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FOOTWEAR HAVING IMPROVED BLOCK COPOLYMER FOXING ADHESION

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ABSTRACT OF THE DISCLOSURE

Footwear assemblies are provided comprising a textile upper, a polymer soling and a block copolymer foxing wherein the foxing adhesion to the upper during wear, especially under wet conditions, is substantially improved by pretreatment of the uppers with polyvinyl chloride.

This invention relates to improvements in the bond strength of foxing to footwear having textile uppers. More particularly it relates to footwear uppers bearing a coating which promotes adhesion especially under wet conditions to foxing comprising block copolymers.

Numerous types of footwear are designed to perform their function under a variety of physical conditions. While it is a reasonably easy task to design a textile top shoe assembly with a high dry strength bond of foxing to fabric, adhesion in wear tests especially under wet conditions, (the so-called "wet peel strength") of polymeric foxing often leaves much to be desired. Textile top shoes are subjected to a number of situations which unless adequately met, result in disintegration of the assembly. Thus, under conditions of rain or perspiration, and especially at the area of flexing, the foxing strip around the base of the upper may tend to separate. Also, when washed in the presence of hot water and detergents, foxing separation may be a severe problem. This is probably due in substantial part to the lack of true adhesion of the foxing material, which is usually non-polar or substantially so, to the textile, which is often polar in character, as in the case of cellulosic fibers and the like. More specifically, the problem of wet peel strength is especially apparent in such footwear as canvas topped shoes. In such articles it is not only important to maintain a high degree of flexibility, improve abrasion resistance and dry peel strength but also and perhaps more importantly to maintain a high level of bond strength when the textiles are subjected to moisture or wet conditions.

It is the usual practice in the trade to laminate two layers of canvas together with a polmeric combining paste and then to bond the canvas laminate to a thermoplastic or elastomeric sole portion of the shoe with a strip applied either simultaneously or subsequently which is known as a foxing strip. This foxing is the strip of material which covers the upper part of the sole edge and the lower edge of the canvas upper where the upper and sole meet. Frequently, the combining paste is made out of vulcanized material such as vulcanized SBR, polychloroprene or with thermoplastic compositions such as polyvinyl chloride and the like. The vulcanized elastomers are highly intractable materials once they have been thermoformed. Moreover, it has been found by experience that these combining paste compositions lack the ability of physically promoting adherence of block polymer foxing especially under wet conditions.

Canvas top shoes and the like must be marketed under highly competitive conditions. Consequently any economies which may be effected in the manufacture of the articles improve the competitive position thereof. The necessity for vulcanizing prior art compositions used as foxing or other footwear components reduces this competitive position and consequently it would be highly desirable to avoid vulcanizing and at the same time to provide improved performance for foxing compounds.

It is an object of the present invention to improve the physical properties of footwear assemblies. It is a particular object of the invention to provide improved footwear as materials to result in superior foxing to fabric bonding especially under wet conditions.

Now, in accordance with the present invention, improved footwear assemblies are provided comprising textile footwear upper bearing a coating of a polymerized vinyl chloride thereon at least in the area contacted by the foxing, said foxing consisting essentially of a block polymer having the general configuration:

$$A—(B—A)_n$$

wherein n is a whole integer from 1 to 5, each A is a polymer block of a monovinyl arene and B is a polymer block of a conjugated diene, each block A having an average molecular weight between about 8,000 and 45,000 and B block haivng an average molecular weight between about 25,000 and 150,000. It has been found that surprisingly improved bonds are obtained of foxing to the textile upper in wear and under wet conditions.

The textile involved in the articles of the present invention may be either woven or non-woven, as the case may be and if two layers of textile are present they may be either similar or dissimilar. While the assembly in its broadest aspects thus contemplates the formation of a storng wet bond of single textile upper to a foxing comprising a block copolymer, a more particular aspect of the invention contemplates the situation in which two textile sheets are combined by means of an intervening combining compound. More particularly, the compositions performing the function of combining compounds comprise not only the block copolymer but compositions in which the block copolymer is modified with one or more ingredients including especially polystyrene, tackifying resins, hydrocarbon extending oils and/or mineral particulate fillers as described hereinafter in greater detail. Other combining compounds may comprise vulcanized SBR, polychloroprene and polyvinyl chloride.

The most important application of the present invention at this time, is in the manufacture of sport shoes generally referred to as tennis shoes or the like. The problem of foxing separation referred to hereinafter is substantially eliminated or largely minimized by the use of the present invention. As the data given hereinafter will show, the application of polymerized vinyl chloride to at least the area of the textile upper contacted by the foxing and thereafter manufacturing shoes such as by injection molding of a block copolymer foxing and a soling onto this upper results in surprisingly improved wet peel strength and performance in wear test of the foxing of the resulting article.

The term "combining compound" is used in the shoe trade for the composition which is utilized for laminating one layer of textile to at least a second layer, resulting in a composite textile especially designed for the preparation of textile shoe uppers.

The block copolymers to be used in foxing, and optionally in soling and combining compounds preferably have the general configuration:

$$A—B—A$$

If the copolymer is not hydrogenated, the blocks A comprise poly(vinyl arene) blocks while the block B is poly (conjugated diene) block. The blocks A normally have number average molecular weights, and determined by intrinsic viscosity measurements which have been correlated with primary molecular weight measurements including osmometry and radiotracer measurements of tri-

tium terminated polymer, of between about 8,000 and 45,000, while the conjugated diene polymer block has a number average molecular weight between about 25,000 and 150,000. If the copolymers are hydrogenated, the molecular weight ranges remain in about the same ranges. Two preferred species of such block copolymers include those having the block configuration polystyrene-polybutadiene-polystyrene and polystyrene - polisoprene-polystyrene as well as their hydrogenated counterparts. The hydrogenated counterpart of the second of the above defined block copolymers is of special interest, not only because of its high stability but because of the elastomeric nature of the hydrogenated mid-section which resembles that of an ethylene-propylene rubber while the end blocks either remain as polyvinyl arene blocks or, if hydrogenated, become saturated blocks made up of polyvinylcyclohexane units. Thus, the fully hydrogenated preferred species has a block configuration which corresponds closely to polyvinylcyclohexane- ethylene-propylene copolymer-polyvinylcyclohexane.

These particular block copolymers have the unique feature of attaining the stress-strain properties of an elastomer without the requirement that it be subjected to curing or vulcanization. Thus, they are sharply differentiated from other rubbers such as natural rubber, polybutadiene, SBR and the like which require vulcanization in order to attain satisfactory stress-strain properties.

The block copolymers of this invention may be the major polymeric material utilized in the foxing but they may, if preferred, be modified by the presence of other components such as plasticizers or other polymeric coating materials. Plasticizers such as rubber extending mineral oils may be employed and polymers such as polystyrene, polyethylene, polypropylene and the like may be incorporated in minor amounts with the block copolymers.

The compositions which are contemplated for the present purpose especially where canvas top sport shoes are concerned include particularly at least foxing compounds which are combinations of 100 parts by weight of the subject block copolymers with 15–150 parts by weight of polystyrene. Normally, still further modifications of such compositions are possible and are utilized for improving the flexibility and reducing the modulus of the compositions if desired as well as for reducing the overall cost. Thus, the presence of 5–150 parts by weight of a hydrocarbon extending oil is also contemplated as is the presence of a substantial amount of an inorganic finely divided particulate solid especially in the order of 5–200 parts by weight per 100 parts of the block copolymer.

In the articles contemplated herein and especially in the case of canvas type shoe uppers, the combining compound utilized for joining two layers of textile together may be the same or different from the composition utilized for the polymerized vinyl chloride coating on at least one of the textile sheets, namely adjacent to the foxing strip around the bottom edge of a shoe upper joining the shoe upper with the shoe soling or at least masking said joint.

One aspect of the present invention involves the modification of the above two component system with polymer extender oils both for the purpose of reducing the cost of the compositions and more particularly for imparting better processing and physical properties thereto. This is especially important as the average molecular weight of the block copolymer increases. In some instance, in the higher molecular weight ranges processing becomes extremely difficult at ordinary processing temperature short of decomposition temperatures in the absence of extender oils. It is preferred that the extender oils be those utilized for extending other polymers and particularly rubbers and that these have no more than about 50% aromatics and greater than about 45% of saturates, usually naphthenic types of hydrocarbons.

The extender oils should be utilized in amounts between about 2 and 300 parts (preferably 5–100 parts) by weight per 100 parts by weight of the block copolymer,

Another important component is a particulate solid, including both fillers, mineral extenders and pigments. These include the various carbon blacks, titanium dioxide, calcium carbonate, clays, as well as mineral pigments such as the earth colors, including the iron oxides and the like. Pigments are normally utilized in as large amounts as possible while still maintaining desired physical properties usually this will be an amount between about 25 and 400 parts by weight per 100 parts by weight of the block copolymer. The compositions of this invention as referred to hereinabove come into play in the incorporation of these particulate solids in that the presence of the polystyrene unaccountably and substantially raises the retention of the particulate solids which otherwise may be loosely held if at all by the block copolymers.

The incorporation of these materials together may take place on the usual polymer processing mills and internal mixers or in an extrusion type of apparatus or may be composited by means of other masterbatching processes, particularly a solution materbatch. In this process a solution of the block copolymer is formed in a solvent which is either a non-solvent or only a partial solvent for polystyrene. Specifically, such a solvent will comprise 21–85% by volume of an open-chain hydrocarbon having from 4–8 carbon atoms per molecule and 79–15% by volume of cyclic hydrocarbon having from 5–8 carbon atoms per molecule. The polymer solution (cement) so formed is then combined with 5–200 parts by weight of polystyrene and 25–400 parts by weight of the finely divided particulate solids per 100 parts by weight of the block copolymer. The mixture is then subjected to coagulating procedure so as to isolate the solid materials from the solvents. This is best effected by forcing the mixture into a vessel containing steam and hot water under such conditions that the solvent is flashed off and the composition becomes suspended in a bath of water in the form of crumbs. These are then separated from the water by screening or decantation and subjected to grinding if necessary to effect relatively uniform particle size after which the particles are subjected to drying procedures as in moving belt drier, expander drier or the like. The use of this particular type of solvent accentuates the effectiveness of the polystyrene in retaining the finely divided particular solids. Apparently, the polystyrene exists under these conditions as a gummy highly swollen material which aids in the incorporation of the particulate solids.

Again referring to sport shoe upper canvases, the term will include those textiles well known in the art for this purpose. While they often are cotton canvases exclusively, they may be combinations of cotton with synthetic materials or regenerated cellulose such as rayon or may comprise at least in part textiles such as polyester, nylon and the like. The present invention moreover contemplates the formation not only of sport shoe uppers but the preparation of innersoles, toe stiffeners, heel stiffeners and cloth interlays.

In accordance with the present invention, the adhesion of block polymer foxing to textile uppers is unexpectedly retained even under wet conditions such as encountered in wet weather, washing, or perspiration by the application of at least a superficial coating or impregnation on at least that part of the upper which is later to be contacted with the foxing compound. The material employed for this purpose is a polymerized vinyl chloride. The polyvinyl chlorides useful in the present assemblies include thermoplastic polymers produced by the polymerization of a monomer mixture containing not less than 70% by weight of vinyl chloride and preferably more than 90% by weight thereof. The monomers may comprise entirely vinyl chloride as the sole monomer. In addition thereto copolymers and interpolymers of vinyl chloride with minor amounts of 1-monoolefinic or vinyl types of comonomers may be utilized. Illustrative comonomers are vinylidene chloride, vinyl acetate, methyl acrylate, styrene, acrylonitrile, methyl methacrylate, ethylene, propylene and others.

While relatively low molecular weight polyvinyl chlorides are preferred, due primarily to the ease of their application, the present invention is not to be restricted to any relatively critical or narrow molecular weight range. The polymers may be characterized in terms of specific viscosity, intrinsic viscosity or by molecular weights, since all of these are related. The molecular weights normally will vary from about 5,000 to about 50,000 and it is preferred that the approximate average molecular weight be between about 10,000 and 25,000. Intrinsic viscosities will usually vary from about 0.12 to about 0.90. As used herein, the terms "specific viscosity" and "intrinsic viscosity" are calculated values derived from viscosity measurements. Solution for viscometric study are prepared by dissolving 0.125 gram of the polyvinyl chloride is 100 cc.'s of cyclohexanone while mildly heating and agitating on a solution roller. The solutions are then filtered into an appropriate Ubbelohde viscometer previously calibrated for the pure solvent. The flow time in seconds for the solution is determined at three dilutions to obtain flow data at a number of concentrations. The ratio of the flow time of the sample to the flow time of the pure solvent is a value known as the "reduced viscosity." When the integer 1 is subtracted from reduced viscosity, one obtains the value known as the "specific viscosity." When the specific viscosity is divided by the concentration and the values obtained plotted against concentration, the extrapolation of the resulting straight line to zero concentration gives the value known as "intrinsic viscosity." Thus, an intrinsic viscosity value of 0.2 corresponds to a molecular weight of approximately 8800 and a value of 1.0 corresponds to a molecular weight of about 58,000. Since the relationship between intrinsic viscosity values and molecular weights is known, the molecular weight of any polyvinyl chloride may be readily estimated from its intrinsic viscosity value. Best foxing adhesion results are obtained when the polyvinyl chloride is applied in amounts between about 0.005 and 0.2 grams/in.^{2} of upper so treated.

The polyvinyl chloride may be applied to the area of the textile upper later to be contacted with the foxing compound by any desired means such as by dipping or spraying in solvent solution or as a latex. The solvent used for the PVC is usually a mixture of ketones such as acetone, methyl ethyl ketone and cyclohexanone, to provide a 1–25% solution.

Example I

A canvas laminate was prepared using as the combining composition a vulcanized SBR. The laminate was cut to the shape of tennis shoe uppers and the area of the canvas to be contacted with the foxing was sprayed with an aerosol of polyvinyl chloride having an average molecular weight in the order of about 15,000, the aerosol propellant being halogenated hydrocarbon. An amount of about 0.04 gram per square inch of polyvinyl chloride was thus deposited in the foxing area of the textile upper. The treated uppers were then fitted into an injection molding shoe manufacturing machine and a block copolymer composition injected into the machine to simultaneously form the soling and the foxing. The composition employed for this purpose was as follows:

	Parts by weight
Polystyrene-polybutadiene-polystyrene block copolymer, having block mol. wts. of 22,000–45,000–22,000	100
Oil	108
Polystyrene	60
TiO_2	15
Clay	75

The shoes so prepared were subjected to three washing and drying cycles. In the washing operation the shoes were washed with a commercial domestic detergent in a domestic washing machine. In the drying operation the domestic drier was set at the warm temperature drying level. Essentially no change in the foxing adhesion was noted after this washing test. Comparable shoes were prepared in which the polyvinyl chloride treatment was omittet, all other conditions of the preparation and assembly being identical. After the same washing and drying cycles, however, it was found that a substantial parting of the foxing from the canvas upper occurred.

In another comparative test, strips cut from shoes prepared as described above were soaked for 30 minutes in a 2% aqueous solution of household detergent at 23° C. and subjected to peel strength tests at 180°, using a separation speed of 0.2 inch per minute. Specimens containing PVC tie coat (0.01 g./in.^{2}) as well as control samples having no tie coat were tested both before and after the soaking period. The results obtained were as follows:

	Peel Strength, p.l.i.	
Sample	Dry	Wet
Control, no tie coat	13	8.5
PVC tie coat	21	15

Example II

Shoes were prepared, utilizing the soling and foxing composition described in Example I. The control comprised a canvas duck upper having no tie coat to promote foxing adhesion. The shoes treated according to the present invention bore either 0.04 (Sample A) or 0.08 (Sample B) g./in.^{2} of PVC on the foxing area of the canvas.

The shoes were worn for the test periods noted below and then examined. In all cases, the control and the treated shoes showed about the same percent wear in the soling and upper. However, as the table below indicates, the treated shoes showed a striking improvement in foxing separation as compared with the untreated control.

	g./in.^{2} PVC	Weeks on Test	Mean foxing Separation Area Ratio Variable/ Control	Mean Maximum Depth of Foxing Separation (inch)
Control	None	4	----------	0.45
Sample A	0.04	4	0.13	0.10
Sample B	0.08	4	0.18	0.20

I claim as my invention:

1. In a shoe assembly comprising a textile upper, a polymeric soling and a foxing, the improvement comprising a superficial coating of a polymerized vinyl chloride at least on the area of the upper which is contacted with the foxing, said foxing comprising a block copolymer having the general configuration

A—B—A

wherein each A is a polymer block of a monovinyl arene and B is a polymer block of a conjugated diene.

2. A shoe assembly according to claim 1 wherein the textile bears between about 0.005 and about 0.2 gram per square inch of polyvinyl chloride in the area of the upper contacted by the foxing.

3. A shoe assembly according to claim 1 wherein the upper comprises a textile laminate combined with a composition comprising a block copolymer as recited in claim 1.

4. A shoe assembly according to claim 1 wherein the foxing composition comprises a block copolymer having the configuration

polystyrene-polybutadiene-polystyrene

5. A process of preparing the shoe assembly of claim 1 wherein the polyvinyl chloride is applied in a ketone medium.

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