United States Patent Office 3,501,855 Patented Mar. 24, 1970

3,501,855

FOOTWEAR HAVING IMPROVED BLOCK COPOLYMER FOXING ADHESION

Glenn R. Himes, Torrance, Calif., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 8, 1968, Ser. No. 719,720
Int. Cl. A43b
U.S. Cl. 36—2.5 4 Claims

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 under wet conditions is substantially improved by pretreatment of the uppers with an amino triazine-aldehyde resin.

This invention relates to improvements in the wet peel strength of foxing to footwear having textile uppers. More particularly it relates to footwear uppers bearing a coating which promotes adhesion of foxing, the latter 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 shoe assembly which will perform satisfactorily under dry conditions, the so-called "wet peel strength" of polymeric foxing often leaves much to be desired. 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. Textile top shoes, in particular, are subjected to a number of situations which unless adequately met, result in disintegration of the assembly. Thus, under rainy conditions, and especially at the area of flexing, the foxing strip around the base of the upper may tend to separate from the textile upper. Also, when washed in the presence of hot water and detergents, foxing separation may be a servere problem. More specifcally 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 peel strength when the textiles are subjected to moisture or wet conditions.

It is the usual practice in the shoe trade to laminate two layers of canvas together with a polymeric combining paste and then to bond (or decorate) 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 part of the canvas upper edge where the upper and sole meet. In many instances in the past, the combining paste has been made out of vulcanized material such as vulcanized SBR or with thermoplastic compositions such as polyvinylchloride and the like. These are highly intractable materials once they have been thermoformed, especially so in the case of the vulcanized elastomers. 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 likes 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 wet peel strength 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 wet peel strength.

Now, in accordance with the present invention, improved footwear assemblies are provided comprising a textile footwear upper bearing a coating of a melamine-aldehyde resin 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

wherein 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 wet peel strengths of foxing to the textile upper are obtained.

While the assembly in its broadest aspects thus contemplates the formation of a high wet peel strength single textile upper bearing a foxing strip comprising a block copolymer; a more particular aspect of the invention contemplates the situation in which two textile layers are combined by means of a intervening combining composition. More particularly, the compositions performing the function of combining compounds may comprise not only the block copolymer referred to above, 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, all as more particularly described hereinafter. Other combining compounds may comprise vulcanized SBR, polychloroprene, or polyvinylchloride.

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 adhesion 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 melamine-aldehyde resin 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 of the resulting article.

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 or more layers of textile are present they may be either similar or dissimilar. The textile upper may be impregnated with a superficial amount of block polymer, if so desired, for the purpose of improving abrasion resistance and reducing water permeability as long as the essential presence of an amino triazinealdehyde resin is applied to the upper at least in the area later contacted by foxing, in conjunction with foxing which comprises essentially the subject class of block copolymers. 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 have the general configuration

A—B—A

If the copolymer is not hydrogenated, the blocks A comprise non-elastomeric poly(vinyl arene) blocks while the block B is an elastomeric poly(conjugated diene) block. The blocks A normally have average molecular weights, as determined by intrinsic viscosity measurements which have been correlated with primary molecular weight measurements, including osmometry and radiotracer measurements of tritium 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-polyisoprene-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 having been 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 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 15–100 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.

One aspect of the present invention involves the modification of the above-foxing composition 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, due to the high molecular weights 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 about 300 parts (preferably 5–130 parts) by weight per 100 parts by weight of the block copolymer.

Another important component is a particulate solid, including fillers, mineral extenders and pigments. These include 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. Fillers 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 polystyrene unaccountably and substantially raises the retention of the particulate solids which otherwise may be loosely held if at all by the block copolymers.

As is usual for elastomer compounds, protection against oxidation degradation is provided by including in the composition one or a mixture of several antioxidants in the amount of approximately 1 part by weight per 100 parts by weight of the block copolymer.

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 masterbatch. 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 a 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 separted 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 acentuates the effectiveness of the polystyrene in retaining the finely divided particulate solids. Apparently, the polystyrene exists under these conditions as a gummy highly swollen material which aids in the incorporation of the particulate solids within the body of the block copolymer.

Again referring to sport shoe uppers, the term will include those textiles well known in the art for this purpose. While they often are cotton canvas 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 nylon and the like. The present invention moreover contemplates the additional presence of intersoles, toe stiffeners, heel stiffeners and cloth interlays.

One of the essential features of the present invention comprises the impregnation or coating or both of at least a portion of the textile upper of the present shoe assemblies with a melamine-aldehyde resin. The area which must be treated with the resin according to the present invention is that area of the textile upper which is later contacted with the block copolymer foxing strip.

The resins utilized in the practice of the present invention may be referred to as acid-cured thermosetting amino

triazine-aldehyde resins. These include those resins formed between an amino triazine and an aldehyde and treated under acidic conditions and at a time and temperature sufficient to form a water-insoluble cured resin coating. While the triazine may be mixed with a variety of proportions of aldehyde to form pre-polymers suitable for acid- and heat-curing, it is preferred that 1–6 mols of aldehyde be used per mol of amino triazine.

Suitable triazines include diamino triazines, triamino triazines, alkyloldiaminotriazines, and alkyl diaminotriazines. Aldehydes such as formaldehyde, propionaldehyde, acetaldehyde, fural and benzaldehyde may be used. Specifically, the preferred resins are formed between melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde in mol ratios between about 1:1 and 1:3. Any alkyl substituents on the triazine molecule preferably have 1–8 carbon atoms.

The resins and their curing systems are known. Curing agents are normally applied to the textile with prepolymers, usually but not necessarily are applied in an aqueous solution, water or other solvent is evaporated and the resin cured to a water-insoluble state by heating at 300–400° F. for 1–30 minutes. Suitable acid-acting catalysts include, for example, mineral acid ammonium salts such as ammonium chloride and mineral acid salts of alkaline earth metals such as magnesium chloride. These are present in amounts varying between about 1 and about 50 parts by weight per 100 parts of prepolymer.

The resin may be modified by the presence of pigments, plasticizers and tackifying resins such as the phenol formaldehyde or coumarone-indene resins. The resin on the area to be later contacted with the foxing strip should be present in an amount based on the area being so treated of between about 0.002 to 0.04 gram per square centimeter. The resin may be applied to the textile as a solution, as an aerosol or as an emulsion.

Especially for use in the preparation of canvas uppers for sport shoes, it is particularly contemplated to utilize a combining composition which is used in the form of either a latex or a cement and in such consistency that the combining composition when deposited on one surface of the canvas essentially remains on that surface and does not cause any appreciable amount of strikethrough. This is primarily for appearance purposes, since the outer surface of the canvas or of the canvas laminate should appear to be unmodified canvas. The consistency specifically employed for this purpose will depend upon the equipment and working conditions encountered in such application and will be easily adjusted by experts in the art. If solvent compositions are utilized, e.g., cements, then readily volatilized hydrocarbon solvents such as cyclohexane or toluene are especially contemplated.

It is epecially contemplated to apply the combining paste on one surface of a first textile layer such as by means of a blading application, then applying a second layer on the top side of the combining paste, passing the laminate so formed between heated rolls or at least over a heated surface to compress the laminate and volatilize any solvent or water which may be present therein to result in a laminate of the two textile, e.g., canvas layers. For the purpose of forming shoe uppers, these layers are then cut by any desired means and the edges stitched to prevent raveling.

In the instance where molded shoe soles are then to be attached to these uppers, the latter are fitted onto suitable forms in an injection molding shoe making machine which is provided with proper spaces and inlets for the injection of the block copolymer utilized in the sole composition, space also being provided in the same machine for the simultaneous formation of a foxing strip around the area of joining the lower part of the canvas upper to the edge of the shoe sole. The treatment of the lower area of the textile upper may take place before or after fitting the uppers on the machine forms provided means are available for heating the treated upper to effect cure of the melamine-aldehyde resin before application of the foxing strip. The conditions are then adjusted such that the shoe soling and foxing composition is injected in a sufficiently thermoplastic condition to allow flow throughout the cavity provided in the machine for the shoe sole and foxing to form in the proper shape. Under these circumstances, sport shoes are prepared having superior wearing property and also superior resistance to foxing separation.

The degree of wetting which shoes are subjected to will vary. For example, this may be due to rainy weather, to washing the shoes for the purpose of removing soil or dirt. Perspiration or body oils may also create a condition similar to other types of moisture and the like which cause the general condition encountered in wet peel.

The wet peel strength is usually determined by an Instron tester at 180° to 80° angle pulled at 0.2 inch per minute at 23° C.

The following examples illustrate the results obtained by the use of the present invention.

EXAMPLE I

Comparative tests were performed on shoe assemblies with and without a resin treatment. Canvas sheeting was laminated with a cured SBR combining paste to form a canvas laminate which was cut into the form of tennis shoe uppers. The area which was to be contacted with the foxing strip was treated with a melamine-formaldehyde prepolymer in aqueous solution.

The 10% solution of prepolymer also contained 3.5% by weight of ammonium chloride and 26% of magnesium chloride based on the weight of prepolymer. After evaporation of the water the treated canvas uppers were heated for 3 minutes at 350–375° F. to cure the resin and then were fixed on a shoe molding machine form and a compound designed for both soling and foxing injected into the mold. The injection molding conditions consisted of a polymer melt temperature of about 400° F., injection pressure of 250 p.s.i. (gauge), pressure within the mold of 90 p.s.i. (gauge). Injection time was about 3 seconds and the formed shoe assembly was held in the mold for approximately one additional minute to allow the thermoplastic rubber compound to become firm through cooling. The compound used for this latter purpose comprised 100 parts by weight of a block copolymer, 108 parts by weight of a naphthenic mineral rubber extending oil, 60 parts by weight of crystal polystyrene, 90 parts by weight of an inorganic filler, namely, clay and titanium dioxide mixture, and 1 part by weight of antioxidant.

In order to test the effectiveness of the melamine-formaldehyde treatment, a parallel test shoe assembly was prepared utilizing all of the same conditions and components with the exception of the melamine-formaldehyde treatment. The resulting shoes were tested in the Instron tester and 0.2 inch per minute under both wet and dry conditions. The shoe assembly having the treatment had a dry peel strength of 11–13.6 pounds per linear inch and a wet peel strength 10–12 p.l.i. Contrasted to this, the shoe assembly in which the melaine-formaldehyde treatment was omitted had a dry peel strength of 11 p.l.i. while its wet peel strength was only 7.2 p.l.i.

The block copolymer used in both shoe assemblies had the structure polystyrene-polybutadiene-polystyrene, the block molecular weights being 23,000–41,000–23,000.

I claim as my invention:

1. In a footwear assembly comprising a textile upper, a polymeric soling and a foxing, the improvement comprising a coating of an acid cured thermoset amino triazine-aldehyde resin 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 0.002 and about 0.04 gram

per square centimeter of a triamino triazine-formaldehyde resin in the area of the textile upper contacted by the foxing.

3. A shoe assembly according to claim 1 wherein the textile upper coprises a canvas laminate and the resin is a melamine-formaldehyde resin.

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

the general configuration polystyrene-polybutadiene-polystyrene.

References Cited

UNITED STATES PATENTS

2,995,839	8/1961	Cronin	36—9
3,414,988	12/1968	Mattos	36—2.5

PATRICK D. LAWSON, Primary Examiner