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FOOTWEAR ASSEMBLY

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4 Claims

ABSTRACT OF THE DISCLOSURE

Footwear assemblies are provided exhibiting improved resistance to foxing separation comprising superficially acetylated textile uppers, a polymeric soling and a foxing strip comprising an essentially non-polar elastomeric block copolymer.

BACKGROUND OF THE INVENTION

In the manufacture of footwear of various types, including canvas top shoes, slippers, sports wear, and the like, it is often a problem to develop a product having all of the physical properties desired and at the same time producing the product at a relatively low cost. Rubber soled shoes made of ordinary rubbers require vulcanization and have a number of properties which are found to be disadvantageous in footwear.

In addition to a textile upper and a polymeric soling injection molded thereon, the shoes contemplated in the present instance have a so-called foxing strip which masks the edge of the sole and the lower boundary of the upper to enhance appearance and improved the adherence of the polymeric sole to the textile upper. The adhesion of this foxing strip to the textile upper presents a serious technical problem, especially when the upper is damp from perspiration, wet weather or washing. The problem arises, in part, because of the difference in polarity between cellulosic textiles normally employed for uppers, such as cotton duck and the like, and the essentially non-polar polymeric compounds which form the soling and foxing strip. As the difference in polarity, expressed by dielectric constant, dipole moment, and solubility parameter, increases, adhesion decreases. An important additional cause for separation is the hydrophilic nature of cellulose which permits water to displace a non-polar material from its surface.

OBJECT OF THE INVENTION

It is an object of the present invention to improve the construction of footwear. It is a particular object of the invention to provide footwear and particularly shoes which do not require vulcanization. It is a special object of the invention to provide footwear comprising cellulosic textile uppers, polymeric soles, and a foxing strip exhibiting improved adherence to the textile upper under a variety of conditions encountered during use. Other objects will become apparent during the following detailed description of the invention.

STATEMENT OF THE INVENTION

Now, in accordance with the present invention, footwear is provided comprising a cellulosic textile upper, a polymeric sole, and a foxing strip wherein the latter comprises as its principal elastomeric component certain block copolymers more fully described hereinafter, and wherein the cellulosic textile is at least superficially esterified at least in the area contacted by the foxing strip, the degree of esterification being restricted to an acetyl content of between about 0.3 and 20% by weight of the treated cellulosic textile.

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When the degree of esterification of the cellulosic uppers is restricted as described above, the textile retains the appearance and characteristics of unmodified cellulose with the important exception that adhesion to the block copolymer foxing strip even under wet conditions is substantially enhanced. At the same time, the superficial extent of the esterification does not degrade the bursting strength or breaking strength of the textile upper as may occur with more fully esterified cellulose uppers. Moreover, the superficially esterified uppers actually exhibit adhesive properties under wet conditions (referred to as wet peel strengths) which are essentially equivalent to the same property tested under dry conditions. The more highly acetylated or esterified cellulose textiles on the other hand show a sharp drop in their breaking strength.

The textile uppers utilized in the production of this general class of footwear are well known in the art of footwear manufacture insofar as the cellulosic nature thereof is concerned. Primarily, the uppers comprise duck of various weights dependent upon the intended end use of the footwear. Thus, sports shoes may comprise a single or multiple layer of cotton duck reinforced with one or more fabrics of the same or of a different material. The textile may be either woven or non-woven but essentially the textile uppers contemplated for the preparation of the superficially esterified materials are largely cellulosic at least on the surface directly contacted by the block copolymer containing foxing strip. Moreover, it is highly preferred that the textile uppers insofar as the area of contact just referred to be essentially free of modifying coatings such as crease resistant or mold resistant coatings so that a direct contact can be made between not only the esterifying agents but also thereafter between the superficially esterified areas and the block copolymer foxing strip.

As is well known, the polymeric chains comprising cellulose are anhydroglucose units linked at the one and four positions with glycosidic bonds with the beta configuration. Therefore, each of the anhydroglucose units has three hydroxyl substituents which are potential sites for esterification. The so-called cellulose triacetate is considered to be a species wherein all of these hydroxyl units have been completely esterified. Secondary acetate (or secondary ester) is regarded as a triacetate which has been hydrolyzed to a lower level of esterification, normally, in the order of about 2.3 to 2.5 to give an acetyl content of 38–40.5%.

Contrasted to the completely esterified ("primary acetate") and the secondary acetates known in the art, the present products may be regarded as superficially esterified cellulose. Moreover, not only is the degree of esterification restricted essentially as referred to hereinbefore, but it is also preferred that the degree of esterification be concentrated at the surface of the textile especially at or near the surface immediately contacted by the foxing strip, although of course the entire textile may be so esterified.

For the purpose of describing the present invention reference will be made to the degree of esterification in terms of weight percent of acetyl groups in the esterified product. It will be understood that the superficially esterified cellulosic textile upper may be non-uniform to the extent that esterification may be on or near the surface and therefore more highly esterified at that point relative to the remainder of the textile but that the description of the extent of esterification will be an average figure for the entire cellulosic portion of the textile.

While the broad concept of the present invention contemplates the superficial extent of esterification to be between about 0.5 to 20%, it is preferred that the degree of esterification on an average basis be between about 1.0

and 5%. The textile retains the appearance of a cotton duck or other cellulosic textile upper and at the same time retains the relatively constant adhesive properties of the textile to the block polymer foxing under both wet and dry conditions.

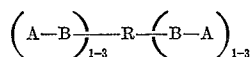
While esterification broadly is considered here, it is especially contemplated that this be acetylation. However, mixed esters such as acetate butyrate derivatives also are contemplated. It is preferred, however, that the acetate predominate in any mixed ester derivatives. Moreover, ether ester celluloses may be employed such as the acetate ethylate of cellulose although on an economic basis the simple ester will be preferred given similar results relative to adherence of the block copolymer foxing strip.

The esterification may take place on the individual fibers or threads prior to assembly of the textile or may occur with only a portion of such fibers; or may occur with respect to either the warp or woof of the textile assuming a woven textile is being considered. On the other hand, it is possible and actually probable that the superficial acetylation will be carried out on the finished textile, either woven or non-woven, prior to or subsequent to assembly as an upper. It is preferred that the conditions of acetylation be selected to not only minimize discoloration but also to prevent or minimize any reduction in breaking strength of the textile or textile fibers.

The general processes of acetylation are broadly known in the cellulose derivative art. Essentially, they comprise the esterification of cellulose in the presence of an acid catalyst such as sulfuric acid or perchloric acid together with an esterifying agent such as acetic anhydride or acetic acid or mixtures thereof. Preferably the esterification is carried out at ambient temperatures or slightly above, the conditions specifically being selected to minimize the disadvantage such as discoloration or strength loss referred to above.

The term "cellulosic" as applied to textile fiber and filament as well as the textile per se may designate either regenerated cellulose (rayon) or cotton fibers either in the form of fiber, yarn, thread, or textile.

The foxing strip and preferably but not essentially the polymeric soling comprise as a major elastomeric component a thermoplastic elastomer polymer which is a block polymer having the general configuration



wherein R is a valence bond or coupling agent residue, each A is a thermoplastic non-elastomeric hydrocarbon polymer block having a glass transition temperature above 25° C. and each B is an elastomeric hydrocarbon polymer block having a glass transition temperature below 10° C. Thus both linear and non-linear polymers are contemplated. Where two blocks B are directly connected, for the present purposes they are to be regarded as a single polymer block. Thus, the essential minimum block copolymer has the structure A—B—A.

The blocks A comprise either homopolymers or copolymers of monovinyl arenes such as styrene or alpha-methyl styrene or copolymers of styrene and a conjugated diene wherein the proportion of monovinyl arene is high enough so that the polymeric end blocks have a characteristically high glass transition temperature. On the other hand, the blocks A may comprise alpha-olefin polymers such as polyethylene, polypropylene, or ethylene-propylene copolymers of such proportion that the resulting polymer block is non-elastomeric. The blocks B, contrasted to the thermoplastic blocks A, are to be regarded as elastomeric at least under the conditions of utility. Primarily, they comprise polymer blocks predominating in conjugated dienes or their hydrogenated counterparts as well as their alpha-olefin equivalents such as ethylene-propylene rubbery copolymer blocks. The polymer may be partially or completely hydrogenated espe-

cially to eliminate at least any residual conjugated diene bonds and to alter solvent sensitivity. In either the non-hydrogenated, partially-hydrogenated or fully-hydrogenated states, however, the block copolymer is essentially non-polar.

The block molecular weights selected for use in the foxing strip polymer should be such that the entire block polymer has the characteristics of a thermoplastic elastomer. By this is meant, an elastomeric composition exhibiting the properties of a vulcanized rubber without being vulcanized at ambient temperatures but which at elevated temperatures exhibits the properties of a thermoplastic polymer and can therefore be processed in thermoplastic processing equipment. The virtue of these polymers aside from this aspect is that scrap portions of any form may be reused simply by reheating and reshaping. This is sharply contrasted to the lack of possibility of reusing vulcanized rubber compositions which require reclaiming.

The individual blocks will differ depending upon the species of monomer utilized in forming the blocks. Thus when the blocks A comprise monovinyl arene polymer blocks or their partially or completely saturated counterparts, the preferred molecular weights may vary from about 9,000 to about 40,000 and preferably from about 14,000 to about 25,000. The blocks B on the other hand when they comprise conjugated diene polymer blocks or their partially or completely saturated counterparts preferably have an average molecular weight between about 40,000 and 125,000 and preferably between about 45,000 and 75,000. Contrasted to the above molecular weight limitations, when the blocks comprise alpha-olefin, the preferred molecular weights of the blocks A are between about 5,000 and about 30,000 while the preferred elastomeric block B made from alpha olefins should be between about 40,000 and about 80,000.

The above described class of block copolymer is essentially in the foxing strip of the shoe assembly. They may be used as the elastomeric or polymeric component of the soling composition as well. Preferably, the soling composition and the foxing strip composition are essentially identical so that they may be formed during an injection molding operation.

The typical species of block copolymers suitable for use in the foxing strip and/or soling compositions are polystyrene-polybutadiene-polystyrene, polystyrene-polyisoprene-polystyrene, polystyrene-hydrogenated polyisoprene-polystyrene, polypropylene-ethylene-propylene rubber-polypropylene, and polyvinylcyclohexane-hydrogenated polyisoprene-polyvinylcyclohexane. Mixtures of these several types of block copolymers may be employed if desired. The specific proportions of the individual blocks as well as the types used will have a major effect upon the physical properties of the resulting block copolymer. Preferably, the high glass-transition polymer end blocks A comprise about 15-55% by weight of the block copolymer.

As stated hereinabove, the soling composition may comprise the same block copolymers as employed in the foxing strip; however, this is not essential since other polymeric materials such as natural rubber or polyvinyl chloride may be used in place or in addition to the block copolymer.

In normal circumstances, when the block copolymers are utilized for either the foxing strip or soling, the composition will be modified with other suitable ingredients. For example, 100 parts by weight of the block copolymer may be modified with 50-85 parts by weight of polystyrene, 60-125 parts by weight of a rubber extending mineral oil of the naphthenic/paraffinic type, and 0-150 parts by weight of a finely divided filler. Moreover, certain resins may be utilized, still further modifying the properties of the foxing or soling compositions or both.

The primary result of the present invention has been the improvement of adhesion of the block copolymer foxing strip to the textile upper which has been superficially

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esterified. This type of result is generally measured by peel tests which are conducted under either wet or dry conditions and with or without flexing tests as well as wear tests in which test shoes are actually worn by persons in normal course of activities.

The following examples illustrate the basis for the present invention.

EXAMPLE I

Cellulose cloth of the type known as 1.35 enameling duck (~7 oz./yd.²) in the form of cloth and also in the form of combined cloth assembled into uppers was treated with 50 parts by weight of acetic anhydride, 40 parts acetic acid and 10 parts zinc chloride for each 10 parts of cloth and tumbled overnight at ambient temperatures on a ball mill. The cloth was air dried. Wet and dry peel test of simulated foxing strip injection molded onto the cloth were made to determine the effect of acetylation. The foxing strip composition was as follows:

	Parts by weight
Polystyrene-polybutadiene-polystyrene block copolymer, block molecular weights 23,000-43,000-23,000	100
Rubber extending mineral oil	108
Polystyrene	60
Filler	90

A control assembly was prepared by molding the same foxing strip composition onto a sample of the unacetylated cloth. The following table shows that substantial improvement was obtained by the acetylation of the cellulose cloth.

Sample	Peel strength, p.l.i.	
	Dry	Wet
Control, no acetylation	9	8
Acetyl cellulose	17	17

Textile shoe uppers were assembled. One pair was used as a comparative control, while a second pair was acetylated. The above composition was injected on both to form soling and foxing. These shoes were subjected to a flexing test under standardized conditions in the presence of water. It was found that the shoe prepared from the acetylated cloth showed essentially no foxing separation after 90,000 flexes. The corresponding control sample (cloth not acetylated) showed about 1.5 square inches of foxing separation after only about 15,000 flexes.

EXAMPLE II

A series of samples was prepared by the superficial acetylation of enameling duck face cloth utilizing perchloric acid as a catalyst. These cloths were tumbled for 10 minutes in a bath (cooled to 20° C.) consisting of 5 parts acetic anhydride, 5 parts acetic acid, 1 part cotton cloth, 0.03 part perchloric acid. The samples were washed in cold water, dried at 100° C., and made into test samples.

Peel strength of a foxing compound is defined as the force (in pounds per linear inch, p.l.i.) required to separate it from the upper material on an injection molded shoe. The sample for peel strength measurement may either be die cut from the area of the sole, near the toe, of an injection-molded blank or a strip of foxing cut from the flex area of a shoe. The sample is partially separated manually, placed in the Instron jaws, and the peel strength measured at a jaw separation of 0.2 inch per minute. The wet peel strength is determined in the same manner after first soaking the sample in a 1% aqueous solution of a detergent (e.g., Tide) for 30 minutes, to insure thorough wetting.

Test samples are prepared by inserting a 7" x 15" sample of the fabric under consideration into the last of the Desma shoe molding machine. A block copolymer shoe sole (women's size 7) is then shot onto this fabric,

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producing a sole with no upper. Dry and wet peel strengths can be obtained from rectangular samples cut from the front portion of this test sample.

The following data was obtained from these blanks.

Sample	Dry Peel	Wet Peel	Percent acetyl	Pretreatment
1	35	27	0.91	A+B
2	35	27	0.89	A+B
3	36.5	28	1.39	B
4	29	20.5	1.36	B
5	31.5	25.0	1.65	None
6	27.0	20.5	1.19	
Control	32.5	6.5		

The different levels of acetylation were obtained by varied pretreatments. The pretreatments consisted of (A) a two hour alkali (2% NaOH) boil and/or (B) a one hour ethanol boil.

EXAMPLE III

This example simulates a continuous acetylation process. Samples of enameling duck face cloth were dipped sequentially in the following solutions: (1) a 60:40 mixture of acetic acid:acetic anhydride at 45° C. for 3 minutes, (2) acetic acid (cooled to 20° C.) for 2 minutes, (3) 3% perchloric acid (catalyst) in glacial acetic acid for 30 seconds at room temperature, and (4) a 60:40 mixture of acetic acid:acetic anhydride (the acetylating bath), maintained at 20-25° C., for 3 minutes. After washing and drying the cloth, the block copolymer composition described in Example I was injection molded onto them. Variation in acetyl levels was obtained by using or omitting the cleansing step [a two-hour alkali boil, and/or steps (1) and (2) (presoaks)].

The following table shows the acetyl levels and dry and wet peel strengths of the injection molded blanks made from the fabric samples described above.

Sample	Pretreatment	Weight percent acetyl	Peel strength, p.l.i.	
			Dry	Wet
Control (no acetylation)	None	0	32.5	6.5
1	do	13.1	40	25.5
2	A	9.66	39.5	30.5
3	A	5.91	36.5	31.5
4	A	4.60	39	17.5
5	A	4.55	32.5	26.0
6	None	2.99	39.5	26.5
7	do	2.87	37.5	26.5

EXAMPLE IV

A commercially acetylated cellulosic cloth having 15% by weight of acetyl content was bonded to the block copolymer composition described in Example I by injection molding. The wet and dry peel strengths were 18 p.l.i. Shoes were made from a similar but non-acetylated upper fabric and a comparative shoe was made utilizing acetylated fabric, the soling and foxing strip being injection molded onto the textile uppers. These were subjected to a flexing test and it was found that the foxing separation rate of the shoes made with a non-acetylated fabric was 10-100 times faster than that of the shoes prepared from the acetylated uppers.

EXAMPLE V

Six pairs of boys sneakers (size 7) were fabricated for wear tests, one shoe of each pair utilizing the acetylated fabric as the textile uppers while the other shoe was

prepared from an untreated cotton duck. The following table gives the results of that program.

Sample	Weeks on test	FSAR	Maximum depth of foxing separation (in.)	
			Acetylated	Control
A-----	9	0	0	0.50
B-----	5	0.35	0.05	0.40
C-----	5	0	0	0.20
D-----	4	0	0	0.20
E-----	7	0.02	0.05	0.35
F-----	5	0.02	0.05	0.60

FSAR, the foxing-fabric separation area ratio, is defined as the ratio of the area of separation of the variable to the area of separation of the control in the region of greatest flex during wear, which is at the ball of the foot. Numbers smaller than unity indicate improvement in foxing-fabric adhesion with acetylation.

EXAMPLE VI

A piece of cotton duck 50" x 108" weighing 816 gms. was boiled in 2% NaOH for 2 hours, washed in dilute acetic acid and water, and dried at 100° C. for 16 hours. A mixture of 2440 gms. of glacial acetic acid and 19.5 gms. of 72% perchloric acid was chilled to 20° C. To this solution was added 2440 gms. of acetic anhydride and the cotton duck, in that order. The reaction mixture was tumbled for 30 minutes. The acetylated fabric was then washed with cold water and then dried at 100° C. for 16 hours. An acetylation level of about 3% was attained.

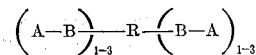
The treated cloth was combined with backing cloth and fabricated into uppers. Injection molded shoes made from the block copolymer described in Example I were mated with shoes of untreated uppers and put out on a wear test. The following table describes the results of these wear tests.

Sample	Weeks on Test	FSAR	Maximum depth of foxing separation (in.)	
			Acetylated	Control
5 A-----	5	0	0	0.40
B-----	5	0	0	0.30
C-----	6	0	0	0.10
D-----	4	Sl. sep.	0	0.10
E-----	5	Sl. sep.	0	0.05
F-----	5	0	0	0.40
G-----	4	0	0	0.50
10 H-----	6	0	0	0.20

We claim as our invention:

1. A footwear assembly comprising:

- a polymeric soling;
- an esterified cellulose textile upper wherein 0.3-20 weight percent of the cellulosic textile upper area contacting a foxing strip comprises lower fatty acyl radicals; and
- a foxing strip comprising an elastomeric block copolymer having the general configuration



wherein R is a linkage of the group consisting of valence bonds and coupling agent residues, each A is a thermoplastic non-elastomeric hydrocarbon polymer block, and each B is an elastomeric hydrocarbon polymer block.

- An assembly according to claim 1 wherein the soling comprises a block copolymer as claimed in claim 1(c).
- An assembly according to claim 1 wherein the soling and foxing polymer has the general configuration polystyrene-polybutadiene-polystyrene.
- An assembly according to claim 1 wherein the area of the textile upper contacting the foxing strip is acetylated to the extent of 0.4-5 weight percent.

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