

[54] METHOD OF TREATING FABRICS	3,268,469	8/1966	Muller et al.	260/29.6
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[22] Filed: Apr. 11, 1973	3,394,028	7/1968	Nachbur et al.	117/138.8
[21] Appl. No.: 349,988	3,401,006	9/1968	Perrino	8/115.6
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117/138 UA, 139.4, 139.5, 143 A; 260/29.6 T,
260/29.6 TA

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[57] **ABSTRACT**
 There is disclosed a process comprising treating knitted and woven textile materials with a polymeric emulsion, and a method of preparing the polymeric emulsion, said emulsion contains a polymeric product derived from a monomer mixture containing a vinyl ester, an ester of an α -mono-olefinically unsaturated carboxylic acid, and α -mono-olefinically unsaturated acid and a bifunctional monomer.

20 Claims, No Drawings

METHOD OF TREATING FABRICS

BACKGROUND OF THE INVENTION

This invention relates to a process for rendering knitted and woven textile materials, particularly thermoplastic fiber-containing textile materials, normally susceptible to snag, picking and pull damage, resistant to such damage. The process includes contacting said material with a pad bath emulsion of a polymeric product as above defined.

Knitted fabrics, particularly those of double knit construction and/or those employing texturized yarn, show a tendency to snag or pull. Snagging is a particularly acute problem in mens' clothing where the retail price of the goods is quite high and a garment repeatedly damaged by snagging eventually becomes unattractive and or unwearable and thus makes the price-life of the garment prohibitive.

Various suggestions have been made in the prior art to solve these problems and various types of articles are offered on the market which are partially resistant to the aforesaid difficulties by the adoption of other than a plain knit structure, for example, through the use of tuck stitches or draw stitches involving the knitting of different parts of a textile article of two different yarns. In such an article, resistance to pulling, snagging and picking may be accomplished by use of one plain knit stitch and another special stitch. To the greater majority of wearers, these textile articles are unacceptable for general use because of the appearance of the garments.

Chemical and adhesive treatments have been utilized in the past to overcome the difficulties of pulling, snagging and picking in woven and knitted garments. Most of these treatments, however, have not been commercially successful because any treatment that has proven to be at all effective, will ordinarily affect the "hand" and/or the stretch characteristics of the garment. The prior art treatments are reputed to reduce snagging and produce a finish highly durable to both washing and dry cleaning. The finishes employed in such treatments include acrylic acid ester emulsions such as poly (ethyl acrylate) or modifications thereof, such as, acrylics cross-linked by methylol, carboxy or epoxy groups (U.S. Pat. Nos. 3,476,581; 3,483,024 and 3,567,498). One such typical example being poly (acrylate) combined with a filler or copolymers of ethylene and vinyl acetate, butyl acrylate and acrylamide and poly (butyl acrylates) containing acrylic acid residues. Problems associated with these acrylate finishes include shade change on dyed fabrics, wet crocking, a stiffer hand and a significant reduction of wash fastness of certain dyes.

Treatment with the above as utilized in the prior art has not been satisfactory because the material after such treatment loses its soft hand and resiliency. Some polymeric materials that are being employed in the prior art have less effect on the hand, but increase resistance to snagging only to a small degree.

In contradistinction to the prior art, the instant process may be applied to dyed or undyed material. In the case of dyed materials, the treatment does not impair, to any appreciable degree, the fastness of the color of the fabric. In the case of undyed materials, the dyeing may be negligibly affected during the process, variables being the dyestuff, dye bath, dye temperature and the like.

Poly (acrylates) as above noted also have other drawbacks, including a stiff hand when the surfactant is leached out of the emulsion during washing of the treated material; lack of moisture re-gain after washings and the like.

An important aspect of the instant invention resides in the use of a polymerizable carboxylic acid, as this component is essential to provide adhesion to the fibers as well as resistance to crocking and improved dry cleaning properties.

It is to be understood that the "emulsion additive" of the instant invention is not chemically the same nor does it function per se as an adjunct to improve hand and abrasion resistance of resin-treated textiles. In other words, the instant emulsion will not be applied along with "permanent press" finishes solely to modify hand or improve abrasion resistance of said permanent press finishes. The instant emulsion is not employed as an additive or coreactant in the production of "durable press" garments produced by the application and subsequent curing of thermosetting resins to the fabric. The emulsion therefore is not employed in the endeavor to improve the abrasion resistance of such fabrics as said term is known in the art. Improving the abrasion resistance of durable press resin treated textiles refers to the wear that occurs at the sleeve cuffs, pants cuffs and shirt collars. Said term does not generically include snagging and pulling as is known in the art to occur specifically to knitted materials, double knits and warp knits of polyester, as well as to knits or wovens of wool, cotton, cotton blends, rayon, acrylates and nylon materials. Accordingly, where knitted articles, cellulose acetate and mixtures thereof, particularly those of double knit construction, have shown a tendency to snag on sharp or pointed objects, treatment with a durable press resin finish will not prevent snagging and pulling, notwithstanding the fact that other resin treated fabrics might be more resistant to abrasion by treatment therewith.

SUMMARY OF THE INVENTION

It is an object of the instant invention to provide a process for rendering knitted and woven textile materials, particularly those containing thermoplastic fibers normally susceptible to snag, picking and pull damage less susceptible thereto while still retaining one or more of the good properties of hand, stretch characteristics, resiliency to dye fastness, resistance to crocking, dry cleaning properties and adhesion to the fabric.

It is also an object of this invention to develop a finish that will significantly reduce the tendency to snag, pick and pull wherein the finish can be applied to a fabric by a finisher in a simple and practical manner.

It is another object of the instant invention to provide a thermoplastic fiber - containing textile material so treated.

It is yet another object of the instant invention to carry out the above mentioned process employing an emulsion containing an interpolymer comprising units of a vinyl ester, an ester of an α -unsaturated carboxylic acid, an α -unsaturated carboxylic acid and a monomer of double functionality.

It is further object of the invention to provide for a novel interpolymer employed in the above defined process.

It is yet a further object of the invention to provide for a process for producing said interpolymer.

It is further object of the instant invention to avoid one or more drawbacks of the prior art.

Other objects and advantages will appear as the description proceeds.

In satisfaction of one or more of the foregoing objects and advantages, there is provided by this invention a process for rendering knitted and woven, particularly thermoplastic fiber-containing materials, more resistant to picking, snagging and pulling, comprising treating same with an aqueous emulsion containing approximately by weight:

I. 20-79% of a vinyl ester;

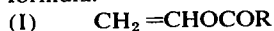
II. 20-79% of an ester of α -unsaturated carboxylic acid,

III. 1-10% of an α -unsaturated carboxylic acid, and

IV. 0.1-2% of a bifunctional monomer

The treated material is thereafter subjected to curing conditions to avoid dye migration and resistance of the size to washing and dry cleaning.

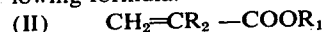
The vinyl esters employed herein have the following formula:



wherein R is a straight or branched chain alkyl radical of 1 to 18 carbons, preferably 1 to 3. The vinyl esters of α -unsaturated monocarboxylic acids may be used to provide the desired kind of final polymer. While vinyl esters may be of small molecular size such as vinyl acetate, vinyl propionate, or vinyl butyrate, esters of larger molecular size may also be used, such vinyl monomers as vinyl caprylate, vinyl laurate, or vinyl stearate. Vinyl acetate or propionate is particularly preferred.

The acrylic ester monomer (or mixtures thereof) employed herein may be any ester of acrylic, methacrylic, α -ethacrylic, or α -chloracrylic acid with a monohydroxylic organic compound referred to herein as a monohydric alcohol, which may be saturated, aromatic or aliphatic, straight or branched chain, substituted or unsubstituted. As examples of suitable monohydroxylic organic compounds which may be employed for esterifying one of the above mentioned acrylic acids, there may be mentioned such alcohols as, methyl, ethyl, propyl, butyl, isobutyl, 2-ethyl hexyl, amyl, hexyl, cyclohexyl, heptyl, dodecyl, octyl, iso tridecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl, oleyl, arachidyl, ceryl, dimethylaminoethyl, tertiary-butylaminoethyl, and benzyl alcohol in addition to phenol, naphthol and the like. These esters are substantially water insoluble.

The ester of the α -unsaturated acid is preferably an alkyl acrylate, in other words, the ester of an α,β -mono-olefinically unsaturated carboxylic acid, i.e., those alkyl esters of acrylic acid wherein the alkyl portion contains about 1 to about 12, preferably 1-8 and optimally 1-4 carbon atoms. The alkyl chain may be a straight or branched chain. The alkyl acrylate monomers used in the preparation are described by the following formula:



wherein R_1 is a straight or branch-chained alkyl radical. A particularly valuable class of these alkyl acrylates are those wherein R_2 has from 1 to 8 carbons. Especially preferred monomers falling within above defined group are methylacrylate, ethylacrylate, n-butylacrylate and 2-ethylhexylacrylate, as these materials are readily available and relatively inexpensive. R_2 may be hydrogen or methyl; in latter case, the monomer is methacrylate and the methyl, ethyl and n-butyl ester are the preferred species.

The α -unsaturated carboxylic acids preferably employed are the α,β -olefinically unsaturated carboxylic acids having from 1-7 carbon atoms, representative members of which include, acrylic acid, methacrylic acid, ethacrylic acid, mesaconic acid, citraconic acid, sorbic acid, maleic acid, crotonic acid and the like and anhydrides thereof. The preferred monomeric acids are the α,β -monoolefinically unsaturated carboxylic acids. The most preferred are the α,β -monoolefinically unsaturated monocarboxylic acids, particularly acrylic and methacrylic acids.

The acrylic acid monomeric units are derived from an α,β -unsaturated acid of the formula:



wherein R is hydrogen or an alkyl group of 1 to about 7 carbon atoms. Illustrative of such compounds are acrylic acid and methacrylic acid as well as those acids wherein R is an alkyl group of 2 to 7 carbon atoms. These compounds and their methods of preparation are well known in the art. Acrylic acid is especially preferred because of its ready availability and the excellent properties of the products obtained therefrom.

The bifunctional monomeric units may be described by the formula:



wherein R is an amine or diamine radical, oxygen, or dicarboxylic acid radical. Diallylphthalate, diallylether, diallylamine are the preferred compounds, which fall into this category.

The comonomers that are useful in this invention include those which cross-link or cure to form a relatively soft film. These monomers should combine softness, resilience and low temperature flexibility with improved wash fastness. They are cross-linkable, which means that they are self cross-linking and react or cure in situ under the curing conditions of this invention set forth hereinafter. The compound or compounds having acid groups that are capable of cross-linking may be reacted in situ during the curing step of this procedure if desired, to form a thermosetting type resin.

The aforesaid cross-linking component (i.e. carboxylic acid) is operative to "lock into" both the substrate and the hydroxyl groups of cellulose where polyester blends are employed; the foregoing, notwithstanding the fact that said substrate is water soluble. The bifunctional monomer (e.g. diallylphthalate) not only improves the dry-cleanability of the fabric, but also contributes to the softness of the hand. In those finishes employing an external cross-linking agent operative to cross-link the straight acrylate, the finish gradually leaches out each time the fiber is washed.

Polymers containing only acrylates or vinyl esters in combination with a non-carboxylic cross-linkable comonomer, are inferior to the polymers of this invention in protecting knit fabrics against mechanical damage.

The process of the present invention may be applied to knitted or woven fabrics and also to fabrics or articles containing wool and/or nylon in admixture with other fibers such as the synthetic protein fibers, cotton, rayon, casein fiber and cellulose acetate.

Among the articles which may be treated according to the present invention are underwear, or outerwear garments, hose socks and stockings, felt, hats, ties, fur-

nishing fabrics, upholstery, gloves, scarves, curtains, etc.

The process of the invention may be applied to a dyed or undyed material. In the case of the undyed material, the dyeing may be effected during the process of the present invention or may be effected subsequent to the treatment. It is, however, preferable that the textile materials treated in accordance with this invention should be free of other finishes, i.e., lanolin, lubricants or the like.

The fabrics or articles so treated in accordance with this invention, show an increased resistance to picking, snagging and pulling.

The term "picking" as used herein refers to the tendency of fabric to have unsightly broken threads and holes, this characteristic being particularly present in knitted goods. The measure of this physical characteristic of fabrics can be carried out on the "Hanes Pick Tester," U.S. Pat. No. 3,044,293. This tester comprises a small cylindrical tumbling device equipped with baffles and with a number of straight pins protruding from the cylinder wall. In the use of this pick testing device, the goods are first inspected and all defects marked and then put into the pick tester and tumbled.

The term "snagging" as used herein refers to the tendency of knitted and woven fabrics to have broken threads and holes or loose loops of thread protruding from the fabric. The measurement of the resistance of the fabric thereto is done with a so-called "Mace-Tester" which comprises a tumbling steel ball having pins protruding from its surface. The pins come in contact with the stretched fabric in a reproducible fashion; after 600 revolutions on the Mace-Tester, the fabric is examined and the defects caused by the tester are determined.

The instant process of applying said finish to such goods, is particularly effective on garments produced from textured textile yarn, polyester knits, polyester double-knits, warp knits, and polyester blends used in knit goods. The finish, when applied to the goods, shows a definite ability to reduce snagging and to permanently modify the hand of the fabric, thus making the fabric particularly attractive for menswear. The finish may be applied at various levels for durable hand building of the fabric and/or to provide varying degrees of anti-snap characteristics.

DETAILED DESCRIPTION

The emulsions prepared and used in accordance with the instant invention have been found to be homogeneous, stable, aqueous emulsions containing the polymeric product as above defined.

The emulsions are characterized by unusually good stability, low to medium viscosities, the ability to deposit a clear transparent film on a glass plate and a polymeric product which is essentially water insoluble and at least about 90% soluble in aromatic solvents, i.e., benzene. The emulsions are further characterized by the ability to be converted to a thermosetting product by heating to about 100° to 180°C for 1 hour to 1 minute, respectively.

In producing the polymeric product contained in said aqueous emulsion, the ratio of each of the monomers may be varied as desired over a wide range. However, for obtaining optimum properties, the following ratios by weight of the monomers are operable:

Monomer	Parts by Weight
(I) Vinylester	20-79
(II) Alkyl acrylate (or methacrylate)	28-79
(III) Unsaturated Acid	0.5-10
(IV) Bifunctional Monomer	0.1-5

though weight ranges of 35 to 55 of Unit I, 40 to 60 of Unit II 1 to 5 of Unit III and 0.1 to 2 of Unit IV are preferred.

The polymers of this invention are conveniently prepared by subjecting a mixture of the aforesaid monomers in the requisite amounts to conditions conducive to vinyl polymerization. This copolymerization may be induced by the action of known free radicals and proceeds exothermically once initiated. Suitable catalysts include organic peroxides and hydroperoxides, alkali metal persulfates and aliphatic azo-compounds, as well as other catalytic free radical compounds known to the art.

The free radical-supplying redox polymerization catalysts useful in the present process are well known in the art. Most of these catalysts are compounds yielding oxygen under the conditions of polymerization, as represented by the inorganic and organic peroxygen or peroxide compounds. As examples of such compounds, there may be mentioned hydrogen peroxide, metal and alkali metal peroxides such as sodium, potassium, barium and zinc peroxide; diacyl peroxides such as diacetyl, dibenzoyl and dilauroyl peroxide; dialkyl peroxides such as di-tertiary-butyl peroxide and cyclohexene peroxide; hydroperoxides such as tertiary-butyl hydroperoxide and p-methane hydroperoxide; peroxygen acids such as performic, persulfuric and peracetic acid and their ammonium, sodium and potassium salts, in addition to systems such as potassium or ammonium persulfate-sodium bisulfite. Other oxygen-yielding compounds or sources include atmospheric oxygen, ozone and the like. If desired, an activating agent such as an alkali metal sulfite or bisulfite can be added to promote the reaction. The catalyst is employed in a catalytically effective amount which may range from about 0.01 to about 2.0, preferably 0.05 to 0.5 parts by weight based on the total weight of the mixture.

The polymerization is preferably carried out in an aqueous media, such as water, thus giving stable, aqueous emulsions containing solid, dispersed particles. The size of these particles may vary between 100 A and 5000 A, but the preferred particle size is 500 A-2500 A.

If desired, an activating agent such as an alkali metal sulfite or bisulfite can be added to the system in which case lower reaction temperatures may be used. Chain regulators, such as mercaptans, can also be employed in the polymerization.

Suitable surface active agents include fatty acid soaps, fatty alcohol sulfates and sulfonates, as well as sulfates and sulfonates of alkylphenoxy poly(ethyleneoxy)ethanol, etc. It has been found that stable emulsions of the type described in this invention can be prepared without the acid of an emulsifying agent or protective colloid, although it has been observed that it is preferable to add such materials to the emulsion recipe in order to obtain high conversions and greater stability of the resultant emulsions. The polymerization should be carried out in the absence of free oxygen,

conveniently under a blanket of a neutral gas, such as nitrogen, argon or the like.

In carrying out the polymerization reaction, the catalyst and the mixture of monomers may be admixed in any order, in increments or otherwise. For better temperature control and preparation of a product with optimum properties, it is, however, preferred to add the monomer and a reducing agent (e.g. sodium meta bisulfite) gradually and/or in increments to the aqueous solution of surfactant containing the catalyst and activator. It is permissible to carry out this reaction at a temperature ranging from about 10°C up to 150°C. However, in order to avoid runaway conditions or undesirable side-reactions, it is preferred to carry out the polymerization at about 40°C to 90°C. The pH of the medium is substantially non-critical, though a pH of below 6.0 and preferably between 3.5 and 4.5 is preferred. Completion of the reaction is determined by cessation of evolution of heat and/or spot analysis for residual monomer and the like. The thus produced aqueous emulsion containing the polymeric product is thereafter applied to the fabric.

The polymeric material described above is utilized in a water base emulsion as the treatment medium in accordance with this invention. In order to carry out the processes, the polymeric material is first diluted to a solids content of from about 5 to about 20% based upon the weight of the emulsion. In the preferred embodiment of this invention the polymeric material will preferably be present in the emulsion in the approximate range of 7 to 12% by weight. Where a viscosity improver can be utilized to obtain a more uniform emulsion, a higher content can be used.

In order to effect even superior adhesion to the fabric or garment substrate, one may add a catalytic initiator to the aqueous emulsion. These catalytic initiators are preferably acid catalysts that are well-known in the textile arts, although in certain instances a basic catalyst may be used. The catalyst most frequently used is oxalic acid.

The amount of catalyst to be utilized above is that conventionally used in activating the reaction between textile resins or polymers and hydroxy groups of cellulose, for example, up to about 5% by weight of an acid acting compound on the fabric with the preferred range being from about 1 to about 2%, based on the weight of the polymer. 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%.

It should be understood that any of the well-known lubricants that are conventionally used to facilitate subsequent processing of fabrics may be added to the polymeric emulsions so long as they are compatible herewith. Likewise, antifoaming agents and other additives that do not affect the hand, stretch or other desirable characteristics of the fabric or garment may be added to the emulsion.

The emulsion may also contain 0 to 3.5% of a softener based on the weight of the fabric, this depending on the particular ratio of monomeric units in the polymeric emulsion and the desired hand of the finished product. Suitable softeners include "Gafstat" AD-510 — a free acid of a complex phosphate ester; "Gafac" RM-710 — a phosphate ester with an aromatic hydrophobic base; "Cutless 50" a blend of polyethylene and cationic softeners and the like.

The process of applying the emulsion may be carried out with existing plant equipment, such as a pad box and roll and drying frames.

Broadly speaking, the process comprises applying the emulsion to the material from a pad bath; the emulsion is padded onto, e.g., polyester fiber such that there is approximately 75–100% wet pick up thereon; times may vary, however, generally a few seconds to 5 minutes or more is adequate.

After cure, there should remain about .1 to 5%, preferably 2–4% polymeric product by weight on the dry weight of the fabric. The pad bath temperature should be ambient to about 50 to 140°F, preferably about 120°F. The drying temperature are about 220° to about 255°F. The curing temperatures are about 285°F to 350°F; time will be approximately 30 seconds where the temperature is about 310°F, greater time being required for lesser temperatures and lesser time being required at the higher temperatures.

In the usual procedure, the aqueous emulsion is applied to the fabric or material. For example, a number of materials may be placed in a suitable container designed for a liquid treatment of this nature, and the articles or materials dipped and preferably submerged in the emulsion bath for a period of time ranging from a few seconds to 5 minutes or more. The emulsion bath may be at room temperature or at a temperature ranging up to about 140°F. After the textile article has been subjected to this treatment for a required length of time, the article is placed in an extractor for the purpose of extracting the excess liquid emulsion that may remain thereon. This extractor may comprise a spin dryer, for example. It should be understood that other means for applying the emulsion of this invention may be utilized, for example, spraying, padding or the like.

Subsequent to extraction, the material is preferably air dried for a period of time ranging approximately from an hour to 24 hours. At the end of this period the polymeric material will usually be present on the material or fabric in a weight percentage varying from about 0.1 to 15%, based on the weight of the material or fabric. During this period of time, due to the initiator which may be present in the emulsion, some curing or cross-linking may take place. It is preferable, though not absolutely necessary, that some curing take place in this stage so that subsequent treatments of the material or fabric may be facilitated, without adhesion of the materials or fabric to the processing equipment.

In an alternative procedure and the one which is preferred for use in accordance with this invention, materials are allowed to dry after treatment with the above described emulsion and extraction for a sufficient period of time to effect the partial cure of this polymeric material.

The final result is a finished fabric having a desirable hand, light fastness, durability and other good fabric qualities. These and other properties may be determined by tests known in the trade.

It is to be understood that the emulsion is equally as effective on warp knit and stretch wovens as it is on double knit polyesters. Also included are the "Banlon" texturized nylon fabrics and "Acrilon" acrylate fabrics as well as rayon-polyester blends.

The following examples are only illustrative of the instant invention; they are in no way to be considered as limiting. All parts, portions and ratios given therein as

well as in the appended claims are by weight unless otherwise specified.

EXAMPLE 1

Preparation of the interpolymer.

Apparatus: 2 liter resin kettle, equipped with mechanical stirrer, reflux condenser, thermometer, gas inlet tube and two graduated dropping funnels.

Procedure: 564 g. distilled water is charged into the resin kettle, 25 g. "Igepal" CO-970, 1 g. ammonium persulfate and 0.5 g. sodium metabisulfite are added and the system is purged with nitrogen. In a flask, 230 g. vinylacetate, 262.5 g. butylacrylate, 7.5 g. methacrylic acid and 0.79 diallyl phthalate are mixed, and that mixture is placed into a graduated dropping funnel. Fifteen % of this mixture is added to the reactor. The other dropping funnel contains 0.5 g. sodium metabisulfite dissolved in 119.5 g. of distilled water.

The reactants are stirred for 10 minutes, then heating is started, and the temperature of the contents of the kettle is raised to 65°C. At this temperature, addition from both graduated dropping funnels is started, and the monomers and activator are added simultaneously over a 2 hour period. When the addition is completed, the mixture is stirred at 65°C for the 15 additional minutes. After which the temperature is raised to 85°C which is maintained for one-half hour. Finally, the temperature is lowered to 25°C and the product, a milky, white latex, is discharged through cheesecloth.

EXAMPLE 2

Apparatus: As described in Example 1

Procedure: 763 g. distilled water is placed in the resin kettle, 5 g C₁₈ hydroxy alkylsulfonate, 5 g. Igepal CO-970 and 10 g acrylic acid are added. The pH of the solution is adjusted to 7.5 with conc. ammonium hydroxide solution. After which 41 g. vinylacetate and 41 g butylacrylate are added and the system is purged with nitrogen.

In a flask, 224 g. vinylacetate, 224 g. butylacrylate and 1 g diallylphthalate are mixed, and the mixture is placed in a dropping funnel.

0.3 g. ammonium persulfate is added to the reaction mixture and heating is started. The temperature is raised to 72°C which is maintained for 30 minutes. After which the addition of the monomers is started, and the contents of the dropping funnel is added over a 2 hour period. When the addition is over, the temperature is held for 1 hour, then 0.3 g. of ammonium persulfate is introduced. The addition of the catalyst is repeated 1 hour later. Finally, the milky white latex is cooled to room temperature, and discharged through cheese-cloth.

EXAMPLE 3

Apparatus: 5 l. kettle, equipped as described in Example 1

Procedure: Similar to Example 1, except that the monomer mixture consists of 486.8 g. butylacrylate, 54.7 g. 2-ethylhexylacrylate, 473.8 g. vinylacetate, 15.4 g. acrylic acid and 7 g. diallyl phthalate.

EXAMPLE 4

Apparatus: As described in Example 1

Procedure: 448 g. distilled water is placed in the kettle. Five gram itaconic acid is dissolved in 85 g. distilled water, and 10 g. of this solution is added to the kettle.

22 g. Igepal CO-970 is charged, and the system is agitated until the solution is clear. 237.5 g. butylacrylate, 100 g. ethylacrylate, 103.5 g. vinylacetate and 1 g. diallylphthalate are mixed in a flask and 25% of this mixture is added to the itaconic acid-surfactant solution. The rest of the monomers are placed in a graduated dropping funnel.

The system is sparged with nitrogen, then 2 g. ammonium persulfate is dissolved in 18 g. distilled water and 1 g. of sodium metabisulfite dissolved in 19 g. distilled water; 5 g. of each solution is added to the reaction mixture.

Heating is started and the contents of the kettle are heated to 50°C. At this temperature gradual addition of monomers, itaconic acid solution and catalyst solution is started. The addition is made over 1½ hour. After the addition is completed, the temperature is allowed to increase, but is not allowed to exceed 65°C. The peak temperature is maintained for 15 minutes. After that the latex is cooled to room temperature, the pH is adjusted to 6.5 with conc. ammonium hydroxide solution, and the polymer is discharged through cheese-cloth.

EXAMPLE 5

Apparatus: As described in Example 1

Procedure: Similar to the one described in Example 1, except the monomer mixture consists of 492.5 g. butylacrylate, 7.5 g. methacrylic acid and 0.7 g. diallyl phthalate.

EXAMPLE 6

Apparatus: as described in Example 1

Procedure: 425 g. distilled water is charged into the reaction kettle. 25 g. Igepal CO-970, 2 g. sodium bicarbonate and 0.15 g. ammonium persulfate are added. The system is purged with nitrogen.

In a flask, 302.5 g. butylacrylate and 247.5 g. vinylacetate are mixed. 15% of this mixture is added to the reaction mixture, and heating is started. The mixture is heated to gentle reflux which is maintained for about 15 minutes (about 83°C). After that gradual addition of the rest of the monomers is started and the monomers are added over 2 hours while maintaining gentle reflux. After the addition, the temperature is maintained for 1 hour, then it is increased to 90°C, which is held for 1 hour. Finally, the latex is cooled and discharged through cheese-cloth.

EXAMPLE 7

Apparatus: Fabric padder, equipped with wringer and pad-bath.

Procedure: The polymer latex of Example 1 is diluted to about 10% solids content and placed in the pan of the padder. A pre-weighed 3 × 13 inch swatch of polyester double-knit fabric is put through the apparatus with a wringer setting which allows a wet pickup of about 80% on the weight of the fabric. After which the text-piece is fastened to a drying-frame and placed in a pre-heated, forced-air oven. The test-piece is kept in the oven at 320°F for 5 minutes.

EXAMPLE 8

(pad bath formulation preparation)

Emulsion of Example 1
"Gaflex" E-cationic polyethylene emulsion
Water

100 gms.
20-40 gms.
1000 gms.

The pad bath is heated to 75°–120°F and padded onto the fabric with the pad roll pressure adjusted to obtain 80% wet pick up. The padded fabric is then dried and cured for 1–2 minutes at temperatures from 250°–350°F. The time should be adjusted so that the fabric temperature equalizes ambient temperature in the final curing stage.

EXAMPLE 9

(pad bath formulation modification)

Emulsion of Example 2	100 gms.
Glycol (e.g. ethylene, propylene, 2,3-dibromobutylene)	1–2 gms.
Softener (optional, depending on hand desired)	20–40 gms.
Water, sufficient to make	1000 gms.

EXAMPLE 10

3 × 13 inch pieces of polyester double knit fabric are treated as described in Example 7, using as pad-baths, polymeric emulsions described in Examples 1 through 6, respectively. Another piece of 3 × 13 inch fabric — dipped into distilled water instead of the polymeric pad-bath is used as control.

The pieces are tested for:

- Snagging (600 revolutions on the Mace-Tester), as is
- Snagging (after washing as per AATTC test method no. 124-1969)
- Snagging (after dry-cleaning as per AATTC test method no. 86-1970)
- Wet-crock (using AATTC test method no. 8-1969)
- Hand

The results are as follows:

Table I

Latex of Example	Wet-Crock	As Is	After Washing	After Dry-Cleaning	Hand
1	Good	Good	Good	Good	Soft
2	Good	Good	Good	Good	Soft
3	Good	Good	Good	Good	Soft
4	Good	Good	Good	Good	Soft
5	Fair	Fair	Good	Fair	Slightly firmer
6	Poor	Poor	Poor	Poor	Soft
Control	Very Poor	Good	Very Poor	Very Poor	Soft

EXAMPLE 11

To determine anti-shrink and fabric stabilization properties of the finish on polyester/cotton blends.

Procedure: In order to determine the effect of the finish on the shrinkage control of cotton, 100% broadcloth cotton and 65/35 polyester/cotton blends are employed. These fabrics are treated with two different types of the interpolymer emulsions. The pad bath formulations are as follows:

Table II

Components	A	B	C	D
Emulsion of Example 1	10.0g	10.0g	—	—
Emulsion of Example 2	—	—	10 g	10 g
Water	90 g	90 g	90 g	90 g
Citric Acid	0.1g	0.1g	1.0g	1.0g
Magnesium Chloride	0.6g	—	0.6g	—

All pad baths are heated to 120°F and applied at 100% wet pick-up on broadcloth cotton and 65/35 polyester cotton. All finishes are pre-dried at 250°F for 5 minutes before the final cure.

Finishes A and C are cured for 12 minutes at 325°F in an attempt to cross-link the finish directly to the cotton. Finishes B and D (no magnesium chloride) are cured for 2 minutes at 325°F in an attempt to cross-link the finish internally without cross-linking to the cotton.

Shrinkage tests are run by boiling the fabrics for 10 minutes, rinsing, extracting and steam pressing to dryness. 10 × 10 inches swatches are used and a 5 inch square is measured off and marked in the center of each swatch just prior to boiling. The results are as follows:

	Broadcloth Cotton	65/35 Polyester/Cotton
A	5" × 4 14/16"	5" × 4 14/16"
B	4 14/16" × 4 14/16"	5" × 4 14/16"
C	5" × 4 29/32"	5" × 4 15/16"
D	5" × 4 26/32"	4 31/32" × 4 14/16"
Control	5" × 4 12/16"	5" × 4 12/16"

(First number being the measurement across the warp)

In all cases the greatest shrinkage takes place in the direction of the warp. It is believed that greater shrinkage control is obtained where cross-linking to the cotton is made.

EXAMPLE 12

Performance tests were run with the finish of Example 1 and two commercially available products, "Vibraflex MF" and "Mace Gard 702".

TABLE III

Evaluation/Finish	Finish Ex. 1	Mace-Gard 702*	Vibraflex MF*
Application % OWF	3.0	3.0	3.0
	(All finishes dried at 250°F, and cured at 350°F for 30 seconds)		
Shade Change	4	3	3
Wet Crocking	3	5	3–4
Dry Crocking	4–5	5	4–5
No. AATCC Wash	3–4	3–4	3
40 hr. Fadometer	2–3	—	—
Solvent Bleeding	3–4	—	—
Acid Perspiration	3–4	—	—
Alkaline Perspiration	3–4	—	—
Hand for Men's Wear	V-Good	Good	Fair to Good
Durability (5 washes)	Hand slightly softer	Hand slightly stiffer	Hand slightly stiffer
Anti-Snag	4–5	2–3	2–3

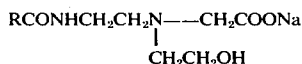
*Polyacrylates

Fabrics are evaluated using a 1-5 scale graduated as follows:

1. Severe change, 2. Marked change, 3. Moderate change, 4. Slight change, 5. Negligible or no change.

The same double knit 100% texturized polyester was used in all above tests, dyed at a 2.0% level with "GENACRON" blue BRL.

Complex fatty amide amphoteric compounds, such as "SOROMINE" AT may be employed in like amounts as softener, either alone or with the aforementioned softeners when both a good hand and antistatic properties are desired. Amphoterics including as a major component thereof, the following compound, are preferred.



wherein R = C₈₋₂₂, preferably C₁₆₋₂₂.

Since it is obvious that numerous changes and modifications can be made in the above described details without departing from the spirit and nature of the invention, it is to be understood that all such changes and modifications are included within the scope of the invention.

We claim:

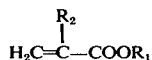
1. A process for treating knitted textile materials, comprising applying to said materials an aqueous emulsion of an interpolymer comprising approximately by weight:

- a. 20 to 79% of a vinyl ester having the formula:



wherein R is a straight or branched chain C₁₋₁₈ alkyl radical;

- b. 20 to 79% of an ester of an α,β -monoolefinically unsaturated carboxylic acid having the formula:



wherein R₁ is straight or branched lower alkyl and R₂ is hydrogen or C₁₋₈ alkyl;

- c. 1 to 10% of an α,β -monoolefinically unsaturated carboxylic acid; and

- d. 0.5 to 2% of a bifunctional monomer having the formula:



wherein R is selected from the group consisting of oxygen, an amine radical, and a dicarboxylic acid radical,

and thereafter subjecting the treated knitted textile materials to curing conditions, whereby 0.1 to 5% by weight of the cured polymeric product per dry weight of the knitted textile material remains on said knitted textile materials.

2. A process as defined in claim 1 wherein unit (a) is vinyl acetate.

3. A process as defined on claim 1 wherein unit (b) is selected from the group consisting of methyl acrylate, ethyl acrylate, n-butylacrylate and 2-ethyl hexylacrylate.

4. A process as defined in claim 3 wherein unit (b) is butylacrylate.

5. A process as defined in claim 3 wherein unit (b) is ethyl acrylate.

6. A process as defined in claim 3 wherein unit (b) is ethyl hexylacrylate.

7. A process as defined in claim 1 wherein unit (c) is a monocarboxylic acid.

8. A process as defined in claim 1 wherein unit (c) is a dicarboxylic acid.

9. A process as defined in claim 7 wherein said acid is acrylic acid.

10. A process as defined in claim 7 wherein said acid is methacrylic acid.

11. A process as defined in claim 7 wherein unit (d) is diallyl phthalate.

12. A process as defined in claim 1 further comprising adding at least one suitable textile softener to said emulsion.

13. A process as defined in claim 1 wherein said textile materials contain thermoplastic fibers.

14. A process as defined in claim 1 wherein said treated materials contain 75-100% of said emulsion based on the weight of said materials.

15. A process as defined in claim 1 wherein the dry weight of said interpolymer on said material after cure is about 2 to 4% by weight of said material.

16. A process as defined in claim 1 wherein said treatment is carried out at temperatures ranging from about 100° to 140°F.

17. A process as defined in claim 1 wherein said curing is carried out at a temperature ranging from about 250° to 360°F for about 30 seconds to 2 minutes.

18. A fibrous textile material normally susceptible to picking snag and pull damage protected against such damage by treatment according to claim 1.

19. A fibrous textile material as defined in claim 16 wherein said materials contain thermoplastic fibers.

20. A material as defined in claim 17 selected from the group consisting of nylon, acrylics, polyester, polyester knits, polyester double knits, cotton-polyester blends and rayon-polyester blends.

* * * * *

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