

UNITED STATES PATENT OFFICE

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WOOLEN TREATMENT AND PRODUCTS
THEREFORJohn B. Rust, West Orange, N. J., assignor to
Montclair Research Corporation, a corporation
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This invention relates to fiber treatment and particularly to processes of treating wool to reduce substantially the shrinkage of wool, to the products obtained by such processes of treatment, and to baths utilized in such treatment.

It is known that it is possible to produce non-felting and non-shrinking wool by chlorination or bromination of wool. There have also been described processes of producing non-felting wools by treatment with alcohol solution of alkalis, by treatment with sulfonyl chloride, nitrosyl chloride, and the like. (However, in this case mixed cotton and woolen goods cannot be treated.)

Treatment with rubber latex in the presence of quaternary ammonium, phosphonium, sulfonium compounds and the application of alkylated methylol melamine at relatively high temperatures have also been described.

In the prior art processes, difficulties are encountered including danger of damage to fibers, reduced wearing qualities, and undesirable hand which are difficult to prevent in most of the prior art processes.

Among the objects of the present invention is the treatment of wool and wool containing fabrics to render them substantially resistant to felting, fulling and shrinkage by a relatively simple process, and particularly wherein danger of damage to fibers, reduced wearing qualities and undesirable hand are eliminated.

Other objects include the production of treating baths enabling the conditioning of wool to produce products of the character set forth above.

Other and further objects and advantages of the present invention will appear from the more detailed description set forth below, it being understood that this more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present process, the wool either as raw wool, yarn, knit, woven goods or mixed goods, is entered into an aqueous conditioned bath containing a polymeric butadiene derivative, and exhausting the bath on the fiber. The bath desirably should contain the butadiene polymer in an amount to give under the conditions of treatment, a wool having from 1% to

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25% of polymer based on the weight of the wool. The bath is conditioned by adding to it sufficient strong electrolyte to allow the deposition of the polymeric butadiene derivative on the wool fibers.

It has been found that in such a bath, no deposition of the polymeric butadiene derivative occurs under ordinary conditions at a pH below 7. However, upon addition of an electrolyte, exhaustion of the bath will take place with varying rapidity depending mainly upon temperature and electrolyte concentration. Without any limitation by way of theoretical considerations, it is believed that a reversal of the electrical charge on the colloidal particles of the polymeric butadiene derivative takes place on addition of the electrolyte, enhancing the affinity of the polymeric butadiene derivative for the fiber. The proportion of electrolyte added would be insufficient to account, on a theoretical basis, for a salting out of the polymeric butadiene derivative particles. Thus the effect must be one of electrical charge rather than precipitation by coagulation. When the electrolyte is added to the treating bath, no coagulation or precipitation occurs even on heating for long periods of time. It is only in the presence of the wool that deposition occurs. This is additional proof that electrical charge of the particle is involved rather than the salt effect.

It is both startling and noteworthy that straight butadiene polymers or butadiene homologue polymers give notably superior non-felting effects than do butadiene copolymers and for this reason the polymeric derivatives from butadiene alone or butadiene homologues alone are preferred to the copolymers. The polymeric butadiene derivatives may be for example, the polymers of butadiene and its lower homologues such as isoprene, dimethyl butadiene, ethyl butadiene, ethoxy and methoxy butadiene, cyanobutadiene, and the like, particularly butadiene-1.3 and its derivatives, since as stated, these produce a much superior non-felting effect than the substantial copolymers with vinyl and methyl substituted vinyl compounds. For example, it has been found that in a series of copolymers of butadiene with methyl methacrylate, as the methyl methacrylate content of the copolymer increased, the non-felting characteristics imparted to the wool fibers decreased so that a butadiene polymer containing no methyl methacrylate renders wool entirely non-

felting whereas a straight methyl methacrylate has no effect upon the felting qualities under the same operating conditions. The same results have been found to be true with every vinyl compound tested. However, vinyl compound may be copolymerized with the butadiene or butadiene derivatives to give compositions which render wool non-felting to a satisfactory degree, the amount of vinyl compound present in the copolymer being regulated to give the result desired. As illustrative of such components that may be noted in producing copolymers there may be used vinyl acetate, methyl methacrylate, ethyl acrylate, styrene, acrylo-nitrile, vinyl pyridine, methacrylonitrile, isopropenyl methyl ketone, vinyl phenyl ketone, vinyl methyl ketone, and the like.

The electrolyte content may vary over substantial limits, but sufficient electrolyte should be present to condition the bath so that the bath although stable in the absence of wool fibers, will deposit the polymer in the presence of the conditioning electrolyte. Thus the electrolyte content may vary between from about 25% to about 500% based on the weight of polymeric butadiene derivative present. As such electrolyte, water-soluble salts may be used, desirably such salts which do not precipitate the polymer. The following are exemplary: sodium sulfate, sodium chloride, sodium bromide, sodium iodide, sodium phosphate, sodium sulfamate, sodium sulfite, sodium bisulfate, sodium bisulfite, sodium nitrate, sodium acetate, and the like, or salts of the above using potassium, lithium, caesium, and so forth, in place of sodium. Salts like zinc chloride may also be used where the coagulation does not appear to be too serious since it occurs in small particulate form, and the particles may be redispersed by stirring. Neutral salts, specifically salts of strong bases and strong acids, particularly inorganic salts, are preferred.

The term "conditioning electrolyte" is used hereinafter to cover such electrolytes which produce the desired deposition of the polymer in baths having a pH below 7.

The operation is desirably carried out at temperatures ranging from 40° C. to the boiling point of the bath. The process can be applied before or after fulling, weaving, scouring and the like operations. In some cases it can be applied in the dye bath. Mixed goods including wool-cotton, wool-rayon, etc., can be treated by this method without any deleterious effect. The wool may be subjected to a pretreatment, as for example, chlorination or bromination before being treated in accordance with the present invention.

In emulsions containing the butadiene polymer, the emulsifying agent may be any anionic emulsifying agent which is stable at a pH below 7. Such emulsifying agents are exemplified by sodium lauryl sulfonate, sodium alkyl naphthalene sulfonates, long chain alkyl sodium sulfonates, sodium dioctyl sulfosuccinate, etc. There may also be used neutral non-cationic emulsifying agents such as mannitol monolaurate, the reaction product of protein degradation products with acid chlorides, ethylene oxide reaction products with fatty acid, fatty alcohols, and the like.

The emulsions of the polymer used in accordance with the present invention are preferably but not necessarily, those which have been carried to a 100% polymerization. When 100% polymerization is obtained, considerable cross-linking has occurred in the polymer with consequent insolubility in organic solvents. Thus a type of

prevulcanization of the polymer has been obtained. It is also possible to vulcanize the polymers with vulcanizing accelerators such as thiuram disulfide, etc., vulcanizing agents such as sulfur, dinitrobenzene, alkyl phenol sulfide, etc., either previous or subsequent to deposition or dyeing, into the wool fibers.

After treatment in accordance with the present invention, the wool is rinsed and dried. Its properties have been altered to such a degree that it no longer has a tendency to felt during washing and consequently is non-shrinking also.

Exemplifying the present invention, the following examples are given:

EXAMPLE 1

An emulsion which contained 27.8% of a butadiene-isopropyl methyl ketone copolymer was made by mixing 20 parts of butadiene, 20 parts of isopropenyl methyl ketone, 100 parts of a buffer solution of about pH 10, 2.5 parts of 30% hydrogen peroxide, and 5 parts of sodium lauryl sulfate (the parts being by weight) and heating at 45° C. for 16 hours with agitation. A conditioned bath was made from 2.8 parts of the above emulsion, 300 parts water, 20 parts of acetic acid and 1 part of sodium sulfate. 15.9 parts of knitted scoured grey goods wool were entered in the bath at 55° C. and boiled for 1½ hours to secure complete exhaustion on the wool. This example represents substantially the minimum amount of electrolyte which may be used to condition the shrinkproofing bath. The treated sample contained 5% of butadiene-isopropenyl methyl ketone copolymer. It was subjected to 6 separate washings in a washing machine with water at 70° C. and with ¼% soap for 1 hour. No felting or shrinking whatsoever was noted in the treated sample whereas with an untreated control, strong felting and shrinking was noted after the second washing.

The method used for testing the non-felting characteristics imparted to wool by the present process involves a series of washings. The treated wool is placed in a large volume of hot (70°-100° C.) water containing ¼ to ½% of neutral soap in a washing machine and washed for 1 hour, after which the wool is rinsed and dried. The number of such treatments which the treated wool can endure before definite signs of felting are noted and taken as a measure of its resistance to felting. This washing procedure is similar to that used to test the permanency of certain cotton finishes and may be considered as quite drastic for wool.

EXAMPLE 2

	Parts
Butadiene	20
Buffer solution at pH 10	50
30% hydrogen peroxide	1.25
Sodium lauryl sulfate	2.5

The mixture was placed in a pressure reactor and heated at 45° C. with agitation for 17 hours. An emulsion was obtained which contained 27% solids. A sample of knitted scoured woolen goods weighing 16.8 parts was entered in a bath containing 3.11 parts of the above emulsion, 200 parts of water and conditioned with 7 parts of sodium sulfate. The bath was heated to 60° C. and rapid deposition of the emulsion occurred on the wool. The wool was rinsed and dried. It had a pleasing soft hand. On subjecting the wool to four washings as described above, no felting whatsoever was observed.

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EXAMPLE 3

A

	Parts
Methyl methacrylate	5
Butadiene	15
Buffer solution at pH 10	50
30% hydrogen peroxide	1.25
Sodium lauryl sulfate	2.5

B

Methyl methacrylate	15
Butadiene	5
Buffer solution at pH 10	50
30% hydrogen peroxide	1.25
Sodium lauryl sulfate	2.5

C

Methyl methacrylate	10
Buffer solution at pH 10	30
30% hydrogen peroxide	.05
Sodium lauryl sulfate	1.5

Emulsions A and B were placed in a pressure reactor and heated at 45° C. with agitation for about 18 hours. Emulsion A had a solids content of 27% and emulsion B had a solids content of 26%.

Emulsion C was agitated rapidly for a period of 8 hours at 60°-65° C. The solids content was found to be 21%.

Using the above emulsions, samples of knitted scoured woolen goods weighing approximately 16.4 parts were placed in a bath containing sufficient emulsion to give .82 part of polymer, 200 parts of water acidified with acetic acid and conditioned with 7 parts of sodium sulfate. The bath was heated to a top temperature of 70° C. and stirred until complete clarity was obtained showing that the polymer had deposited entirely upon the wool fibers. The treated pieces were subjected to five washings as described in Example 1. The pieces treated with emulsion A showed substantially no felting; that treated with emulsion B felted to a considerable degree but not as much as an untreated control; whereas the swatch of wool treated with emulsion C felted just as much as an untreated piece.

EXAMPLE 4

	Parts
Isoprene	10
Isopropenyl methyl ketone	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

The reactants were sealed in a pressure reactor and heated at 45° C. with agitation for about 17 hours. An emulsion was obtained which contained 32% solids. A knitted woolen swatch weighing 16.5 parts was treated with a bath consisting of 2.6 parts of the above emulsion, 200 parts of acidified water and conditioned with 5 parts of sodium sulfate. The wool was entered into the bath at 50° C. and stirred and heated at 50-60° C. until the bath was clear. The woolen piece was subjected to four washings as described in Example 1. Substantially no felting or shrinkage was noted.

EXAMPLE 5

	Parts
Butadiene	10
Styrene	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

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The mixture was reacted in a pressure reactor at 40° C. with constant agitation for 20 hours. An emulsion was formed containing 26.7 per cent of solids. 1.6 parts of beta phenyl naphthylamine was added as an antioxidant. A piece of knitted scoured wool weighing 10 parts was treated in a bath containing 100 parts of water, .05 part acetic acid, 3.8 parts of the above emulsion and conditioned with 3.5 parts of sodium sulfate. The wool was entered at about 50° C. and taken to the boiling point, whereupon the bath cleared up in a very minutes. Before washing the woolen piece has the dimensions of 19.1 x 11.1 cm. After six washings such as described in Example 1, substantially no felting was observed and the woolen piece showed the dimensions of 18.7 x 11.6 cm.

EXAMPLE 6

	Parts
Butadiene	10
Acrylonitrile	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

A stable emulsion containing 26.7 per cent solids was made by heating the above ingredients in a pressure reactor at 45° C. for about 15 hours. 1.6 parts beta phenyl naphthylamine were added as an antioxidant. A swatch of wool weighing 9.6 parts was treated in a bath consisting of 100 parts of water, 3.6 parts of the above emulsion, .5 part acetic acid and conditioned with 3.5 parts of sodium sulfate. The wool was treated in the bath at 60° C. until practically complete exhaustion was obtained. The treated wool was subjected to three washings as described in Example 1. Slight felting was noticed. It was then subjected to three additional washings under the same conditions, whereupon very bad felting occurred.

The above example illustrates that under certain conditions and with certain types of vinyl polymer considerable effect is obtained by using a substantial amount of the vinyl derivative as interpolymers. Thus in the case of Example 5, where 50% of styrene was used, only slight felting was obtained after six washings, whereas in Example 6, where 50% of acrylonitrile was used, extremely bad felting was obtained after six washings. The next example will also illustrate this fact to some degree.

EXAMPLE 7

	Parts
Butadiene	10
Methyl methacrylate	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

Polymerization of the emulsion was obtained in a pressure reactor at 45° C. for about 15 hours. A piece of knitted scoured wool weighing 9.1 parts was treated in a conditioned bath containing 100 parts water, 3.4 parts above emulsion, .5 part acetic acid, 3.5 parts sodium sulfate. The wool was treated at 60° C. until clearing of the bath occurred. Before treatment the wool had the dimensions of 15.7 x 9.7 cm. It was then subjected to six washings as described in Example 1. Considerable felting was noticed in this time but the dimensions were found to be 16 x 8.9 cm.

EXAMPLE 8

A piece of knitted scoured wool weighing 16.2 parts was treated in a bath consisting of 200

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parts of water, 3.2 parts of a commercial emulsion of polyvinyl acetate containing 50% solids, 2 parts of 10% sulphuric acid solution and 6 parts of sodium sulfate. The wool was treated in this bath at 55° C. Uneven deposition of the polymer occurred with some coagulation on the surface of the wool. The treated wool was subjected to six washings as described in Example 1 with subsequent extreme felting, as bad as an untreated control. The dimensions of the woolen piece before washings was 15.5 x 13.7 cm. After six washings the dimensions were 11.8 x 10.2 cm.

EXAMPLE 9

	Parts
Isoprene	10
Methyl methacrylate	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

An emulsion was obtained containing 30% solids by polymerizing the mixture in a pressure reactor at 45° C. for about 17 hours. A piece of wool weighing 8.7 parts was treated in the bath consisting of 100 parts of acidified water, 1.5 parts of above emulsion and conditioned with 3.5 parts of sodium sulfate. The wool was entered at 50° C. and heated at 50°-60° C. until the bath was exhausted. The treated wool was then subjected to three washings as described in Example 1. A medium felting was observed which became considerable after six washings.

EXAMPLE 10

	Parts
Isoprene	20
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

The ingredients were emulsified and polymerized in a pressure reactor at 45° C. for about 16 hours. A solids content of 22% was found. A piece of wool was treated in a bath containing sufficient of the above emulsion to produce a 10% increase in the weight of the wool. The bath was acidified and conditioned with an electrolyte consisting of sodium sulfate. The wool was entered into the bath at 55° C. and heated with agitation at 55°-60° C. for about 20 minutes, in which time the bath became entirely clear. The wool piece possessed a pleasing soft hand. On subjecting the treated wool to six washings, as described in Example 1, no felting whatsoever of the wool was observed.

EXAMPLE 11

	Parts
Butadiene	10
Ethyl acrylate	10
Buffer solution at pH 10	50
30% hydrogen peroxide	2.5
Sodium lauryl sulfate	2.5

An emulsion was obtained by polymerizing the above mixture in a pressure reactor at 40° C. for 20 hours. A stable emulsion containing 26.7 parts solids was obtained. A piece of knitted scoured but unfinished raw wool was treated in a bath containing sufficient of the above emulsion to allow an increase of 10% in the weight of the wool. The bath was acidified and conditioned with an electrolyte composed of sodium sulfate. The wool was entered in the bath at 55° C. and heated with agitation at 55°-60° C. until complete exhaustion was obtained. The treated wool

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was subjected to six washings as described in Example 1. Very bad felting was obtained on this treatment, medium felting being obtained even after three washings. This was slightly better than an untreated control.

EXAMPLE 12

A. (80% butadiene)

	Parts
Butadiene	32
Styrene	8
Buffer solution at pH 10	100
30% hydrogen peroxide	5
Sodium lauryl sulfate	5

B. (70% butadiene)

	Parts
Butadiene	28
Styrene	12
Buffer solution at pH 10	100
30% hydrogen peroxide	5
Sodium lauryl sulfate	5

C. (60% butadiene)

	Parts
Butadiene	24
Styrene	16
Buffer solution at pH 10	100
30% hydrogen peroxide	5
Sodium lauryl sulfate	5

D. (40% butadiene)

	Parts
Butadiene	16
Styrene	24
Buffer solution at pH 10	100
30% hydrogen peroxide	5
Sodium lauryl sulfate	5

The above emulsions were formed by heating the mixture in a pressure reactor at 45° C. for about 17 hours with agitation. Substantially complete polymerization occurred with a subsequent solids content of approximately 30%. 3.5 parts of beta phenyl naphthylamine was incorporated in each emulsion as an antioxidant.

Pieces of wool weighing approximately 10 parts were treated in a bath consisting of 3 parts of the given emulsion, 145 parts of water, 1 part 50% sulphuric acid and conditioned with 3 parts of sodium sulfate. The wool was entered in the bath at 55° C. and kept at 55° C. until complete deposition on the fibers occurred. The wool pieces were subjected to washings as described in Example 1. That treated with emulsion A showed no felting after six washings; that treated with emulsion B showed substantially no felting after six washings; the wool treated with emulsion C felted to a slight extent after six washings; whereas that treated with emulsion D was rather badly felted after six washings.

EXAMPLE 13

A treating bath was made by mixing 150 parts water, 4.4 parts of a butadiene emulsion containing 30% solids, 3 parts of acetic acid and conditioned with 1 part of sodium chloride. The bath was heated to 55° C. and a swatch of wool weighing 16.4 parts was placed in the bath. The wool was treated with good agitation for 15 minutes at 60° C. Exhaustion of the bath occurred in this time. The treated wool was subjected to 6 washings as described in Example 1. No felting was observed. Before washing the wool had a measurement of 17.4 x 12.8 cm. After the six washings the dimensions were 17 x 12.1 cm.

EXAMPLE 14

A treating bath was made by mixing 4.7 parts of a butadiene polymer emulsion containing 30% solids with 150 parts of water and 3 parts of acetic acid. 1 part of zinc chloride was added. Rapid clouding of the bath occurred and if allowed to stand for several hours the polymer separated out completely. However, 17.6 parts of wool were treated in this bath at 60° C. Complete exhaustion occurred. The treated wool was subjected to 6 washings as described in Example 1, during which considerable felting was noted.

EXAMPLE 15

150 parts of water, 3.5 parts of a butadiene polymer emulsion containing 30% solids were mixed with 3 parts of acetic acid and conditioned with 1 part of sodium acetate. The bath was heated to 55° C. and 13.2 parts of wool were entered. The bath was heated for ½ hour at 60° C. without complete exhaustion. Another 1 part of sodium acetate was added and heating continued at 60° C. for 20 minutes, after which complete exhaustion was secured. The wool was subjected to 6 washings as described in Example 1. No felting was noticed after these washings.

The treatment of wool fibers is particularly emphasized herein although other animal fibers such as silk and protein fibers such as "Aralac" (a casein fiber) may also be treated in accordance with the present invention.

Having thus set forth my invention, I claim:

1. The method of treating wool which comprises heating the wool in an aqueous emulsion at a temperature of from 40° C. to the boiling point of the bath containing a synthetic butadiene polymer of 100% polymerization and a non-cationic emulsifying agent in the presence of at least 25% by weight on the polymer of a water-soluble neutral salt of an alkali metal as conditioning electrolyte, the pH of the bath being below 7 to give deposition of from 1 to 25% by weight of polymer on the wool, the bath being substantially stable in the absence of the wool, the amount of the butadiene polymer being sufficient to give substantial shrinkproofing properties to the wool while retaining substantially its normal hand.

2. A bath for treating wool to give shrinkproofing with substantially normal hand which comprises an aqueous substantially stable emulsion containing a synthetic butadiene polymer of 100% polymerization, in amount to give 1 to 25% by weight of polymer deposition on the wool, a non-cationic emulsifying agent, and at least 25%

by weight on the polymer of a water-soluble neutral salt of an alkali metal as conditioning electrolyte, the pH of the bath being below 7.

3. A bath for treating wool to give shrinkproofing with substantially normal hand which comprises an aqueous substantially stable emulsion containing a synthetic homo-butadiene polymer of 100% polymerization, in amount to give 1 to 25% by weight of polymer deposition on the wool, a noncationic emulsifying agent, and at least 25% by weight on the polymer of a water-soluble neutral salt of an alkali metal as conditioning electrolyte, the pH of the bath being below 7.

4. A bath for treating wool to give shrinkproofing with substantially normal hand which comprises an aqueous substantially stable emulsion containing a synthetic butadiene polymer of 100% polymerization, in amount to give 1 to 25% by weight of polymer deposition on the wool, an anionic emulsifying agent, and at least 25% by weight on the polymer of a water-soluble neutral salt of an alkali metal as conditioning electrolyte, the pH of the bath being below 7.

5. A bath for treating wool to give shrinkproofing with substantially normal hand which comprises an aqueous substantially stable emulsion containing a synthetic butadiene polymer of 100% polymerization, in amount to give 1 to 25% by weight of polymer deposition on the wool, a neutral non-cationic emulsifying agent, and at least 25% by weight on the polymer of a water-soluble neutral salt of an alkali metal as conditioning electrolyte, the pH of the bath being below 7.

6. The method as set forth in claim 1 in which the polymer is butadiene 1.3 polymer, the emulsifying agent is sodium lauryl sulphate, and conditioning electrolyte is sodium sulphate.

JOHN B. RUST.

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