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3,476,581

TREATMENT OF TEXTILES WITH CROSS-LINKABLE ACRYLIC POLYMERS AND THE RESULTING PRODUCTS

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7 Claims

ABSTRACT OF THE DISCLOSURE

A process for treating sheer knit or woven textile articles to improve their resistance to pulling, snagging and picking comprising applying an aqueous acrylic polymeric emulsion containing ester groups to a textile article, drying the treated textile article to partially cross-link the polymer, and curing the acrylic polymer under textile resin curing conditions so as to cross-link the polymer and to obtain a soft, resilient coating on the textile article.

This invention relates to a process and resulting article wherein a textile material is treated with a polymeric emulsion to increase the material's resistance to pulling, snagging and picking.

In the production of knitting or weaving of sheer garments such as sheer knitted stockings some difficulties arise that are peculiar to the art. Due to the deviation of production elements such as sinkers and needles in knitting machines, stitch formation of an irregular type will result in articles that will run, snag or pull when worn.

Various suggestions have been made in the prior art to solve these problems and various types of articles including stockings are offered on the market which are resistant to the aforesaid difficulties by the adoption of other than 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 may be produced. 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 prior art to overcome the difficulties of pulling, snagging and picking in woven and knitted fine denier sheer garments. None of these treatments have been really commercially successful because any treatment that is proven to be effective will affect the "hand" and/or the stretch characteristics of the garments.

On object of the present invention is to provide textile articles including sheer stockings which have exceptional resistance to picking, running or snagging, while demonstrating excellent "hand" and stretch characteristics.

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

According to the present invention a process is provided for treating a textile article with an aqueous liquid wherein the liquid contains a polymeric substance comprised of at least some acrylic monomers, some of which are esters.

The polymers and copolymers that are useful in this invention are those acrylic emulsion polymers that cross-link or cure to form a relatively soft film. These polymers should combine softness, resilience and low temperature flexibility with improved dry cleaning fastness and excellent wash fastness. These polymers should be cross-

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linkable which means that should either be self cross-linking or possible of reacting or curing in situ with a nitrogenous or other type of external cross-linking agent, under the curing conditions of this invention set forth hereinafter. The compound or compounds having groups that are capable of cross-linking may be reacted in situ with the acrylic monomer during the curing step of this procedure if desired, to form a thermosetting type resin.

The process of the present invention may be applied to knitted or woven fabrics or articles and is applicable to wool or nylon or mixtures of these materials, and also to fabrics or articles containing wool and/or nylon in admixture with other fibers such as the synthetic protein fibers, e.g., material known under the name "Ardil" and the ethylene glycol terephthalic polyesters, e.g., material known under the name "Terylene," cotton, rayon, casein fiber, cellulose acetate, e.g., the viscose rayon material known under the name "Fibro."

Among the articles which may be treated according to the present invention are underwear, or outerwear garments, hose, half-hose, quarter-hose, three-quarter hose, socks and stockings, felts, hats, ties, furnishing fabrics, upholstery for motor cars, 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 this treatment. It is, however, preferable that the textile materials treated in accordance with this invention should be free of other finishes, i.e. lanolin or the like.

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

The term "picking" as used herein refers to the tendency of sheer fabrics to have unsightly broken threads and holes, this characteristic particularly being present in knitted stockings and the like. The measurement of this physical characteristic of fabrics particularly stockings can be carried out on the Hanes Pick Tester, U.S. Patent 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 stockings are first board inspected and all defects marked and then put into the pick tester and tumbled for three minutes at approximately 18.8 r.p.m. The straight pins hold the hose as well as the baffles in the tumbler thus giving hose a tumbling action. After three minutes in the tester the samples are removed and inspected for defects. Defects are classified as to their location in the hose (boot or welt). The additional defect totals are recorded.

The process of this invention is particularly beneficial in treating garments or fabrics produced from textured textile yarn. One of the textured yarns that is particularly difficult to work with and has been proven to give a relatively high number of picks, pulls and snags in woven or sheer knitted garments is "AGILON"® yarn or any equivalent edge-crimped yarn. AGILON® yarns as produced in accordance with the method and apparatus as set forth in U.S. Patent 2,919,534 to Bolinger et al. or by the apparatus set forth in Patent No. 2,977,746 to Klein, particularly shows improved results when finished in accordance with the process of this invention. It is known that AGILON® stockings, particularly those knitted from multifilament yarn, i.e., 15 denier, 3 filament will demonstrate between 10 and 20 picks per hose when tested on the Hanes pick tester described above. After treatment according to the process of this invention, the AGILON® stockings will generally when tested on a Hanes pick tester demonstrate from one to five picks per hose, under the same conditions.

Garments made from yarn produced from other tex-

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turing methods such as the Pinlon process, covered in part by Patents 2,914,810, 3,153,272 and 3,174,206 will show marked improvement when finished in accordance with the process of this invention.

Yarns made by other texturing processes such as "Spunize" or by other gear crimping, stuffer box or false twist crimping methods can be treated beneficially in accordance with this invention and will improve the pick, pull and snag resistance of the garments that are so treated.

The polymers that are most useful in this invention are those known to the art as the acrylics, including particularly the acrylates. These polymers may be homopolymers or copolymers so long as the acrylate chain has both ester groups and groups that are capable of cross-linking with the polymeric chain under properly catalyzed conditions. It is, however, preferred that copolymers be utilized for the most part. In general, the polymers utilized in this invention will have molecular weights ranging from about a few hundred, i.e. three hundred to about three million and be comprised from an acrylic monomer having ester groups and a side chain group that is comprised of compounds selected from the group having epoxide, carboxyl and/or methylol groups. Among the most preferred polymers are the acrylates and particularly the alkyl acrylate monomers such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, pentylacrylate and the like up to and including 12 carbon atoms alkyl acrylates. Within this particular group poly-n-butylacrylate having a molecular weight in the range of one thousand to one million is the preferred species.

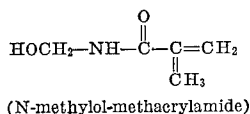
Any of the above acrylic monomers may be reacted with any copolymerizable compounds containing epoxide groups, carboxyl groups or methylol groups. Compounds having functional groups that can be cross-linked are preferably n-methylolacrylamide, glycidyl acrylate, acrylic acid and methacrylic acid. These co-monomers that can react in the copolymerization process or in situ to form a side chain group having an epoxy, carboxy and/or methylol group are usually present in an amount ranging from 0.5 percent to 10 percent by weight of the polymeric material formed.

In addition to the above compounds that have functional groups that can be cross-linked, particularly where the crosslinking takes place in an in situ reaction, acrylic anhydride, glycol esters of acrylic or methacrylic acid and acrylamide may be used.

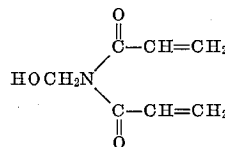
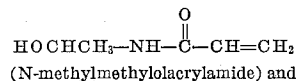
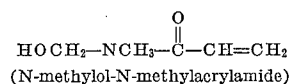
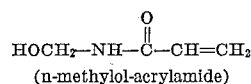
The backbone of the polymeric chain may be comprised of any of the acrylic monomers set out in the book entitled "Reaction Of The Acrylic Esters," reprinted from Chapter VI Monomeric Acrylic Esters by E. H. Riddle, published by the Reinhold Publishing Corporation, 430 Park Avenue, New York (Sp-182 copyright 1954 by the Reinhold Publishing Corporation).

The polymerization or copolymerization of these acrylic monomers may be carried out with either a persulfate or peroxide catalyst or with a redox catalyst system in accordance with the recipes and formulations set forth in the publication entitled "Emulsion Polymerization Of Monomeric Acrylic Esters," published by Rohm and Haas Company, Special Products, Washington Square, Philadelphia 5, Pennsylvania (Sp-154 Published in April 1960, superseding Sp-154 dated May 1959). In these polymerization and copolymerization reactions which are generally well-known in the prior art the cross-linkable monomer should be present in the emulsion reaction in the general range of 0.2% to 20%, by weight, of the acrylic monomer.

Among the preferred cross-linkable compounds characterized above are the methylol acrylamides, e.g.:

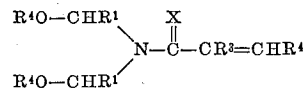


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Additional suitable methylol acrylamides include those having more than one methylol group, such as shown in the following formulae:

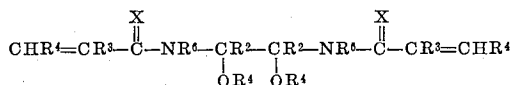
(VI)



wherein R¹ is selected from hydrogen, lower alkyl and the residue of an aldehyde; R³ is selected from hydrogen and methyl; R⁴ is selected from hydrogen and lower alkyl; and X is selected from oxygen and sulfur.

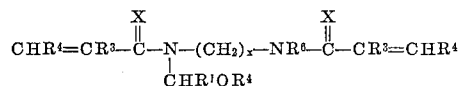
Other acrylamide compounds may be utilized, e.g., alkylene-bisacrylamides to provide compounds of the following formulae:

(VII)



wherein R³, R⁴ and X are as before, R⁶ being hydrogen, lower alkyl or CHR¹OR⁴ wherein R¹ is as before at least one R⁶ being CHR¹OR⁴. Typical compounds include that derived from acrylamide and glyoxal and the N-methylol, di-N-methylol derivatives thereof.

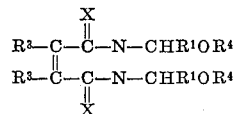
(VIII)



wherein R³, R⁴, R⁶ and X are as before, and x=1,6 e.g., N-methylol-methylene-bis-(acrylamide), methylene-bis-(N-methylol acrylamide) and the like.

Additional, but less preferred, compounds include:

(IX)



wherein R¹, R³, R⁴ and X are as given above, e.g., as wherein R¹ and R³ are hydrogen and X is oxygen.

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

The latent base acting catalyst utilized herein preferably comprises alkali-metal salts, such as alkali-metal carbonates like sodium carbonate which is neutral to moldly alkaline, for example pH of about 8.5 on the

fabric but decomposes at temperatures in excess of about 80° C. to form the stronger base sodium carbonate, which will initiate substantial reaction at the elevated temperatures utilized during curing. Sodium carbonate may be utilized if desired since the pH of 9.5 in the fabric produced by this compound in normal condition is generally insufficient to initiate the desired degree of reaction under normal temperature conditions.

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

Additional base acting catalysts include potassium bicarbonate, potassium carbonate, sodium silicate, alkali metal phosphates, 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 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%.

The amount of catalyst to be utilized will 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 polymeric material described above is utilized in a water base emulsion as the treatment medium for sheer fabrics and garments in accordance with this invention. In order to carry out the processes of this invention the polymeric material is first diluted in an aqueous emulsion. The polymer may be present in an amount ranging from about 0.1% to 46% solids by weight, based upon the weight of the aqueous emulsion. In the preferred embodiment of this invention the polymeric material is primarily insoluble in water and will preferably be present in the emulsion in the approximate range of 0.3 to 28% solids, by weight, based upon the weight of the emulsion. Where a viscosity improver can be utilized to obtain a more uniform emulsion a higher solid content can be used.

In order to effect cross-linking of the polymer and in order to accomplish good adhesion to the fabric or garment substrate it is necessary to add a catalytic initiator to the aqueous emulsion for the reaction. These catalytic initiators are preferably acid catalysts that are well-known in the textile arts, although in certain instances and depending upon the polymers or copolymers selected, a basic catalyst may be used. Among the catalysts most frequently used are oxalic acid and diammonium phosphate.

It should be understood that any of the well-known lubricants that are conventionally used to facilitate subsequent processing of fabrics or stocking may be added to the polymeric emulsions so long as they are compatible therewith, i.e. Lanogel 41®. 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.

After the desired emulsion has been prepared and brought to the proper consistency either by the dilution of a polymeric material that may be a powder or granular or by the addition of the polymeric material to water

to form an aqueous emulsion and after the catalyst has been added in a proper concentration usually ranging from 0.1% to 20%, by weight, based upon the weight of the emulsion, the process of treating the garments or fabrics is commenced.

In the usual procedure the aqueous emulsion is applied to the fabric or garment. For example, a number of stockings or other sheer fabrics or garments may be placed in a suitable container that is designed for a liquid treatment of this nature, and the articles or garments dipped and preferably submerged in the emulsion bath for a period of time ranging from a few seconds to five minutes or more. The emulsion bath may be at room temperature or at a temperature ranging from about 50° F. to 125° 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 therein. This extractor may comprise a spin dryer, for example. It should be understood that other means for applying the emulsion for this invention may be utilized, for example, spraying, vapor treatment or the like. Subsequent to extraction the garments are 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 garment or fabric in a weight percentage varying from about 0.1 to 10%, based on the weight of the garment or fabric. During this period of time due to the catalytic initiator present in the emulsion, some curing or cross-linking will take place. It is preferable, though not absolutely necessary, that some curing take place in this stage so that subsequent treatments of the garments or fabric may be facilitated, without adhesion of the garments or fabrics to the processing equipment. For example, in the further processing of stockings which involves "boarding" if some curing is allowed at room temperature prior to curing in a subsequent step at higher temperature boarding may be accomplished much more quickly and with less difficulty than otherwise.

Where stockings are processed according to this invention a number of alternative boarding procedures may be used. In this first procedure to be described the stockings may be boarded while wet. Here a light coating of oil or equivalent are placed on the boards with a subsequent removal of any excess oil. The boards are then preheated to varying temperatures in the range of approximately 200 to 300° F., most preferably 240 to 260° F. Heating of the boards may be accomplished as in conventional boarding processes i.e., by use of steam. The hose are then placed on the hot boards and are allowed to remain on the boards until all welts are dry. The period of time involved in this boarding procedure will vary from approximately one to five minutes. The hose are then preferably vacuumed for a few seconds and the dry hose removed from the boards.

In an alternative procedure and the one which is preferred for use in accordance with this invention garments, including hose 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. In this procedure the boards are coated with a light oil such as knitting oil. In any respect, such oil is removed. The hose are then placed on hot boards and allowed to remain there for a period ranging from one to five minutes at the above temperatures. Again, the dry hose are vacuumed for a few seconds and removed from the boards.

A typical procedure for the preparation of the polymers of the type that are useful in this invention is as follows:

To a 1000 ml. round bottom five-neck flask equipped with a thermometer, a stirrer (a) with a half moon paddle, a water cooled condenser and four more openings, the addition of the chemicals listed below is started.

At first 75% of the water and of the emulsifiers and all of the sodium bicarbonate are introduced in the flask (this is the initial charge); the rest of the chemicals, except the oxidizing agent, ammonium persulfate and the reducing agent Formopon are used to form a preemulsion. The preemulsion must be stable in order to assure uniform and consistent addition of the chemicals. This is done by obtaining the maximum viscosity of the emulsion system upon slow addition of the acrylates to the water phase, where the emulsifiers were already dissolved, and with slow stirring, an oil in water stable preemulsion is formed. The speed of the stirrer was 110-116 r.p.m. until about the last 10-15 ml. of the preemulsion at which point the speed was increased to 125 r.p.m. Of this preemulsion 25% is added to the reaction flask after the initial charge is sparged with nitrogen for one hour and forty-five minutes at the rate of ca. 60 bubbles per minute. One hour and forty-five minutes later the reducing agent is added, followed by the addition of 68.3% of the oxidizing agent (ammonium persulfate) five minutes later. At this point the temperature begins to rise, the emulsion looks blue, and at 29° C. the addition of the balance of the preemulsion is resumed, at ca. 55-65 drops per minute. The reaction temperature is kept $53 \pm 2^\circ$ C. and may be regulated to a great extent by the rate of addition of the preemulsion. When the reaction temperature began to drop (even after an increase in preemulsion addition rate), then, the reaction temperature was allowed to drop to $45 \pm 1^\circ$ C., while the rate of addition of the preemulsion was slowed down gradually. At this point 1 ml. of the oxidizing agent was added and the temperature began to rise; this was followed by an increase of the rate of addition of the preemulsion to about 65 drops per minute. As the viscosity of the reaction increased the rate of stirring was increased, so as to maintain a slight vortex in the polymerization reaction. While the exotherm was being dissipated, again the same procedure was used, that is, reducing the rate addition of the preemulsion before the last portion of the oxidizing agent was added; the rate of addition was once more increased and the exotherm was sufficient to complete the preemulsion addition. Ten minutes after all the preemulsion was added the temperature reached the maximum of 54° C. At this point a slight drop in temperature was observed (53.7° C.), vacuum was applied for thirty minutes. This brought the temperature down to 32° C. The reaction was stopped and the amount of coagulum was estimated to be <0.1 gm. Upon dilution and stirring no cobweb formation was observed. A film made from this polymer was practically clear (with very few and small ripples) and extremely soft and slightly tacky.

The chemicals used in this preparation are as follows:

Chemicals Used	Synonym	Weight or Volume
1 H ₂ O	Water	158.5 gms.
2 Triton X-405 (70%)		8.70 gms.
3 CH ₃ (CH ₂)COOSO ₃ Na(20%)	Sodium Lauryl Sulfate (Sipex UB)	5.90 gms.
4 NaHCO ₃	Sodium bicarbonate	0.10 gms.
5 CH ₂ CHCOONHCH ₂ OH(60%)	N-methylol acrylamide	4.54 gms.
6 CH ₂ C(CH ₃)COOCH ₃	Methyl methacrylate	2.73 gms.
7 CH ₂ CH ₂ CH ₂ CHCOOC ₂ H ₅	Butyl acrylate	118.61 gms.
8 CH ₂ C(CH ₃)COOH	Methacrylic acid	1.34 gms.
9 NaHSO ₂ CH ₂ O ₂ H ₂ O	Formopon	2.93 ml.
10 (NH ₄) ₂ S ₂ O ₈ (6%)	Ammonium persulfate	5.86 ml.

A typical polymer of this type is now made by the Rohm and Haas, Co. under the name E-287.

The following example is illustrative of the concept of invention and is not to be considered as limiting thereof. Further, it should be understood that those persons skilled in the textile art will be able from a study of this specification to make many variations and modifications

not specifically described herein but further within the scope and spirit of the invention.

EXAMPLE

Thirty-six grams of an n-butyl acrylate with self cross-linking methylol groups of the type prepared above (46% solids) was mixed with one gallon of water. One dozen ladies' hose were put into a cotton dye bag and submerged in the emulsion and agitated for five minutes. The dozen hose in the cotton dye bag were removed and extracted for one minute, then air dried at room temperature for a few hours. Hose were cured by boarding at 255° F. for one and one-half minutes. Hanes pick test results on 36 tests gave an average value of 3.41 picks per hose, which is a three to four times improvement over current commercial finishes. The pick test procedure used in this example is as follows:

- (1) Code or number each hose to be tested.
- (2) Pull each hose over board and identify each pick that might be in the hose. Use an ink felt pin for marking these picks.
- (3) Enter six (6) hose into pick tests on each cycle.
- (4) Run pick tests for three (3) minutes or a clock setting of 14 on the rack clock.
- (5) When machine is stopped, remove hose from machine-being careful not to further snag the hose.
- (6) Pull each hose over board and count and record all picks in hose. Identify each pick in order that it will not be counted again.
- (7) Run hose through tests for six (6) times on procedure above.
- (8) At end of six (6) cycles, total all picks per stocking and get an average of picks per hose. Record results on forms provided.

Having thus described the invention what is claimed is:

1. The method of treating a stocking comprising applying an aqueous emulsion of a cross-linkable polyacrylate polymer to the stocking, drying the stocking to partially cross-link the polymer, boarding the dried stocking in the presence of steam and curing the partially cross-linked polymer to a cross-linked condition by heating to obtain a stocking with a soft cross-linked polyacrylate coating, said cross-linkable polymer having a cross-linkable member selected from the group consisting of methylol, carboxy and epoxy groups.

2. The method of claim 1 wherein the polymer is poly-n-butylacrylate (having a cross-linkage member selected from the group consisting of methylol, carboxy and epoxy groups).

3. The method of claim 2 wherein the stocking is boarded at a temperature in the range of 240 to 260° F. (in the presence of steam).

4. The method of claim 3 wherein the cross-linkable member is N-methylol-acrylamide.

5. A nylon stocking treated according to the process of claim 1.

6. The stocking of claim 5 wherein the yarn comprising the stocking is produced from textured yarn.

7. The stocking of claim 6 wherein the yarn is textured by an edge-crimping process.

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U.S. Cl. X.R.

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