patent wherein, instead of reacting the polymeric acid with a polyol or an epoxide, the polymeric acid is reacted with the reaction product of a polyol and a polyisocyanate. U.S. Pat. No. 3,125,405 to Gardon is directed to the manufacture of a permanent-press garment. N-methylol acrylamide is applied to the fabric with a free radical acid catalyst and the N-methylol acrylamide is cross-linked with the cellulose molecule. Additionally, extra monomers and polymers are as set forth in the patent which may be incorporated in the treating solution. U.S. Pat. No. 3,246,946 to Gardon likewise is directed to the production of durable-press garments. N-methylol acrylamide is employed in conjunction with one or more condensates of an aldehyde and a free radical acid catalyst whereby the reactants are cross-linked with the cellulose molecule. Extra monomers and polymers may be added to the treating solution. U.S. Pat. No. 3,090,704 to Collins et al. is directed to a terpolymer for rendering the fabric soil-resistant. The terpolymer consists of (1) a compound having incorporated therein a cross-linking component, (2) a compound having incorporated therein an anionic component, e.g., an alkali metal salt of an aromatic sulfonic acid, and (3) a compound having a component therein that contains a strong nonionizable, nonhydratable permanent or induced dipole. U.S. Pat. No. 2,876,141 to Matthews employs a solution containing (1) mineral oil, (2) base cordage oil, (3) oleic acid, and (4) a cationic wetting agent, e.g., trimethyl- β -oleamidoethyl ammonium sulfate in an effort to improve the soil resistance of the fabric treated.

The above brief abstracts are set forth to provide an indication of prior research effort directed to attaining a soil-resistant fabric or a fabric having soil-release properties. The problem heretofore confronted with fabrics having incorporated therein synthetic fibers has been that the synthetic fibers while hydrophobic are oleophilic and therefore whereas oil and grime may become embedded in the fiber, its hydrophobic properties prevent water from entering the fiber to remove the contaminates therefrom. The efforts of this invention have been directed to the modification of the properties of synthetic and/or natural fibers in such a manner that the soil and oily contaminates may be easily removed.

Additionally, by incorporating the process of the present invention with that of a process to render a garment resistant to

creasing, a garment is produced that has both durable-press and soil-release properties. In other words, the ultimate garment is a utopia for the consumer and for the housewife who is confronted with the problem of rendering the garment clean for further wearing.

In view of the above comments it should be evident to one skilled in the art that the problem confronted has been that of rendering a garment clean if the garment contains synthetic and/or natural fibers as described herein. Accordingly, by virtue of the teachings of the present invention, the problems historically present with the use of garments having incorporated therein both cellulosic fibers and synthetically produced fibers are alleviated.

It is therefore an object of the present invention to provide a substrate having soil-release properties.

Still another object of the present invention is to provide a process for treating a substrate whereby said substrate easily releases soil when contacted with a detergent solution.

Still further another object of the present invention is to treat a substrate in such a manner that after said substrate is soiled and subjected to washing, less soil and grime from the wash water will be redeposited thereon.

A further object of the present invention is to provide a durable-press fabric having soil-release properties.

Another object of the present invention is to provide a process for treating a fabric in such a manner that it has both durable-press and soil-release properties.

Still another object of the present invention is to treat fabric in such a manner that after a garment produced therefrom is soiled and subjected to washing, soil and grime from the wash water will not be redeposited onto the garment.

Still further another object of the present invention is to provide a treatment for fabric such that garments produced therefrom will not become discolored due to repeated wearing and washing.

Another object of the present invention is to treat fabric in such a manner that a garment produced therefrom has excellent wash-and-wear and soil-release properties.

These and other objects may be readily seen from the following detailed description of the present invention.

Generally speaking, the present invention relates to a process for treating a substrate comprising applying thereto a film-forming synthetic acid polymer and a condensation product of ethylene oxide and an alkyl phenol, said condensation product being employed in an amount equivalent to about 1 to 10 percent by weight of the application emulsion, and effecting the formation of a film on said substrate.

Soil removal ability is improved on an organic substrate when the acid polymer and condensation product are applied thereto. Suitable substrates, 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.

Textile materials are preferred substrates and those which can be treated according to the process of the invention are those in which the anhydroglucose molecules are chemically substantially unmodified. The term "textile material" thus comprises 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 cellulosic containing textile fabrics either knitted, woven, or nonwoven, 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 materials containing both cellulosic and noncellulosic fibers, especially, if the noncellulosic 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), polyamide such as poly(hexamethylene adipamide) or acrylic fibers, such as polyacrylonitrile, and copolymers containing at least about 85 percent combined acrylonitrile filaments or fibers, with cotton or rayon. It should be pointed out, however, that textile material containing only noncellulosic 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 polyester fibers are 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 most primarily directed to fabrics containing a substantial portion of synthetic fibers, but is not limited thereto. Instead, it has been determined that the present process can be very successfully employed with cellulosic fabrics, fabrics containing synthetic fibers and cellulosic fibers, and fabrics containing only synthetic fibers.

In many instances when the substrate is a textile material, an aminoplast textile resin will also be applied with the acid polymer. Very unexpectedly, it has been observed that when the textile resin, the acid polymer and ethoxylated alkyl phenol are 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 comprising applying thereto an aminoplast textile resin, a textile resin catalyst, a film-forming synthetic acid polymer and a condensation product of ethylene oxide and an alkyl phenol, said condensation product being present in the amount of about 1 to 10 percent by weight of the application emulsion, and said acid polymer comprising at least 10 weight percent acid calculated as acrylic acid; and effecting the formation of a film around the fibers making up the textile material and curing of 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

Additional base-acting catalysts include potassium bicarbonate, potassium carbonate, sodium silicate, alkali metal phosphates, such as sodium or potassium 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 percent by weight of an acid-acting catalyst in the application bath with the preferred range being from about 1 percent to about 7 percent. A preferred range for the base-acting catalyst is again the conventional amount and is generally between about 0.2 percent to about 16 percent, preferably about 2 to 16 percent. 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 per se 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 an 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 those 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 will also be hereinafter referred to as an "acid polymer." This acid polymer may be selected from a large number of synthetically produced compounds provided certain limitations are met. The acid polymer employed must be 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 be at least partially insoluble in water. The film, if water-soluble, would, of course, be easily washed from the fabric. The polymer from which the film is formed may, however, be water-soluble if applied with a textile resin, for during the curing process, the polymer if water-soluble, is transformed to a water-insoluble film. Furthermore, when the acid polymer is applied to a substrate without a textile resin, it may likewise be water-soluble if the substrate is such that the soil removal is only required once. Acid content of the film is likewise important and at least 10 weight percent of the acid polymer from which the film is formed must be acid-calculated as acrylic acid and preferably at least 20 weight percent. The results obtained from using acid polymers containing 10 weight percent acid give improved results as may be seen from Table III. For commercial acceptance, however, these should preferably be at least 20 weight percent acid in the soil-release polymer calculated as acrylic acid. Again reference is made to Table III. It has further been observed that all of the acid polymers that afford soil release have a carbon atom to acid group ratio in the repeat group in the range of 2:1 to 30:1, and that an air-dried film cast therefrom has a water of imbibition of at least 89 percent.

Synthetically produced acid polymers within the scope of the present invention may be prepared from any of the polymerizable organic acids, i.e., those having reactive points of unsaturation. These polymers may be homopolymers of the acids, or interpolymers of the acid and other monomers copolymerizable therewith so long as at least 10 weight percent acid monomer is present in the polymer. Exemplary of polymerizable acids that may be used are acrylic acid, maleic acid, fumaric acid, methacrylic acid, itaconic acid, crotonic acid, cinnamic acid, polymerizable sulfonic acids, polymerizable phosphoric acids, etc. Monomers that may be interpolymerized with the acids include any monomers capable of copolymerizing with the acids and which will not detrimentally affect the film-forming properties of the polymer. Suitable monomers include, esters of the above acids prepared by reacting the particular acid with an alkyl alcohol, e.g., ethyl acrylate, methyl acrylate, propyl acrylate, isopropyl acrylate, methyl methacrylate, ethyl methacrylate, 2-ethylhexyl acrylate, butyl acrylate, etc.; alkyl fumarates, maleates, crotonates, cinnamates, etc.; vinyl halides; monomers having vinylidene groups; e.g., styrene, acrylonitrile, methylstyrene; substituted vinyl monomers, e.g., chlorostyrene; butadiene, etc. In all of the polymers prepared from the above-listed monomers, there must be at least 10 weight percent acid calculated as acrylic acid. It should be noted that various mixtures of the above polymers will work according to the process of the present invention and hence should be considered within the scope of the present invention. Furthermore, salts of the acid polymers, e.g., sodium, potassium, lithium, ammonium, etc., will afford the desired soil-release characteristics.

Examples of some of the synthetic acid polymers that may be used according to the present invention are polymerization products of:

ethyl acrylate:acrylic acid
ethyl acrylate:acrylic acid:acrylamide
butyl acrylate:acrylic acid
ethyl acrylate:methacrylic acid
ethyl acrylate:itaconic acid
methyl methacrylate:acrylic acid
2-ethyl hexyl acrylate:acrylic acid
butyl acrylate:acrylic acid:acrylamide
ethyl acrylate:acrylic acid:N-methylol acrylamide
ethyl acrylate:acrylic acid:styrene
ethyl acrylate:acrylic acid:hydroxy propyl methacrylate
ethyl acrylate:acrylic acid:divinyl benzene
ethyl acrylate:acrylic acid:allyl acrylamide
ethyl acrylate:acrylic acid:glycidyl acrylate
ethyl acrylate:itaconic acid

ethyl acrylate:sodium styrene sulfonate
 ethyl acrylate:crotonic acid
 styrene:acrylic acid
 ethyl acrylate:acrylic acid:hydroxy ethyl methacrylate
 hydroxy ethyl methacrylate:acrylic acid:acrylamide
 butyl acrylate:ethyl acrylate:acrylic acid
 and the like.

Some acid polymers work better than others, however, and these are preferred. Examples of the preferred acid polymers includes (1) copolymers of ethyl acrylate and acrylic acid that are prepared by polymerizing a comonomer mixture of from about 50 to 80 parts of ethyl acrylate and about 20 to 50 parts of acrylic acid; (2) copolymers of propyl or isopropyl acrylate and acrylic acid wherein the copolymers are prepared by polymerizing a monomer mixture of from about 40 to 57 parts propyl or isopropyl acrylate and about 43 to 60 parts of acrylic acid; (3) copolymers of butyl acrylate and acrylic acid prepared by polymerizing a comonomer mixture of from about 30 to 70 parts of butyl acrylate and about 70 to 30 parts of acrylic acid; (4) copolymers of 2-ethyl-hexylacrylate and acrylic acid prepared by polymerizing a comonomer mixture of from about 10 to 40 parts of 2-ethyl hexyl acrylate and about 60 to 90 parts of acrylic acid; (5) copolymers substantially identical to the ones listed above with the exception that methacrylic acid is substituted for acrylic acid and the esters are methacrylates instead of acrylates; (6) a copolymer of ethyl acrylate and itaconic acid prepared by polymerizing a monomer mixture comprising about 70 parts ethyl acrylate and about 30 parts itaconic acid; (7) copolymers of the acrylic acid set forth above wherein the acrylates are substituted by methacrylates; (8) a copolymer of acrylamide and acrylic acid prepared by polymerizing a monomer mixture comprising about 10 parts acrylamide and about 90 parts acrylic acid; and (9) terpolymers comprising ethyl acrylate, acrylic acid and acrylamide prepared from monomer mixtures of ethyl acrylate, at least 10 parts acrylic acid and up to 20 parts acrylamide.

The acid polymers suitable for use in practicing the present invention form a hydrophilic film upon drying and afford soil release ability at that point. For unknown reasons, further treatments and/or ingredients will enhance the soil-release ability of the substrate. If the substrate having the acid polymer thereon is subjected to textile resin curing conditions, the durability of the soil-release ability is enhanced. Likewise, the presence of a textile resin catalyst during the textile resin curing conditions further improves soil-release ability. Still further, the soil-release finish is much more lasting on a substrate when the acid polymer is subjected to textile resin curing conditions in the presence of an aminoplast textile resin. It is known that the film covers the hydrophobic synthetic fiber contents of the textile material without any reaction therewith. What is not understood, however, is the durability of the soil-release characteristic. While it is known that there is some reaction between the acid polymer and the textile resin, the reaction mechanism is very speculative. Furthermore, there may be some cross-linking between the cellulose molecules and the acid polymer or there may be just an enhanced physical bond between the textile resin and the acid polymer above and beyond their reactivity.

Soil-release polymers, like the textile resins, give some improvement at very low levels on the fabric. Accordingly, as the amount of soil-release polymer is increased, the ability of the fabric to release soil increases. Thus, the upper limit on the amount of soil-release polymer is determined by economics and resulting adverse effects on the fabric, e.g., the hand of the fabric. Furthermore, practically speaking there is a set range of soil-release polymer indicated by commercial success.

The acid polymers, as a general rule, are emulsion polymers containing varying amounts of solids, normally in the range of about 25 to 50 weight percent. The polymer emulsion should be present in the pad bath or other application medium in the range of about 2.5 to 40 weight percent. Otherwise stated, there should be from about 0.25 to 5.0 weight percent of acid

polymer solids applied to the substrate, based on dry weight, and preferably 1.0 to 1.5 weight percent.

The above-defined acid polymers afford a good soil-release characteristic to a substrate. It has now been very unexpectedly discovered that when certain amounts of condensation products of ethylene oxide and an alkyl phenol are added to the pad bath or are otherwise applied to the cellulosic containing fabric with the acid polymer, a substantially improved soil-release ability is realized.

These condensation products act synergistically with the acid polymers and simultaneously therewith assist in stabilizing the pad bath emulsion. While normally these condensation products are employed as surfactants, they are employed here in greater proportions, and all surfactants do not add to the soil-release ability. It has been discovered that only a very limited number of surfactants add to the soil-release ability and these are certain of the condensation products of ethylene oxide and an alkyl phenol.

Among the ethylene oxide, alkyl phenol condensates that add to the soil-release characteristics are those where the alkyl group contains from three to 14 carbon atoms. Additionally, there should be at least 3 moles of ethylene oxide per mole of alkyl phenol and preferably at least 8 moles of ethylene oxide per mole of alkyl phenol.

Exemplary of suitable condensates that act synergistically with the acid polymer are reaction products of the following: 3.5 moles of ethylene oxide per mole of propyl phenol; 8.0 moles of ethylene oxide per mole of nonyl phenol; 7.5 moles of ethylene oxide per mole of hexyl phenol; 9.5 moles of ethylene oxide per mole of nonyl phenol; 10.0 moles of ethylene oxide per mole of dodecyl phenol; 5.0 moles of ethylene oxide per mole of heptyl phenol; 6.5 moles of ethylene oxide per mole of butyl phenol; 4.0 moles of ethylene oxide per mole of isopropyl phenol; 6.0 moles of ethylene oxide per mole of 2-ethyl hexyl phenol; 9.0 moles of ethylene oxide per mole of nonyl phenol; 5.5 moles of ethylene oxide per mole of octyl phenol; 7.0 moles of ethylene oxide per mole of octyl phenol; 10.0 moles of ethylene oxide per mole of nonyl phenol; 11.0 moles of ethylene oxide per mole of tetradecyl phenol; and 9.0 moles of ethylene oxide per mole of propyl phenol; 30.0 moles of ethylene per mole of nonyl phenol; 20.0 moles of ethylene per mole of octyl phenol; etc.

The pad bath solution should contain at least one percent of the ethylene oxide, alkyl phenol condensate. The soil-release ability of the treated textile material improves directly with the amount of condensate in the pad bath. Practically speaking, however, the upper limit on the amount of condensate to be added to the pad bath is determined by the hand of the textile material. Around 10 weight percent, the material becomes very sticky. Preferably, therefore, the amount of condensate product added to the pad bath ranges from about 1 to 10 weight percent and most preferably from about 1.5 to 3 weight percent.

The solution used to impregnate the textile material according to the present invention is not limited to including only the possible ingredients heretofore mentioned, e.g., textile resin, textile resin catalyst acid polymer and ethoxylated alkylphenol. In addition, other ingredients may be employed such as, for example, softeners, etc., and numerous other compounds that enhance the physical characteristics of the fabric. The solution may be applied to the substrate in any suitable manner. For instance, padding of the solution onto fabric is preferred because of ease of operation at that particular stage of the development. The ingredients may be sprayed on as liquids; the substrate may be treated with vapors of the compounds if convenient; the substrate may be dipped, etc.

In general, the applicator system is adjusted to provide from 30 to 100 weight percent wet pickup by the fabric from the pad bath. Preferably, however, it has been determined that best results are obtained by providing a wet pickup of from 40 to 60 weight percent from the pad bath.

When the aminoplast textile resin is applied to the substrate, e.g., textile material, along with the acid polymer and ethoxy-

lated alkyl phenol they may be simultaneously applied from the same pad bath. Simultaneous application is not required though and the same results may be realized by first applying the soil-release polymer and ethoxylated alkyl phenol followed by separate application of the textile resin and curing of the textile resin. Insofar as separate application is concerned, however, where the textile resin is applied first and cured and the soil-release polymer and ethoxylated alkyl phenol are added separately thereafter, initial soil-release ability is outstanding, but not nearly so durable as the simultaneous application or the separate addition where textile resin, soil-release polymer and ethoxylated alkyl phenol are present during curing of the textile resin.

According to the desires of the individual, and the dictates of the ultimate product, separate or simultaneous application of the textile resin, the ethoxylated alkyl phenol and the soil-release polymer may be employed. For instance, when treating a textile fabric which is to be converted into work clothes, it would be desirable to have as durable a finish as possible so that the soil-release properties will be as long lasting as possible. In this situation, either a simultaneous addition or a separate addition where the ethoxylated alkyl phenol and soil-release polymer are added first would be desired. On the other hand, where the ultimate article of manufacture is not one that will be washed or cleaned on a weekly basis, for instance, the desirable property might possibly be to have a very superior initial soil-release property. An example would be upholstery for automobiles, seat covers, wall coverings, etc. For these items it may be more desirable to first apply the textile resin and separately after curing of the textile resin apply the soil-release polymer and ethoxylated alkyl phenol or just apply the soil-release polymer, etc., as described herein, if a textile resin is not desired. It must be emphasized, however, that under such conditions the soil-release properties are less durable than those attained by the aforesaid simultaneous means of application.

Advantages afforded by the process of the present invention are available for substrates treated in almost any form, e.g., films, sheets, fibers, yarns, threads, fabrics or the ultimate product, e.g., a garment, etc. The presensitizing embodiment, i.e., the textile resin treatment, when employed is most advantageously conducted on substrates in the fabric, etc., form.

Garments made from the fabrics treated according to the process of the present invention require no additional steps than normal for the preparation of the conventional durable-press garments. In other words, the garment may be folded and pressed on conventional equipment, for example, a Hoffman press. The pressing cycle utilized is standard in the industry and generally involves pressing of the garment for a short period of time, followed by a curing operation in an oven. Alternatively, the garment may be set in a desired configuration under hot, dry conditions, such as by hot pressing without steaming, for example, at temperatures of up to about 200 C. for as long as necessary to cure the resin.

In general, the textile resin when employed may be selected from several general types. According to the type resin selected, one of the following processes may be generally followed to achieve the novel garments produced by the present invention. In each type procedure, the methods of application and order of application of textile resin soil-release polymer, ethoxylated alkyl phenol, catalysts, etc., may be varied as described supra.

TYPE I

1. Apply textile resin having one type functional groups, textile resin catalyst, soil-release polymer and ethoxylated alkyl phenol to fabric.
2. Dry fabric at temperatures that is insufficient to initiate catalysis of the textile resin.
3. Make garment from fabric.
4. Press garment to produce creases where desired.
5. Subject garment to temperature sufficient to catalyze and cure the textile resin.

TYPE II

1. Apply textile resin having more than one type of functional groups, textile resin catalysts for each type functional group, soil-release polymer and ethoxylated alkyl phenol to fabric.
2. Subject fabric to conditions whereby one type of functional group reacts and remaining functional groups remain dormant.
3. Prepare garment from the fabric.
4. Press creases where desired in garment.
5. Subject fabric to conditions whereby the remaining functional groups are reacted with the cellulose.

TYPE III

1. Apply textile resin having more than one type of functional groups, one type being sites of ethylenic unsaturation, a textile resin catalyst, a soil-release polymer and an ethoxylated alkyl phenol to the fabric.
2. Dry the fabric at temperatures such that the textile resin catalyst remains dormant.
3. Subject the fabric to irradiation.
4. Make a garment from the fabric.
5. Product desired creases in the garments.
6. Subject the garments to textile resin curing conditions.

In each of the above types of procedures, the ultimate curing of the textile resin may be accomplished prior to the manufacture of the garment whereby a good wash-and-wear fabric having soil-release properties is produced.

Procedures of Types I, II and III, as is evident, relate to the process of the present invention being applied to a textile material to afford said textile material soil-release and durable-press or wash-and-wear characteristics. Otherwise than above shown, the acid polymer, textile resin catalyst, ethoxylated alkyl phenol, etc., are just applied to the desired substrate and dried, subjected to textile resin curing conditions, etc., according to the specifications described herein.

The drying temperatures that are insufficient to initiate the catalysis are, of course, dependent upon the particular catalyst being employed. In general, however, the drying step is conducted at a rate of approximately 10 to 70 yards per minute at temperatures ranging from about 225° to 300° F. preferably in a tenter frame. The drying temperature range overlaps to some degree with the curing temperature range set forth below. When drying in the overlapping portion of the drying and curing ranges, it is important that there be no premature curing of the textile resin. Time is the prime variable and when drying the substrate in the higher end of the drying temperature range, care must be taken to avoid heating the substrate for a time sufficient to initiate catalysis that would at least partially cure the textile resin.

Irradiation techniques may be employed according to the process of the present invention when an aminoplast resin having ethylenic unsaturation is applied to the textile material. An insulating core transformer, operated at a potential varying between 100,000 electron volts and 500,000 electron volts may be successfully used to irradiate the textile material. Such a transformer is commercially available from High Voltage Engineering Corporation, Burlington, Mass. The amount of ionizing irradiation necessary according to the present invention is at least 32 electron volts for each ion pair formed. Thus irradiation of 32 volts and above is effective. Both high energy particle and ionizing irradiation are useful according to the present invention. The preferred dosage of irradiation according to the present invention is in the range of 1000 rads to 100 megarads, a rad being the amount of high energy irradiation of the type which results in energy absorption of 100 ergs per gram of absorbing material. More preferably, however, the irradiation dosage ranges from 0.5 to 5 megarads.

Curing of the textile resin is accomplished by subjecting the textile material having the textile resin thereon to conditions such that the catalyst initiates a cross-linking reaction between functional groups of the resin and hydroxyl groups of the cellulose in the textile material and converts the resin to the ther-

moset state. When a 100 percent synthetic fabric is treated, the resin adheres to the material and is converted to a thermoset state. Temperature is the prime mover and generally a temperature in the range of 130° C. to about 200° C. is sufficient. The curing medium that supports the necessary temperature may be any substance that is inert to both the fabric and the ingredients applied thereto, e.g., hot air, steam, etc. In the instance where the textile resin possesses two different types of functional groups, there are actually two curing steps, the first being conducted at a temperature lower than the second and insufficient to initiate the second type of catalysis, e.g., a first partial curing step to initiate alkaline catalysis and a subsequent curing step to initiate acid catalysis and also convert the resin to the thermoset state.

The duration of the various processing steps varies diversely with the particular ingredients employed. In each situation, however, the treatment time is that necessary to sufficiently cause reaction of and/or curing of the textile resin.

Trademarks and abbreviations used throughout the specification and examples are set forth below:

Dacron T—54—	A polyester fiber manufactured by E. I. du Pont de Nemours & Co.
Dacron T—56—	A polyester fiber manufactured by E. I. du Pont de Nemours & Co.
Dacron T—64—	A polyester fiber manufactured by E. I. du Pont de Nemours & Co.
Fortrel—	A polyester fiber produced by Cellanese Fiber Company
Kodel—	A polyester fiber manufactured by Eastman Kodak Company
Orlon—	A polyacrylonitrile fiber manufactured by E. I. du Pont de Nemours & Co.
Acrilan—	A polyacrylic fiber manufactured by Chemstrand Corporation, a division of Monsanto Company
Nylon 20—	A polyamide fiber manufactured by E. I. du Pont de Nemours & Co.
NMA—	N-methylol acrylamide (60% aqueous solution)
DHDMEU—	Dihydroxy dimethylol ethylene urea (50% aqueous solution)
SRP—	Copolymer of 70 parts ethyl acrylate: 30 parts acrylic acid (25% aqueous emulsion)
Profine—	Mixture of glycerol monostearate, and polyethylene glycol monostearates
R—1—	A commercial uron resin manufactured by Rohm & Haas
Syn-Soft A—20—	A polyethylene emulsion (20% solids) manufactured by Sylvan Chemical Co., Paeolet, South Carolina
Alipal CO—436—	An ammonium salt of a sulfated alkyl phenoxy poly(ethyleneoxy) ethanol manufactured by General Aniline and Film Corporation
Triton X200—	A sodium alkyl aryl sulfonate 30% solids) manufactured by Rohm & Haas
Triton X202—	A sodium alkyl aryl sulfonate (28% solids) manufactured by Rohm & Haas

The following examples are not intended to limit the scope of the present invention, but merely to provide direction to one skilled in the art. Several of the examples set forth below represent subject matter that is claimed in a concurrently filed companion application, Ser. No. 570,169, now U.S. Pat. No. 3,377,249. These examples do not include the specified ethoxylated alkyl phenols, but if from 1 to 10 percent of one of these ethoxylated alkyl phenols was added an improvement in soil release would be realized. Unless otherwise stated, parts are by weight.

EXAMPLE 1

A pad bath solution was prepared by dispersing in water the following ingredients: 17 percent N-methylol acrylamide (60 percent aqueous solution); 4 percent zinc nitrate (50 percent aqueous solution of $(Zn(NO_3)_2 \cdot 6H_2O)$); 3 percent Synsoft A-20; and 0.25 percent Alipal CO-436. The above composition was padded onto samples of Dacron/cotton (65/35) fabric to

50 percent wet pickup and the fabric dried on a tenter frame at 13 yards per minute at a temperature of 250° to 280° F. Moisture content of the dried fabric tested 5 percent. The dried fabric was then subjected to irradiation in an insulated core transformer manufactured by the High Voltage Engineering Corporation of Burlington, Mass.

Fabric was passed through the irradiation equipment at 40 yards per minute at a setting on the transformer of 500 kilovolts and 15 milliamps, the fabric being arranged in a 5-pass festoon during irradiation to produce a dosage of 2 megarads. Several pairs of men's slacks were then prepared from the treated fabric and pressed on a Hoffman press in the conventional manner and then pressed on a hot-head press at a cycle of 5 seconds stream, 10 seconds bake and 5 seconds vacuum. The pressed slacks were then suspended from a continuously moving conveyor in an oven and cured for 15 minutes at 325° F. After several washings, the pressed slacks retained all creases unimpaired.

EXAMPLE 2

The procedure followed in Example 1 was repeated with the exception that 100 percent cotton fabric was treated rather than the 65/35 Dacron/cotton. After curing and repeated washing, the creases in the cotton slacks remained as originally pressed into the garments.

EXAMPLE 3

Example 1 was again repeated with the exception that a 100 percent Dacron fabric was treated. Again, after repeated washings, creases in the slacks remained unimpaired.

EXAMPLE 4

The following pad bath was prepared: 25 percent dihydroxy dimethylol ethylene urea; 4.3 percent magnesium chloride ($MgCl_2 \cdot 6_2O$); 3 percent Syn-Soft A-20; 0.2 percent Triton X-200; and 68.5 percent water. The above emulsion was padded onto a Dacron/cotton (65/35) fabric at 50 percent pickup and the fabric was dried at a temperature ranging from 250° to 275° F. on a tenter frame. Moisture content of the dried fabric tested 5.6 percent. Men's slacks were prepared from the treated Dacron/cotton fabric and subjected to the identical pressing and curing condition set forth in Example 1. Creases in the slacks remained unimpaired after several washes.

EXAMPLE 5

Example 4 was repeated with the exception that a 100 percent cotton fabric was treated instead of the 65/35 Dacron/cotton. After repeated washings, the creases in the slacks remained unimpaired.

EXAMPLE 6

Example 4 was again repeated, but a 100 percent Dacron fabric was treated in lieu of the Dacron/cotton blend. Creases produced during the pressing cycle of the procedure were very durable to repeated washings.

EXAMPLE 7

Samples of Dacron/cotton (65/35) fabric were treated with a pad bath emulsion of the following formulation: 20 percent N-methylol acrylamide (50 percent aqueous solution); 10 percent emulsion copolymer of ethyl acrylate:acrylic acid (70:30); 5 percent magnesium chloride catalyst; and 65 percent water. A pad bath solution prepared according to the above recipe was padded onto the Dacron/cotton fabric at 50 percent pickup and the fabric dried at temperatures ranging from 200° to 280° F. to achieve a fabric moisture content of approximately 5 percent. The dried fabric was then given an irradiation dosage of two megarads and converted into men's slacks. Slacks prepared from the treated Dacron/cotton fabric were then pressed and cured identically to those procedures

described in Example 1. After several washes, the creases produced in the slacks by the Hoffman press remained substantially unimpaired, indicating that the presence of the ethyl acrylate acrylic acid copolymer did not adversely affect the durable-press characteristics of the treated fabric.

EXAMPLE 8

The procedure described in Example 7 was repeated with the exception that 100 percent cotton fabric was treated instead of 65/35 Dacron/cotton fabric. Similar durable-press results were obtained.

EXAMPLE 9

Slacks were made from 100 percent Dacron that was treated according to the procedures described in Example 8. After repeated washings the creases in the slacks were virtually as sharp as when they were originally produced in the garment before curing in the oven.

EXAMPLE 10

A pad bath solution was prepared according to the following formulation: 24 percent dihydroxy dimethylol ethylene urea (50 percent aqueous solution); 10 percent copolymer of ethyl acrylate acrylic acid (70:30); 5 percent zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$); 6 percent Profine; 0.2 percent Triton X-202; and 54.8 percent water. The pad bath solution according to the above recipe was padded onto Dacron/cotton (65/35) fabric at 50 percent pickup. The fabric was then dried at temperatures ranging from 245° to 280° F. on a tenter frame. Several pairs of men's slacks were made up from the treated Dacron/cotton (65/35) fabric after which creases were produced and the garments cured according to the procedures described in Example 1. After several washings the durability of the creases was evident by their inertness to the washing operation.

EXAMPLE 11

Cotton fabric was substituted for the Dacron/cotton fabric in Example 10 and the procedures thereof were repeated. Creases in the slacks were unaffected by the repeated washings.

EXAMPLE 12

The Dacron/cotton fabric of Example 10 was replaced by 100 percent Dacron and Example 10 was repeated. Several washings showed no effect on the creases in the Dacron slacks.

EXAMPLE 13

A pad bath solution was prepared according to the following recipe: 10 percent copolymer of ethyl acrylate:acrylic acid

(70:30); 5 percent zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$); and 85 percent water. The above emulsion was padded onto Dacron/cotton (65/35) fabric at 50 percent pickup and the fabric dried at a temperature ranging from 250° to 275° F. Men's slacks were prepared from the treated fabric and pressed and cured as per the procedures defined in Example 1.

EXAMPLE 14

Example 13 was repeated except that 100 percent cotton fabric was used in place of the Dacron/cotton fabric.

EXAMPLE 15

Example 13 was repeated except that 100 percent Dacron was treated in lieu of the Dacron/cotton fabric.

EXAMPLE 16

A pad bath according to the following formulation was prepared: 10 percent copolymer of ethyl acrylate:acrylic acid (70:30); and 90 percent water. Dacron/cotton (65/35) fabric was padded with 50 percent pickup of the above emulsion, and dried at a temperature of 250° to 275° F. The fabric was then used to make several pairs of men's slacks, which were processed according to Example 1.

EXAMPLE 17

Example 16 was repeated except that a 100 percent cotton fabric was treated in lieu of the Dacron/cotton fabric.

EXAMPLE 18

Example 16 was repeated, but using a 100 percent Dacron fabric.

EXAMPLE 19

Two sets of slacks were taken from each of the groups treated as described in Examples 1-18. In each case, the slacks were identified by the number of the example, and further identified by suffixes A and B. Slacks in Group A were stained with a No. 6 crude oil and subjected to one home washing in a Kenmore automatic washer, using one cup of Tide, a commercial detergent, and a water temperature of 140° F. The slacks in Group B were first washed five times under wash conditions identical to those for Group A. The Group B slacks, after the fifth wash were then stained with a No. 6 crude oil and subjected to one further wash under the same wash conditions as set forth above. After each wash, the slacks were dried in a Kenmore dryer at a temperature of from about 150° to 165° F. for approximately 40 minutes. After the designated number of washings, the residual oil stains in the slacks were compared to a set of standards having numerical ratings from 1.0 to 5.0, 1.0 being very poor and 5.0 representing virtually complete removal of the stain. Ratings for the tested slacks are set forth below in Table I and are indicative

TABLE I

[Soil release data for cotton, dacron/cotton and dacron fabrics]

Sample	Fabric	Treatment	Soil release rating		
			Control*	1 Wash	Control* 5 Washes
1.....	Dacron/cotton (65/35)	NMA	1.5	1.7	1.7
2.....	Cotton	NMA	1.8	1.9	1.9
3.....	Dacron	NMA	1.0	1.0	1.0
4.....	Dacron/cotton (65/35)	DHDMEU	1.5	1.7	1.7
5.....	Cotton	DHDMEU	1.7	1.8	1.8
6.....	Dacron	DHDMEU	1.0	1.0	1.0
7.....	Dacron/cotton (65/35)	SRP and NMA	*2.7	4.5	*2.8
8.....	Cotton	NMA and SRP	*3.5	4.2	*3.7
9.....	Dacron	NMA and SRP	*1.4	4.0	*1.5
10.....	Dacron/cotton (65/35)	DHDMEU and SRP	3.3	3.6	3.6
11.....	Cotton	DHDMEU and SRP	3.3	3.0	3.0
12.....	Dacron	DHDMEU and SRP	3.1	2.0	2.0
13.....	Dacron/cotton (65/35)	SRP	4.5	4.0	4.0
14.....	Cotton	SRP	4.6	3.0	3.0
15.....	Dacron	SRP	3.5	1.6	1.6
16.....	Dacron/cotton (65/35)	SRP**	4.2	4.3	4.3
17.....	Cotton	SRP**	4.5	2.9	2.9
18.....	Dacron	SRP**	2.0	1.8	1.8

*No treatment was rendered to control samples.

**No catalyst in pad bath.

of the soil-release property of the fabrics. Controls for the various fabrics are also included and represent slacks made from the fabric that was untreated; and the slacks were just pressed as per normal procedures.

From the data set forth in Table I the following conclusions may be drawn: (a) soil-release ability for cotton, Dacron/cotton and Dacron fabrics is substantially improved when the soil-release polymer is added, (b) the finish afforded the fabric by the soil-release polymer is enhanced when the soil-release polymer is deployed with a textile resin and a textile resin catalyst and the treated fabric cured; (c) soil-release ability of each of the fabrics is reduced when only the textile resin is employed to afford the fabric with a durable-press property, whereas the addition of the soil-release polymer more than compensates for the reduction brought about by the textile resin alone.

Test washes for obtaining soil-release data were conducted using the commercial detergent Tide, marketed by Proctor and Gamble. This particular detergent does not however, contribute specifically to the soil-release ability. Numerous of the commercial detergents were rated against one commercial detergent as a standard. There was only a slight difference in these detergents noted, so one cup full of any of them should perform satisfactorily.

EXAMPLE 20

To evaluate the breadth of the present invention regarding the fabrics which may be improved as to soil release, a number of fabrics were soiled with a No. 6 crude oil, washed one time in a Kenmore automatic washer with one cup of Tide at a wash water temperature of 140° F. The fabric was then dried for approximately 40 minutes at a temperature of from about 150° to about 165° F. and rated against the soil-release standards referred to above. Samples of the same fabrics were padded with an emulsion containing 12 percent dihydroxy dimethylol ethylene urea; 10 percent copolymer of ethyl acrylate:acrylic acid (70:30); 5 percent zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$); and 73 percent water. The samples were then cured in a conventional garment cure oven for 15 minutes at 180° C. Each of the fabric samples was then stained with a No. 6 crude oil and washed in a Kenmore automatic washer as prescribed above. Each of the samples were rated against standards described above and tabulated in Table II.

TABLE II

SOIL RELEASE DATA		
Fabric	Untreated Control	DHDMEL and SRP
Dacron T-54	1.4	4.0
Dacron T-56	2.8	4.5
Dacron T-64	2.4	4.2
Viscose	4.0	4.0
Cotton	3.5	4.2
Fortrel	1.3	4.4
Kodel	1.2	4.0
Orlon	3.8	4.3
Acrilan	4.0	4.2
Nylon 20	3.4	4.6
Acetate	3.6	4.4
Polypropylene	2.5	3.5

From Table II it is evident that with the exception of viscose, every type fabric treated showed improvement in soil-release ability. Moreover, the sample of viscose fabric was not resin-treated and as pointed out supra resin treatment reduces

the soil-release ability of the fabric. Hence, were the fabric resin-treated so as to afford durable-press properties to the fabric, then some soil-release improvement would be evident. Magnitude of improvement of soil release with the various fabrics was dependent primarily on the original soil-release ability. For example, in the case of cotton as compared to any of the Dacrons, the improvement is not nearly so great, for the cotton originally had much better soil release than the Dacron. Improvement is shown, however, in every instance.

Having determined that a copolymer of ethyl acrylate:acrylic acid (70:30) afforded superior soil-release properties to the various fabrics, it was incumbent to establish the limits of operability of the soil-release polymers. Such efforts have been expanded in two ways. First the composition range of the ethyl acrylate:acrylic acid copolymer system was investigated, and secondly, other polymer systems were tested for their soil-release ability. Table III sets forth soil-release performance for various ethyl acrylate:acrylic acid compositions and Table IV sets forth soil-release performance of various other copolymers and terpolymer systems.

EXAMPLE 21

A series of copolymers of ethyl acrylate and acrylic acid were prepared having varied proportions of acrylate and acid. Each of these polymers was then divided into two parts, A and B. Part A of each polymer was padded onto Dacron/cotton (65/35) fabric and the other part used to make films. The pad baths containing the various ethyl acrylate acrylic acid polymers had the following formulation: 10% ethyl acrylate acrylic acid polymer; and 90 percent water.

After drying the impregnated fabric, and curing the fabric, samples of the fabric were stained with a No. 6 crude oil and washed and further samples were first washed five times, then stained and washed once more. After the staining and washing, each sample was rated for soil-release ability by comparison with the standards discussed supra. Results of the soil-release tests are reported in Table III. Part B of each polymer sample as stated above was made into a film. After the film was cast and air-dried, it was then immersed in water for 16 hours to determine the water of imbibition thereof. Water of imbibition is reported for each polymer as percent water absorbed after 16 hours per weight of the film. Water of imbibition data is also reported in Table III.

Additionally, pad baths were prepared containing the following ingredients: 18 percent N-methylol acrylamide; 10 percent ethyl acrylate:acrylic acid polymer; 4 percent zinc nitrate; and 68 percent water. The ethyl acrylate:acrylic acid polymer composition varied in the pad baths prepared as identified in Table III. After padding the emulsion onto Dacron/cotton (65/35) fabric the fabric was dried at temperatures ranging from 250° to 275° F., subjected to an irradiation dosage of 3 megarads and cured for 30 minutes at 130° C. The fabric was then stained, washed and rated identically to the above fabric where only the soil-release polymer was applied. Data is reported in Table III.

TABLE III

[Soil release ability and water of imbibition data for ethyl acrylate acrylic acid copolymers]

Polymer composition	Polymer composition			
	Ethyl acrylate (percent)	Acrylic acid (percent)	Stain (a)/(b), 1 wash	Stain and wash (a)/(b), 5 washes
100	0	1.5/1.5	1.5/1.8	49.
90	10	2.5/2.0	2.0/2.2	89.
80	20	3.7/3.0	3.0/3.2	167.
70	30	4.3/4.0	3.0/4.0	312.
60	40	3.7/3.4	3.0/3.6	Water soluble.
50	50	3.5/3.0	3.0/3.2	Do.
30	70	4.5	3.0	Do.
20	80	3.8	3.0	Do.
10	90	3.8	3.0	Do.
0	100	4.0/2.8	3.0/3.0	Do.
Untreated	Control	2.6/1.5 (c)	2.7/1.7 (c)	Do.

NOTE.—(a)=Polymer only padded onto fabric; (b)=Resin, catalyst and polymer padded; (c)=Resin treated only (n methylol acrylamide).

TABLE V

[Soil release and water of imbibition data for acid polymers]

Polymer	Soil release rating, 1 wash/5 washes	Water of imbibition, wt. percent increase
Methyl acrylate: acrylic acid (69:31).....	3.6/3.0	252
Ethyl acrylate: acrylic acid: divinyl benzene (67.5:30:2.5).....	3.7/3.0	397
Ethyl acrylate: acrylic acid: acrylamide (66.7:29.7:3.6).....	3.9/3.3	359
Ethyl acrylate: sodium styrene sulfonate (70:30).....	3.0/3.1	211
Ethyl acrylate: acrylic acid: acrylamide (78.2:18.1:3.7).....	3.6/3.5	126

Study of data set forth in Table III indicates that an acrylic acid content of less than 10 percent is undesirable for promoting soil release from the Dacron/cotton fabric. Moreover the water of imbibition data corresponding to the polymer compositions provides an excellent criteria for determining whether the polymer will successfully afford soil-release properties to a fabric when the polymer contains more than 10 percent acid. When the water of imbibition of the film falls below 89 percent, then there is insufficient water absorption to remove the oily soil from the garment during washing. Also, in the situation where the polymer is normally water-soluble, one would surmise that the polymer would not provide good soil-release properties since it would be removed by the wash water. This thesis is only partially true, for when the polymer is added with or prior to the textile resin and subjected to the textile resin curing conditions, then the water solubility of the polymer is significantly modified, probably by virtue of the unidentifiable reaction between the textile resin and the acid polymer.

EXAMPLE 22

A series of polymers were padded onto a Dacron/cotton (65/35) fabric in the following pad bath formulation: 16 percent N-methylol acrylamide; 10 percent polymer; 4 percent zinc nitrate catalyst; and 70 percent water. The various formulations were padded onto the fabric and the fabric was dried, irradiated, cured, stained, washed and rated as previously described. The specific polymers employed in the pad bath formulation and the soil release data are reported in Table IV.

TABLE IV

Soil Release Data For Various Polymers Padded Onto Dacron/Cotton (65/35) Fabric Along With Resin and Catalyst

Polymer	Soil Release Rating Stain and 1 Wash
Butyl Acrylate:acrylic acid (12:88)	3.4
Butyl acrylate:acrylic acid (30:70)	3.5
Butyl acrylate:acrylic acid (80:20)	2.2
Butyl acrylate:acrylic acid (88:12)	2.3
Ethyl acrylate: methacrylic acid (70:30)	3.8
Ethyl acrylate: itaconic acid (70:30)	3.4
Methyl methacrylate: acrylic acid (70:30)	3.6
Acrylamide: acrylic acid (10:90)	3.2
Ethyl acrylate: acrylic acid: acrylamide (50:38:12)	2.5
Ethyl acrylate: acrylic acid: acrylamide (65:30:5)	3.9
Resin control	1.6
Untreated Control	2.8

EXAMPLE 23

In further attempting to define the polymers that successfully afford soil release, the water of imbibition was determined for films prepared from a group of polymers. The films were cast air-dried, and immersed in excess water for a period of 16 hours. Water absorbed by the film was then determined and is reported in Table V as weight percent increase. Also, each of the polymers, as set forth in Table V was incorporated into a pad bath of the following recipe: 10 percent polymer, 18

percent N-methylol acrylamide, 4 percent zinc nitrate catalyst ($Zn(NO_3)_2 \cdot 6H_2O$) and 68 percent water.

Two samples each of Dacron/cotton (65/35) fabric was padded with the formulations prepared, dried and cured. Each sample was then stained with No. 6 crude oil and each set of samples given the 1 and 5 washes as described in Example 1. After washing, the stains were rated against the soil-release standards. Data is reported in Table V along with water of imbibition.

In furtherance of establishing the operability of the soil-release polymers of the present invention, a more quantitative test was followed to indicate soil-release properties of the treated fabric.

EXAMPLE 24

A sample of Dacron/cotton (65/35) fabric was padded with a pad bath emulsion comprising 18 percent N-methylol acrylamide (60 percent aqueous solution); 10 percent copolymer of ethyl acrylate: acrylic acid (70:30); 4.3 percent zinc nitrate (50 percent solution of $Zn(NO_3)_2 \cdot 6H_2O$); 2 percent Syn-Fac N-905 and 4 percent Profine at 50 percent pickup. The fabric was then dried on a tenter frame at 13 yards per minute at temperatures ranging from 240° to 270° F.; subjected to irradiation by the method described in Example 1 and cured by the procedures prescribed in Example 1. A second sample of Dacron/cotton (65/35) fabric having been treated by a conventional method to impart durable-press properties was compared to the above-treated fabric. Both the conventional durable-press fabrics were soiled with a radioactive sebacious soil, then washed once in a conventional automatic washing machine with one cup of "ALL," a commercial detergent in wash water having a temperature of 105° F., and tested to determine the amount of soil remaining on the fabric. Data is reported in Table VI.

TABLE VI

Radioactive Soil Release Data On Soil Release Treated-Durable Press Dacron/Cotton (65/35) vs. Untreated Durable Press Dacron/Cotton (65/35)

Soiling Tests	Conventional Durable Press	Durable Press & Soil Release
Sebacious Soil Pickup	5.9%	5.7%
Soil Retention, 105° Wash in "ALL"	82%	25%

The above data shows positively that the fabric treated to have both durable-press and soil-release characteristics is vastly superior to the conventional durable-press fabric in releasing soil during a conventional wash cycle.

EXAMPLE 25

Earlier in the specification, information is set forth relevant to the order of application of the textile resin and the soil-release polymer. Tests were conducted to determine criticality, if any, of the order of application and/or whether there is any synergism between the various compounds in the pad bath. Dacron/cotton (65/35) fabric was used in each test. Pad

baths included aqueous emulsions of the materials set forth in Table VII. In cases where drying, irradiation and/or curing are indicated, procedures were followed as set forth in Example 1. Three sets of samples were prepared in each instance, one of which was stained with No. 6 crude oil and washed as described supra, one of which was washed five times, stained and washed once more and the third of which was washed 10 times, stained and given a further wash. These data provide comparison of the normal soil-release compositions with those that include the ethoxylated alkyl phenol, Syn-Fac N-905. These data, of course, further provide good readings on both initial soil-release ability and durability of the soil-release finish. After the final wash, each of the samples was compared to the soil-release rating standards and given a numerical rating of 1.0 to 5.0, 5.0 being complete removal of the stain. Data are recorded in Table VII.

TABLE VII

[Study of effect of soil release when ethylene oxide-alkyl phenol condensate added]

Sample	Pad bath	Cure*	Pad bath	Irradiation, 1 rr	Cure*	Wash	Pad bath	Cure*	Soil release rating after—		
									1 wash	5 washes	10 washes
1.....	BX			+	+				1.1	1.3	1.9
2.....	BXF			+	+				3.1	3.2	3.3
3.....	BXFG			+	+				3.5	3.4	3.2
4.....	BX			+	+	+	F	+	4.0	3.0	2.9
5.....	BX			+	+	+	FG	+	4.9	3.1	3.0
6.....	183X	+							1.5	1.7	2.0
7.....	183XF	+							3.4	3.1	3.0
8.....	183XFG	+							4.0	3.6	3.5
9.....	183X	+				+	F	+	3.9	3.0	3.0
10.....	183X	+				+	FG	+	4.5	3.1	2.9

*Cured 340° F. for 15 minutes.

NOTE.—B=15% N-methylol acrylamide (60% solution); X=4.3% zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$); F=10% copolymer of ethyl acrylate:acrylic acid (70:30) (25% emulsion); G=2.3% Syn-Fac N-905; 183=24% dimethylol dihydroxy ethylene urea.

The data in Table VII support two propositions, namely that the addition of an ethylene oxide alkyl phenol condensate (Syn-Fac N-905) improves the soil release from Dacron/cotton fabric, and that addition of the acid polymer after the textile resin has been added and cured yields excellent initial soil release. The soil release accompanying the separate acid polymer addition after curing of the textile resin, while better initially than when the resin and acid polymer are added together, is not nearly so durable. The improved soil-release results realized by the addition apply both when the resin and acid polymer are added together and also when they are added separately as shown in Table VII.

EXAMPLE 26

The following pad bath formulation was prepared and padded onto Dacron/cotton (65/35) fabric at 50 percent wet pickup: 24 percent dihydroxy dimethylol ethylene urea (50 percent aqueous solution); 10 percent copolymer of ethyl acrylate:acrylic acid (70:30) 25 percent aqueous emulsion; 4.3 percent zinc nitrate catalyst; 4.0 percent Profine; 2.3 percent various ethylene oxide-alkyl phenol condensates as set forth in Table VIII; 55.4 percent water.

The various treated fabric samples were dried and then cured at 345° F. for 15 minutes. Samples treated with each of the pad baths were divided into two batches. One batch of each fabric sample was stained with No. 6 crude oil, washed, dried and rated as described supra. The other batch of each

fabric sample was washed five times, stained, washed, dried and rated as described supra. Ratings of the various samples are reported in Table VIII. The control was treated with the pad bath formulation set forth above, but without any ethylene oxide alkyl phenol condensate.

EXAMPLE 27

The following experiment was conducted to determine the ability of fabrics treated by the process of the present invention to repel deposition of oily materials and grime from dirty wash water. The following pad bath was prepared and labeled formulation A: 24 percent R-1, 6.6 percent magnesium chloride catalyst, 3 percent Profine, 2.3 percent Syn-Fac N-905 and 64.7 percent water. A second pad bath labeled formulation B, was prepared identical to the above-identified for-

35 mulation with the exception that 10 percent of a soil-release polymer, a copolymer of ethyl acrylate:acrylic acid (70:30), was included and the amount of water was reduced proportionately, i.e., (54.7 percent present). These formulations 40 were padded onto Dacron/cotton (65/35) shirting. The fabric was then dried and precured at 325° F. for 1½ minutes, after which shirts were tailored from the fabric. The shirts were then labeled A (formulation A) and B (formulation B) and subjected to five home washings in a Kenmore automatic 45 washer using one cup of Tide and wash water of 140° F. Prior to placing shirts A and B in the same washer, a quantity of oil and dirt was put into the water. After the five washes, the shirts were tested in a Hunter color meter manufactured by Hunter Associates Laboratory, Inc., 5421 Briar Ridge Road, 50 McLean, Va., to determine the comparative soil pickup by the shirts in the washer.

The Hunter instrument employs a polychromatic light source and a matched set of barrier-layer photoelectric cells. One photoelectric cell is illuminated directly by the light source while the other photoelectric cell is illuminated by light 55 reflected from a fabric sample. Measurements are made of the degree of unbalance existing between the photoelectric cells, from the current generated by the photoelectric cell receiving direct illumination and the current generated by the photoelectric cell receiving fabric-reflected illumination. 60 Values may be read from digital dials on the device of three

TABLE VIII

[Soil release data for formulations containing ethylene oxide-alkyl phenol condensates]

Sample	Ethylene oxide-alkyl phenol condensate	Soil release rating	
		Stain and wash	5 washes, stain and wash
1.....	6.0 moles ethylene oxide/mole 2-ethyl hexyl phenol...	4.1	3.6
2.....	7.5 moles ethylene oxide/mole hexyl phenol.....	4.2	3.6
3.....	14.0 moles ethylene oxide/mole nonyl phenol.....	4.4	3.8
4.....	5.0 moles ethylene oxide/mole heptyl phenol.....	3.9	3.3
5.....	12.0 moles ethylene oxide/mole nonyl phenol.....	4.3	3.9
6.....	11.0 moles ethylene oxide/mole tetradecyl phenol....	4.1	3.6
7.....	30.0 moles ethylene oxide/mole nonyl-phenol.....	4.6	3.8
8.....	20.0 moles ethylene oxide/mole octyl phenol.....	4.4	3.9
Control.....	None.....	3.8	3.6

visually uniform color scales, the three readings being L, *a*, and *b* wherein:

L measures lightness and varies from 100 for perfect white to zero for black;

a measures redness when plus, gray when zero, and greenness when minus;

b measures yellowness when plus, gray when zero, and blueness when minus.

A value for whiteness (*W*) may be computed from these values by means of the following formula: $W=L-3b$.

Likewise additional shirts labeled A and B were sent out to a commercial laundry and tested for whiteness after 10 commercial washings without soil addition. Data are reported in Table IX.

TABLE IX
Soil Redeposition Data for White Shirts

Treatment	Treatment	Wash	L	a	b	W
Shirt A	R-1	Oily	83.4	+2.5	+3.1	74.1
Shirt B	R-1+SRP	do	88.6	+2.7	+0.4	87.4
Shirt A	R-1	Normal commercial	91.8	+1.7	-2.5	99.3
Shirt B	R-1+SRP	do	92.1	+1.6	-3.3	102.0
Control	None	None				110.7

From the data in Table IX it is therefore evident that all of the shirts lost some of their whiteness after the washings. Shirt B in both the oily washes and the commercial washes retained their whiteness better than Shirt A in each type wash. This positively indicates that less soil was deposited from the wash water onto Shirt B, the shirt having the soil-release polymers applied thereto.

EXAMPLE 28

A pad bath formulation was prepared to include 10 weight percent of a copolymer of ethyl acrylate:acrylic acid (70:30) 4 weight percent zinc nitrate catalyst and 86 weight percent water. This formulation was padded onto a Dacron/cotton (65/35) fabric, the fabric dried at 325° F. for 15 minutes. A further formulation containing the above ingredients plus 2.3 weight percent of a condensation product of 9.5 moles of ethylene oxide per mole of nonyl phenol was prepared, padded onto Dacron/cotton (65.35) fabric. The fabric was then cured at 325° F. for 15 minutes. Both fabric samples were then stained, washed, dried and rated as described in Example 1. Soil-release ratings appear in Table X.

TABLE X

Soil Release Data for Formulations Containing an Ethylene Oxide-Alkyl Phenol Condensate

Sample	Treatment	Stain & Wash	Soil Release Rating	
			Wash 5 times	Stain & Wash
1	AP*	4.3	3.0	
2	AP+C**	4.8	3.2	

* Acid Polymer

** Acid Polymer and Condensate

These data show soil-release improvement when the ethylene oxide, alkyl phenol condensate is added to the formulation.

That which is claimed is:

1. A process for imparting soil-release and durable-press

characteristics to a textile material comprising applying thereto an aminoplast textile resin, a textile resin catalyst, a synthetic acid copolymer comprising at least 20 percent acid calculated as acrylic acid and about 1 to 10 percent based on the weight of the above components of an ethoxylated alkyl phenol, said ethoxylated alkyl phenol having at least three repeating ethoxy groups in the side chain and about three to 14 carbon atoms in the alkyl group, and curing the textile resin; the proportion of acid polymer solids on said textile material being from about 0.25 to about 5.0 weight percent based on the dry weight of the textile material.

2. The process as defined in claim 1 wherein the ethoxylated alkyl phenol has about 3 to 30 repeating ethoxy groups in the side chain.

3. The process as defined in claim 1 wherein the ethoxylated alkyl phenol is prepared by reacting ethylene oxide and nonyl phenol in a molar ratio of 9.5:1 respectively.

4. The process as defined in claim 1 wherein the textile material is a cellulosic-containing material.

5. The process as defined in claim 1 wherein the acid copolymer is prepared by emulsion polymerizing a monomeric mixture comprising an acrylic ester and an acrylic acid.

6. The process as defined in claim 1 wherein the acid copolymer is prepared by emulsion polymerizing a monomeric mixture comprising about 50 to 80 parts of an acrylic ester and about 20 to 50 parts of an acrylic acid.

7. The process as defined in claim 1 wherein the textile material comprises a blend of cellulosic and polyester fibers, the textile resin is N-methylol acrylamide or dihydroxy dimethylol ethylene urea, the acid copolymer is prepared by emulsion polymerizing a monomeric mixture comprising an acrylic ester and an acrylic acid, and the textile material is heated to a temperature in the range of about 130° to 200° C. for about 1 to 30 minutes to cure the aminoplast resin thereon.

8. A process for imparting soil-release and durable-press characteristics to a polyester/cellulosic textile material which comprises applying thereto an aqueous dispersion comprising (a) about 2 to 30 percent of an aminoplast textile resin, (b) about 2.5 to 40 percent of a synthetic acid copolymer which is stable under the conditions of application, said copolymer being prepared by emulsion polymerizing a monomeric mixture comprising an acrylic ester and an acrylic acid, (c) up to 15 percent of a catalyst selected from the group consisting of zinc nitrate and magnesium chloride and (d) about 1 to 10 percent of an ethoxylated alkyl phenol having at least three repeating ethoxy groups in the side chain and about three to 14 carbon atoms in the alkyl group; and heating said textile material at a temperature in the range of about 130° to 200° C. for about 1 to 30 minutes to cure the aminoplast resin thereon; the proportion of acid copolymer solids on said textile material being from about 0.25 to about 5.0 weight percent based on the dry weight of the textile material.

9. A process for imparting) textile and durable-press characteristics to a polyethylene terephthalate/cotton (65/35) textile material which comprises:

a. applying thereto an aqueous dispersion consisting essentially of about 2 to 30 percent of an aqueous solution comprising N-methylol acrylamide or dihydroxy dimethylol ethylene urea, about 1 to 15 percent of an aqueous solution of a catalyst selected from the group consisting of zinc nitrate and magnesium chloride, about 2.5 to 40 percent of an aqueous emulsion of a synthetic acid copolymer prepared by polymerizing a monomeric mixture comprising an acrylic ester and at least 20 weight percent of an acrylic acid, about 1 to 10 percent of an ethoxylated alkyl phenol having at least three repeating ethoxy groups in the side chain and about three to 14 carbon atoms in the alkyl group, and water; said aqueous dispersion being applied to the textile material in the range of 30 to 70 weight percent of the textile material; the proportion of acid copolymer solids on said textile material being from about 0.25 to about 5.0 weight percent based on the dry weight of the textile material.

- b. drying the textile material at a temperature in the range of about 225° F. to 300° F. for a time insufficient to initiate curing of the textile resin; and
- c. heating the textile material at a temperature in the range of about 130° C. to 200° C. for a time sufficient to cure the textile resin; the proportion of acid copolymer solids on said textile material being from about 0.25 to about 5.0 weight percent based on the dry weight of the textile material.

10. A process for imparting soil-release and durable-press characteristics to a textile material comprising linear polyester and cellulosic fibers, which comprises applying thereto N-methylol acrylamide, an acid textile resin catalyst, about 1 to 10 percent of an ethoxylated alkyl phenol having at least three repeating ethoxy groups in the side chain and about three to 14 carbon atoms in the alkyl group, and a synthetic acid emulsion copolymer which is stable under the conditions of appli-

cation, subjecting said textile material to high-energy irradiation to effect addition polymerization of the vinyl group of said N-methylol acrylamide with itself and with the cellulose, and heating said textile material to react the methylol group of said N-methylol acrylamide with the hydroxy groups of the cellulose under the influence of said acid catalyst; said acid emulsion copolymer comprising at least 20 weight percent acid calculated as acrylic acid and the proportion of acid copolymer solids on said textile material being from about 0.25 to about 5.0 weight percent based on the dry weight of the textile material.

11. A textile material having soil-release and durable-press characteristics, prepared according to the process of claim 1.

12. A cellulosic-containing textile material having soil-release and durable-press characteristics, prepared according to the process of claim 7.

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