FOOTWEAR HAVING IMPROVED BLOCK COPOLYMER FOXING ADHESION

Jon W. Martin, Los Alamitos, Calif., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 6, 1968, Ser. No. 719,755

U.S. Cl. 36—2.5

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 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 thermformed. 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 having 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 strong 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 forming 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 and obvious 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 upper.

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. The molecular weight range of the polyvinylcyclohexane units. Thus, the fully hydrogenated 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 obtain satisfactory stress-strain properties.

The block copolymers of this invention may be the major polymeric material utilized in the foaming 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 poly

Another important component is a particulate solid, including both fillers, mineral extenders and pigments. These include the various carbon blacks, titanium dioxide, calcium carbonate, and other fillers which 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-poly styrene - polisoprene-poly styrene as well as their hydrogenated counterparts. The block copolymer, counter part 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 remain as polyvinylarene blocks or, if hydrogenated, become saturated blocks made up of polyvinylcyclohexane units. Thus, the fully hydrogenated 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 obtain satisfactory stress-strain properties.

The block copolymers of this invention may be the major polymeric material utilized in the foaming 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 poly
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. In 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 value 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 8000 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 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 foxed was sprayed with an aerosol of polyvinyl chloride having an average molecular weight 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 fit into an injection molding shoe manufacturing machine and a block copolymer composition injected into the machine to simultaneously form the soled and the foxing. The composition employed for this purpose was as follows:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>100</td>
</tr>
<tr>
<td>Oil</td>
<td>108</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>60</td>
</tr>
<tr>
<td>TIO₂</td>
<td>15</td>
</tr>
<tr>
<td>Clay</td>
<td>75</td>
</tr>
</tbody>
</table>

The shoes so prepared were subjected to three washing and drying cycles. In the washing operation the shoes were washed with a commercial household 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 omitted; all other conditions of the preparation and assembly being identical. After the same washing and drying cycles, however, it was found that a substantial part 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:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control, no tie coat</td>
<td>13</td>
<td>8.5</td>
</tr>
<tr>
<td>PVC tie coat</td>
<td>21</td>
<td>15</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>g/in.²</th>
<th>PVC Weeks on Test</th>
<th>Mean foxing Separation Area Ratio Variable/ Control</th>
<th>Mean Maximum Depth of Foxing Separation (inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.04</td>
<td>4</td>
<td>0.13</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.08</td>
<td>4</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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 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.

References Cited

UNITED STATES PATENTS

3,145,487 8/1964 Cronin 36—14 X
3,217,345 11/1965 Snitzer 36—14 X
3,573,150 3/1971 Fears et al. 250—92.8

PATRICK D. LAWSON, Primary Examiner