April 13, 1965 H. G. DAVIS, JR., ETAL 3,177,597

OUTSOLE AND METHOD OF ATTACHING SAME

Filed Sept. 19, 1961 2 Sheets-Sheet 1

Fig. 1

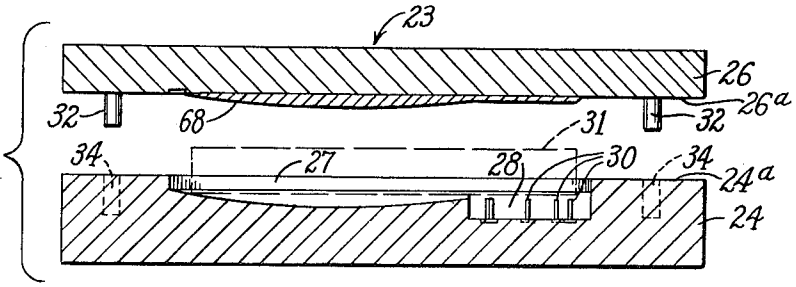


Fig. 2

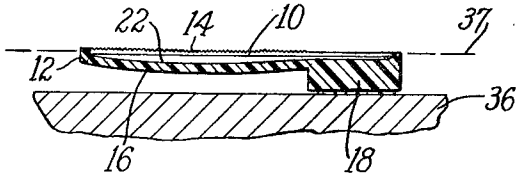


Fig. 3

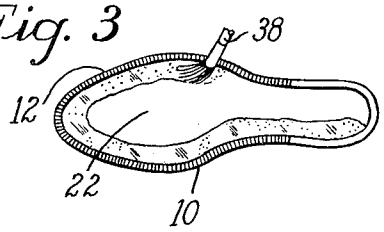


Fig. 4

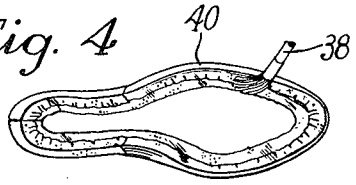


Fig. 5

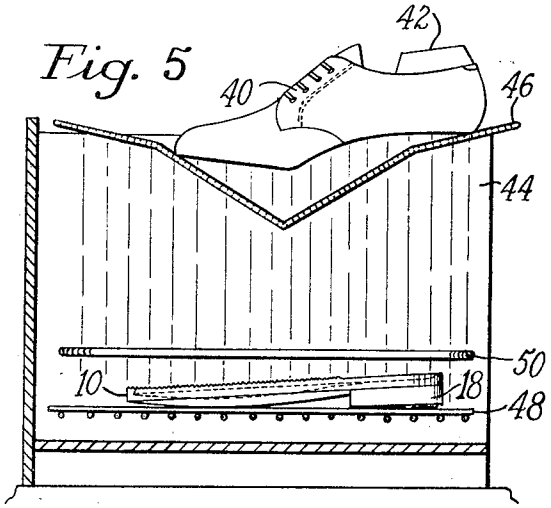
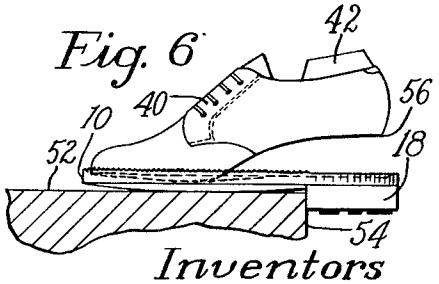


Fig. 6



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April 13, 1965 H. G. DAVIS, JR., ETAL 3,177,597

OUTSOLE AND METHOD OF ATTACHING SAME

Filed Sept. 19, 1961 2 Sheets-Sheet 2

Fig. 7

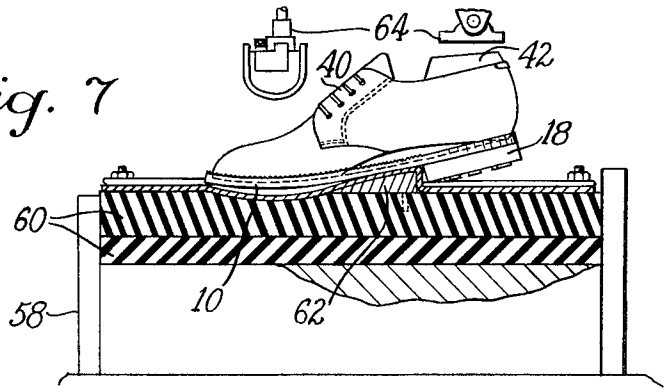


Fig. 8

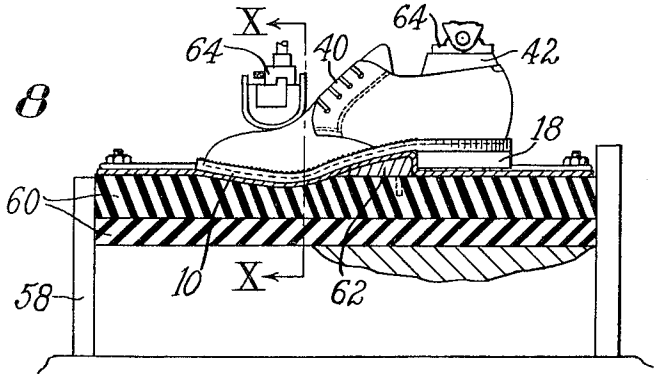


Fig. 9

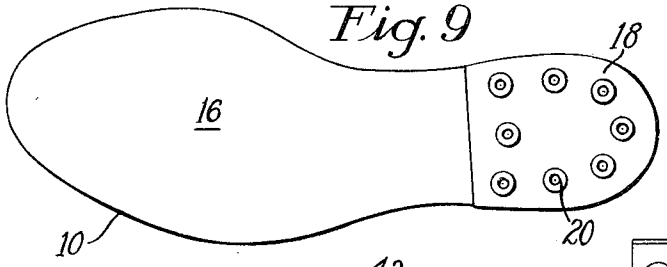


Fig. 10

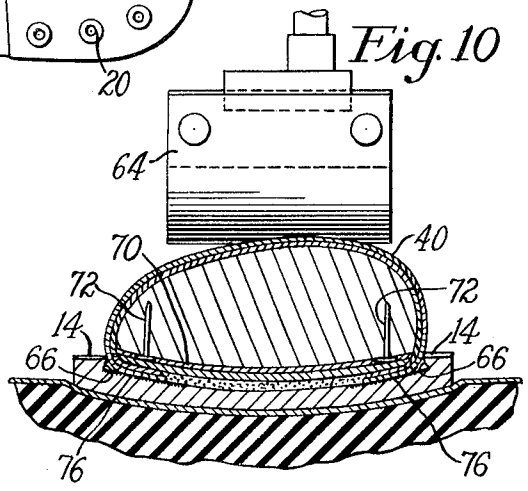
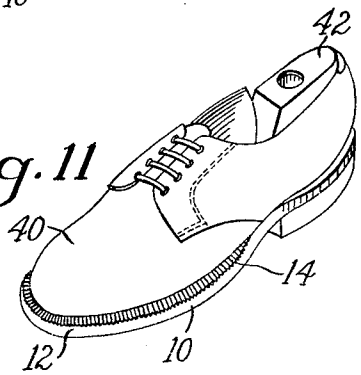


Fig. 11



United States Patent Office 3,177,597 Patented Apr. 13, 1965

3,177,597

OUTSOLE AND METHOD OF ATTACHING SAME

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Filed Sept. 19, 1961, Ser. No. 139,256
11 Claims. (Cl. 36—19.5)

This invention is directed to attaching outsoles to shoe uppers, and more particularly to a method for adhesively attaching outsoles, molded from plasticized polyvinyl chloride resins, to shoe uppers.

Welded shoes are commonly manufactured with flat lasted shoe uppers, the uppers being applied to a last with the marginal portions of the uppers carried over the bottom of the last about a ridge forming a break line between the bottom surface of the last and the contoured sides of the last. To secure the overlasted marginal portions of the shoe upper in place, the last carries an insole to which the overlasted marginal upper portions are cemented, stapled or otherwise attached. Thereafter, the overlasted marginal upper portions of the shoe upper are readied and given a coating of adhesive. An outsole which is obtained as a result of being molded directly or from being cut out of a sheet of molded thermoplastic material is also readied and coated with adhesive. The adhesively coated outsole is applied to the bottom of the shoe upper and the assembly is presented to a press which is operated to conform the outsole with the bottom of the shoe upper supported by the last. Thereafter, and if necessary, the projecting portions of the adhesively attached outsole are trimmed to form a contour bearing a definite relationship with the last break line, and the resulting edges are finished and set in accordance with acceptable shoemaking practices.

Formerly, the thermoplastic material from which outsoles were molded for use in making welded shoes, were rubber, either natural or synthetic. Now, to a large extent, rubber is being replaced by other polymeric materials, particularly plasticized polyvinyl chlorides which contribute properties of economy, processing and wearing qualities at least as good as those obtained using rubber. To be more specific, outsoles can be conveniently molded from plasticized polyvinyl chloride, including homopolymers or copolymers of the same containing vinyl acetate in copolymerized form to exhibit properties of flexibility and resilience at least as good as those exhibited by natural or synthetic rubbers. The properties of flexibility and resiliency are particularly important in shoe outsole materials.

In referring to the outsoles as "molded" or "premolded," it is intended throughout this presentation to include those which can be obtained directly from the practice of conventional molding processes, such as injection, slush, etc. molding as well as outsoles which can be obtained by processes in which sheets of plasticized polyvinyl chloride are initially prepared by molding, calendering, extruding, casting and the outsole or outsole blanks then cut from the same.

Because of the resiliency obtainable in outsoles constituted of plasticized polyvinyl chloride, certain difficulties can arise during manufacture of welded shoes including the same. In particular, it can be difficult to effect strong, permanent adhesive attachment between outsoles constituted of plasticized polyvinyl chloride and shoe uppers by a method which relies upon thermoplastic adhesives and conventional conditions of temperature, pressure and time. To illustrate, in the manufacture of welded shoes, it has been found that a plasticized polyvinyl chloride outsole, after being conformed with the contour of the overlasted upper, exhibits a strong tendency to straighten out and return to the alignment or orientation originally molded in it. Due to this, the adhesive bond between the outsole and the overlasted margin of the upper is subjected to heavy stress after attachment to the upper, with the result that the bond which results from using ordinary thermoplastic adhesives, represented by natural and synthetic rubber adhesives etc. is very often ruptured.

Another difficulty often had in welded shoes using plasticized polyvinyl chloride outsoles comes as a result of the plasticizer migrating to the surface. This can take place before, during or after attachment is carried out, and, the quantity of plasticizer migrated can be sufficient to adversely affect adhesive bonding provided by the thermoplastic adhesive to the point that peeling or softening of the same takes place with separation of the adhered components from one another. To remedy this, in many cases it has become customary to rely upon cured-type cements. This expedient, however, is less than satisfactory in that the pot life of the curing type cement can be short; parts coated with curing type cements must be asembled before the curing of the cement has progressed too far; and full-strength of curing-type cements is not obtained until curing is complete. Accordingly, in using cured-type cement time is extremely critical.

It is a principal object of the present invention to provide a method for attaching outsoles of plasticized polyvinyl chloride to shoe uppers in the manufacture of welded shoes in which a strong, permanent adhesive bond is obtained between the adhesively attached components using a thermoplastic adhesive and without the need for relying on extreme conditions of temperature, pressure and time.

Another object is that of providing a method for attaching plasticized polyvinyl chloride outsoles to shoe uppers in the manufacture of welded shoes in which the adhesive bond obtained between the adhesively attached components by relying on a thermoplastic adhesive is not significantly affected by plasticizer migrated to the surface of outsoles.

These and other objects of the present invention are obtained in a method for adhesively attaching a shoe upper to an outsole constituted of plasticized polyvinyl chloride, both homopolymers and copolymers of the same containing copolymerized vinyl acetate and mixtures of the same, which method comprises (*a*) applying to the outsole a solution of an essentially linear polyesterurethane elastomer in a selected, volatilizable, normally liquid, organic solvent capable of solvating both the said elastomer and the said polymeric material, (*b*) evaporating the said solvent after surface portions of the outsole have become at least partially dissolved in the said solvent, (*c*) softening the polyesterurethane film remaining deposited on said outsole by solvent, heat or other type of activation and (*d*) contacting the softened polyesterurethane carried on the outsole under pressure to a coating of said polyesterurethane applied to said shoe upper.

In order to illustrate the method of the present invention, the following drawings are included in which

FIG. 1 is a lengthwise sectional elevation of a mold which can be used in producing outsoles for use in practice of the present invention;

FIG. 2 is a view in side elevation and in section of an outsole obtained by molding plasticized polyvinyl chloride resin in the mold illustrated in FIG. 1;

FIG. 3 is a plan view of the outsole shown in FIG. 2 illustrating the manner of applying adhesive to the same;

FIG. 4 is a bottom plan view of a lasted shoe upper illustrating the manner of applying adhesive to the same;

FIG. 5 is a sectional elevation of a heater in which an outsole and a shoe upper are located in the process of thermally activating the linear polyesterurethane elastomer coatings;

FIG. 6 is a sectional side elevation of a support on which an outsole and a shoe upper are located in the process of preliminarily aligning the same relative to one another;

FIG. 7 is a sectional side elevation of a pad box in an outsole attaching machine to which the preliminarily fitted outsole and shoe upper are presented;

FIG. 8 is a similar view of the pad box shown in FIG. 7 and a shoe thereon during the process of permanent outsole attachment;

FIG. 9 is a bottom plan view of the outsole of FIG. 2;

FIG. 10 is a sectional view on an enlarged scale along the line X—X of FIG. 8; and

FIG. 11 is a perspective view of a completed shoe manufactured in accordance with the method of the present invention.

Referring particularly to the drawings, an outsole premolded from plasticized polyvinyl chloride is shown at **10** in FIGS. 2, 3 and 10. In these figures, outsole **10** is shown including an edge **12**, a flat raised marginal surface **14**, and a tread surface **16**. Outsole **10** as shown also includes an integrally molded block heel **18** formed with suitable configuration on its tread surface and imitation nail holes **20**.

To assist in fitting outsole **10** preliminary to and during the attaching operation, essentially the entire length of the same is formed with a central recess **22** of a length and width slightly less than that of a shoe bottom to which it is to be attached. For further convenience, the inner surface of the central recess **22** in a direction widthwise of the outsole can be formed with a concave curvature corresponding to the transverse curvature of the bottom of a shoe upper to which it is to be attached.

Outsole **10**, as described, can be obtained by molding plasticized polyvinyl chloride resin in a two-part mold, generally referred to as **23** in FIG. 1. As illustrated there a hollow die **24** and a cover plate **26** are designed for use together. Both the die **24** and the cover plate **26** have flat mating surfaces **24***a* and **26***a* respectively, the plane of which coincides with that of the raised marginal portion **14** of outsole **10**. The hollow **27** in die **24** is provided with a heel cavity **28**, the bottom surface of which is provided with a suitable configuration to imitate a nailed-on heel. For this purpose a series of pins **30** are mounted to project upwardly within the heel cavity. To provide plasticized polyvinyl chloride resin for molding, a biscuit **31** of this material is inserted between the die **24** and cover plate **26** and heat and pressure, from a source not shown, is applied to the mold parts. To assist in properly aligning the cover plate **26** with the hollow die **24** during molding, two or more positioning pins **32** project downwardly from the cover plate **26** into openings **34** in the die **24**.

When the plasticized polyvinyl chloride outsole **10** is laid with the breast of the heel against a table or other flat surface **36** as shown in FIG. 4, and pressure is applied from above on the heel portion of the outsole **10**, the marginal surface **14** rises into a plane **37** parallel to the table surface **36**. Advantage is taken of this characteristic of the outsole to maintain its upper raised marginal surface **14** in a single flat plane to assist in fitting the same to the bottom of the shoe upper.

In order to attach outsole **10** to the bottom of a flat lasted shoe upper, a solution of an essentially linear polyesterurethane elastomer is applied to the top surface of outsole **10** by a brush **38** or any other suitable means as shown in FIG. 3; as shown in FIG. 4, an inturned area of a flat-lasted shoe upper **40** supported on a last **42** can also be provided with an application of the solution of

the same elastomer which is applied to the outsole. After the elastomer solution, and more particularly the solvent portion of the same has had an opportunity to dissolve a surface portion of the outsole **10** and to evaporate both outsole **10** and shoe upper **40** are introduced into a heater formed by an enclosure **44** having a shoe upper support **46** and a sole supporting grid **48**. Both shoe upper **40** and outsole **10** are introduced into the heater with the coated surfaces facing toward an electrical heating unit **50**. The purpose for inserting the outsole and the shoe upper in the activating heater can be twofold. In the first instance, excess solvent, which remains from the elastomer solution previously applied can be evaporated, and secondly, and more important, the polyesterurethane is heat softened or thermally activated to an adhesive condition. Because the solvent, which will be described in detail further on, volatilizes readily at comparatively low temperatures, for instance room temperature to 40° C., with the lower temperatures in that range being preferred, there is generally no necessity to rely on heater **44** for the purpose of volatilizing the solvent. If it does become necessary to do so in order to obtain a predetermined amount of solvation of the plasticized polyvinyl chloride in outsole **10** and facilitate intermingling of the same with the elastomer, then heating at a convenient temperature can be carried out sequentially or simultaneously with the heating step designed to adhesively activate the said elastomer. Activation, that is adhesive activation which connotes mobility and pressure sensitivity exhibited on the part of the elastomer, can be obtained by providing the elastomer with a surface temperature of 50–80° C. by heating for a period of about 30 seconds. Electrical heating unit **50** is operated then to provide such a surface temperature. In addition to this, outsole **10** is shown as being placed closer to unit **50** in order to better facilitate intermingling of the previously solvated surface portions of the same with the heat activated polyesterurethane elastomer.

After activation of polyesterurethane elastomer is obtained, outsole **10** and shoe upper **40** are removed from heater **44**. Immediately, the flat forward portion of outsole **10** is laid on a fitting bench **52** having a front vertical surface **54** against which the breast of heel **18** is engaged, and, the forepart portion of shoe upper **40** then is brought directly over the toe end of the recess **22** and the tip of the shoe toe of upper **40** inserted in the recess. As soon as the tip is inserted in the recess, the heel end of shoe upper **40** is depressed projecting the forepart of the bottom of shoe upper **40** into the recess with the result that the shoe upper **40** and outsole **10** assume the positions of FIG. 6, the parts being temporarily secured in these positions by the adhesively activated polyesterurethane elastomer. It now remains for the operator to fit the heel end of the shoe upper within the rearward end of the recess **22**.

To fit the heel end of the shoe upper **40** into recess **22** requires some manipulation of the parts, since the outsole **10** is somewhat shorter than the measurement taken along the curved bottom surface of the shoe upper running from the tip of the toe of the same to a corner of the shoe upper **40**. The rearward corner of the shoe upper, being supported by the heel brake line of the last **42**, is indicated at **56** and this corner must be brought into the recess **22**.

In order to fit the corner **56** at the heel end of shoe upper **40** in the rearward end of recess **22** in this step, the plasticized polyvinyl chloride outsole blank **10** is stretched by application of forwardly directed force on the heel end of the shoe upper while the toe end of the shoe upper is temporarily secured by the heat-activated elastomer within the forward end of the recess **22**, the heel **18** being held against the flat vertical surface **54** of fitting table **52**. The corner **56** then having been inserted within the recess **22**, the straight central portion of the outsole bridges across the inwardly curved shank of the shoe between the

corner 56 and the ball of the shoe upper. This is the relationship of the shoe upper 40 and the outsole 10 indicated in FIG. 7.

After having inserted the toe of the shoe upper and the rearward corner 56 of the heel within the recess 22 of the outsole 10, the shoe assembly, that is the temporarily secured shoe upper and outsole is introduced into a sole attaching press having a pad box 58, as shown in FIG. 7. Within the pad box 58 is a series of pads 60 and a wedge 62 conforming with the space between the heel 18 and the shank portion of a completed shoe. When first introduced into the press, the shoe assembly rests principally on the wedge 62. As soon as the attaching operation is started, the pad box 58 is raised to bring the shoe assembly into engagement with the toe and heel abutments 64 which press the shoe assembly against the pads 60. The pressure of the pads against the tread surface of the outsole blank improves the final fit of the parts and insures accurate conformity of recess 22 in the outsole blank with the bottom of shoe upper 40. The application of pressure by the pressing pad 60 besides expanding the outsole to conform with the shoe upper also serves to facilitate permanent attachment between the shoe upper and the outsole with the polyesterurethane elastomer serving as the adhesive. This is the condition of the parts illustrated in FIGS. 8 and 10.

As a means for further defining the outline of the recess 22 in the outsole as well as to assist in providing a predetermined spread of the solution of polyesterurethane elastomer during the attaching operation and to improve the fit of the shoe within the recess 22, the raised marginal surface of the outsole surrounding the recess is formed with an inturned fin-like lip 66, see FIG. 10. About the heel of the outsole the lip 66 is less sharp than about the forepart, since there is less flexure of the shoe along the heel and less opportunity for smearing adhesive composition on exposed surfaces.

To produce the fin-like lip 66 and the recess 22, the cover plate 26 of mold 23 has secured to its under surface an insert 68 having rounded edges and graded thicknesses from its edges to its central area, the dimensions of insert 68 being smaller than the hollow in the die 24, see again FIG. 1.

For the purpose of reinforcing the corner of the shoe upper supported by the break line of the last, the last has mounted on its tread surface a metal sheet 70 formed with abrupt edges and secured in place by nails 72. This is shown in FIG. 10 together with the unitary adhesive line 76 which results on intercontacting of the activated polyesterurethane elastomer carried on outsole 10 and shoe upper 40.

After the pressure on the tread surface of the outsole 10 has been released by the pad 60 in the attaching press, the outsole tends to contract bringing the lip 66 into close, firm contact with the corner of the shoe upper surrounding the break line of last 42, the lip 66 serving to restrict the contracting movement of the outsole and to be compressed by the shoe upper somewhat in forming a close fit therewith. The result of the entire process, therefore, is to produce a shoe illustrated in FIG. 11 having its upper 40 and outsole 10 assembled together with the raised marginal surface 14 imprinted with imitation stitch indentations and hugging closely to the upper without leaving any appreciable crevice within which foreign materials, water or other liquids may enter.

DISCUSSION OF MATERIALS

The outsoles designed for use in the present invention are molded from plasticized polyvinyl chloride resins. The intended polyvinyl chloride resins include those which are obtained by homopolymerizing vinyl chloride or copolymerizing the same with vinyl acetate. If desired, other elastomeric polymeric materials, either in polymerizable or polymerized form, can be admixed or blended with the plasticized polyvinyl cholrides to obtain polyvinyl chloride resins exhibiting slightly different properties but which can still be used in molding the outsole blanks. Representative of these materials are polymers of butadiene-acrylonitrile, vinylidene chloride, chloroprene, isoprene, etc. If used, these materials should be maintained in comparatively low amounts, specifically on the order of up to 10% by weight based on the total weight of resin.

Generally speaking, polyvinyl chloride resins are rigid in nature; those having molecular and intrinsic viscosities ranging .83 to 1.30 are recommended as a starting point in providing resins from which to mold outsole blanks.

Because of the performance required of outsoles, they can be expected to be subjected to a wide variety of wearing, weather and other conditions, plus the fact that marketing of shoes can be enhanced by providing outsoles in various colors, it can become important that the polyvinyl chloride resin from which the outsoles are molded evidence a certain amount of internal plasticity. As an instance, polyvinyl chloride resins tend to darken on prolonged exposure to heat or sunlight which calls for remedial steps as are had by the incorporation of small amounts of stabilizers such as lead stearate, lead oleate, barium-cadmium laurate, barium and cadmium alkyl aryl phosphites, barium ricinoleate, cadmium ethyl hexanoate, tin mercaptide, triaryl phosphates, and the like. In another instance it can be desirable to incorporate fillers, inorganic such as carbon black, titanium dioxide, calcium carbonate, etc., organic such as nylon or rayon threads, fibers and the like. Again, it is common practice to incorporate pigments to obtain outsoles in a variety of colors. When it is desirable to do any of these, copolymers of vinyl chloride copolymerized with vinyl acetate are recommended for consideration as containing inherently greater internal plasticity than polyvinyl chloride homopolymers. Copolymers of polyvinyl chloride containing up to 15% by weight of copolymerized vinyl acetate based on the total weight of copolymer have sufficient internal plasticity to facilitate incorporation of sufficient quantities of the various fillers and additives relied upon to contribute improvement in wearing qualities plus attractiveness of color in outsoles designed for ordinary wearing conditions.

Flexibility is a necessary attribute in outsoles. To obtain this, plasticizers are incorporated in the polyvinyl chloride resin. Plasticizers which perform well for this purpose include normally liquid esters of polybasic acids, the latter intended to include acid-anhydrides as well. Representatives of these ester plasticizers are the phthalic anhydride esters, such as dibutyl phthalate, dicapryl phthalate, diethyl phthalate, dioctyl phthalate which further includes di-2-ethylhexyl phthalate, etc.; adipic acid esters such as di-2-ethylhexyl adipate; lauric acid esters, such as glyceryl monolaurate and polyethylene glycol dilaurate; oleic acid esters, such as diethylene glycol monooleate; also ricinoleic and acetylricinoleic acid esters, sebacic acid esters; benzoic acid esters such as diethylene glycol dibenzoate; stearic acid esters; phosphoric acid esters such as tricresyl phosphate and triphenyl phosphates. Illustrative of other plasticizers which operate are the epoxided esters such as epoxidized tallate, as well as the varous resinous plasticizers. The plasticizers can be used singly or in mixtures and amounts of the same will vary depending upon the identity of the polyvinyl chloride polymer, the particular plasticizer or plasticizers used and the amount of flexibility desired in the outsoles to be molded from the same. In polyvinyl chloride polymers having the particular range defined above, the plasticizer content can be generally stated to range about 50 to 100% by weight of the polyvinyl chloride resin with good flexibility resulting. Recommended plasticizers include di-2-ethylhexyl phthalate; tricresyl phosphate; epoxidized tallate.

In order to provide adhesive attachment between a shoe upper and a plasticized polyvinyl chloride outsole,

the present invention relies principally upon an essentially linear polyesterurethane elastomer. The term "principally" is intended to take into account that some adhesion or improvement of the same can be obtained from the surface portions of the plasticized polyvinyl chloride of the outsole which becomes dissolved by the solvent portion of the polyesterurethane elastomer solution which is applied to the same and which as a result can become intermingled with the polyesterurethane elastomer.

The polyesterurethane elastomers intended for use in the present invention are essentially linear, or substantially free of crosslinking while, nevertheless, exhibiting the properties of cross-linked polyurethane vulcanizates. They can be generally described as being obtained from reacting 1.0 mol of a particular essentially linear hydroxyl terminated polyester having a molecular weight of from 600 to 1200 and an acid number of less than 10 with about 1.1 to 3.1 mols of a diphenyl diisocyanate in the presence of about 0.1 to 2.1 mols of a free glycol containing 4 to 10 carbon atoms, the reactants and the reaction being essentially free of moisture. The particular polyester can be obtained from esterifying an aliphatic dibasic acid such as adipic, succinic, pimelic, or preferably those of the formula: HOOC—R—COOH where R is an alkylene radical containing 2–8 carbon atoms and more, preferably adipic acid and anhydrides thereof, with a glycol in the mol radio of greater than 1.0 mol of glycol per 1.0 mol of the acid. The glycol used in preparation of the polyester is chosen from straight chain glycols containing 4 to 10 carbon atoms with preference directed to butanediol-1,4. The polyester obtained as a result of esterifying the preferred reactants is the hydroxyl poly (tetramethylene adipate). The same glycol, butanediol-1,4, is preferred for use as the free glycol, and the amount of same to be used depends upon the weight of the polyester. The preferred diphenyl diisocyanate is the diphenyl methane-p,p′ diisocyanate. The amount of the diisocyanate to be used will be that which is the mol equivalents to the total of the polyester and the free glycol which together have a hydroxyl number of 185 to 250, in order that essentially no free isocyanate or hydroxyl groups remain after reaction is carried out.

In order for the linear polyesterurethane elastomer to be sufficiently linear for use in the present invention it must be soluble, that is dissolve completely in the strong organic solvents: tetrahydrofuran, dimethylformamide, dioxane and cyclohexanone, and in addition to be soluble in methyl ethyl ketone. This dictates that the polyesterurethane elastomer to be used be one in which the polyester reactant has a molecular weight approaching the lower limit for the same in the range prescribed above. By contrast, and making them particularly attractive for adhesives with which to adhesively attach outsoles to shoe uppers, the prescribed linear elastomeric polyurethanes are highly resistant to solvation by the more common solvents such as hydrocarbons, gasoline and the like. Further, these elastomers can be readily molded and melt when heated. This particular elastomer when used as presently prescribed provides a strong permanent adhesive bond between the shoe uppers and outsole blank in the manufacture of welded shoes.

For application to the outsole, the linear polyesterurethan elastomer is dissolved in a volatilizable, normally liquid organic solvent having the capacity to solvate both the elastomer and the plasticized polyvinyl chloride from which the outsole blank is molded. Requiring that the solvent have the capacity to dissolve the plasticized polyvinyl chloride, takes into account the intention that upon its application to the outsole, it will dissolve a portion of the surface of the plasticized polyvinyl chloride, allowing it to become intermingled with the elastomer to provide improvement in adhesion between the outsole blank and the shoe upper. Specifically, the solvents to be used are tetrahydrofuran, dimethylformamide; and mixtures of the same containing up to 35 parts by weight methyl ethyl ketone as determined on total weight of solvent with preference being directed to the use of tetrahydrofuran as the solvent. The prescribed solvents have boiling points ranging between about 60 to 160° C. and as a result are in a liquid state at normal conditions of temperature and pressure. They are also readily volatilizable at temperatures convenient for their use in the present invention, i.e., room temperature to 40° C. Because of this, times ranging from less than 5 seconds to 5 minutes are sufficient in which the solvent will solvate enough of the surface portions of the plasticized polyvinyl chloride of the outsole to facilitate intermingling of the same with the polyesterurethane elastomer. Solutions of the polyesterurethane elastomer which can be applied to the outsoles with good adhesion results, include those having dissolved 5.0 to 30.0% by weight and more preferably 10 to 20% by weight of the polyesterurethane elastomer determined on the weight of the solution and which have viscosities ranging from about 50 to 50,000, and more preferably 400 to 2500 centipoises.

The polyesterurethane solution can also include various non-reactive fillers such as silicon dioxide, clay, carbon black, polyvinyl chloride and other synthetic resins, and the like, designed to extend and vary certain of the physical properties of the solution such as viscosity, thermal sensitivity, color, etc.

The essentially linear polyesterurethane elastomer previously described for application to the outsoles can also be applied to the shoe upper to form there a complementary adhesive deposit of the elastomer. Additionally, the linear polyesteurethane elastomer can be applied to the shoe upper in other forms using other convenient methods for its application if so desired. If the shoe upper is molded from a plasticized polyvinyl chloride resin rather than being made of the more conventional leather or cloth construction, then it is recommended the elastomer solution prescribed for application to the outsole be again used.

The following examples are included for the purpose of further illustrating the present invention:

Example 1.—Preparation of molded outsoles from plasticized polyvinyl chloride(s)

Following are formulations used in providing plasticized polyvinyl chloride resins from which to mold outsoles:

Formulations	A, p.p.w.	B, p.p.w.	C, p.p.w.
COMPONENTS			
Polyvinyl chloride homopolymer, Intrinsic Viscosity 1.04	100.0	-------	90.0
Copolymer of vinyl chloride and vinyl acetate (96-4%) Intrinsic Viscosity 1.14	-------	100.0	-------
Copolymer of butadiene and acrylonitrile (57-43%)	-------	-------	10.0
Di-2-ethyl hexyl phthalate	52.5	45.0	60.0
Epoxidized tallate M.W. 416; Epoxide Equivalent 293.0; Sp. Gr. 0.9221/20° C.; B.P. 215° C.; F.P. 14.5° C	17.5	15.0	20.0
Barium-cadmium laurate (Stabilizer)	2.0	2.0	2.0
Carbon Black (25% in plasticized polyvinyl chloride resin), Sp. Gr. 1.46/25° C	1.8	1.8	1.8
Totals	173.8	163.8	183.8

Each of the formulations can be provided as a molding compound by a process which involves first charging the resin, plasticizer(s) and stabilizer into a screw-type blender and blending with heating to 90° C. for about 90 minutes. The carbon black is then charged to the blender and the temperature of the mix allowed to drop to 42–45° C. before blending continued for a period of 30 minutes. Thereafter the mix is allowed to cool and removed from the blender.

Immediately prior to molding, the blended formulations are charged into an extruder, colloided at 175–180° C. prior to extruding, sheeting biscuiting and charging into

molds of the type shown in the drawings. Molding temperatures of 195–205° C. can be used.

Example 2.—Preparation of linear polyesterurethane elastomer and solution of the same

A heated autoclave is charged with 800 grams (1.0 mol) of hydroxyl poly (tetramethylene adipate), molecular weight 800, hydroxyl number of 140, and 9.0 grams (0.1 mol) of butanediol-1,4. The charge is heated to melting with stirring for 20 minutes under a pressure of 5 to 6 mm. Hg and a temperature of 100 to 110° C. To the resulting mixture is then charged 275 grams (1.1 mol) of diphenyl methane p,p′ diisocyanate. The resulting mixture is stirred for about one minute and is then poured into a stainless-steel container, hermetically sealed, and the container placed in an oven 140° C. for 3.5 hours. The container is then removed, allowed to cool to room temperature and is then opened.

The polyesterurethane elastomer removed from the container is linear as reflected by being readily soluble in tetrahydrofuran, dimethylformamide, dioxane and cyclohexanone and in methyl ethyl ketone. However, it is essentially insoluble in gasoline. The polyesterurethane elastomer obtained has a specific gravity of 1.20; Shore hardness (*a*) 68–75; tensile strength 5000–6000; modulus at 300% of 300–475; and ultimate elongation of 700–825.

Portions of the methyl ethyl ketone-soluble linear polyesterurethane elastomer obtained above are cut into small pieces and dissolved into tetrahydrofuran at room temperature accompanied by stirring. The amount of elastomer used is 15% by weight calculated on total solution weight. The elastomer solutions which are obtained as a result have viscosities of 600–1100 centipoises.

Example 3

(A) *Sole attaching.*—The marginal sections of the bottoms of shoe uppers lasted essentially of leather components are provided with coatings of the elastomer solution described in Example 2. The marginal portions of shoe outsoles, molded from formulation A of Example 1 are similarly coated with the solution. In each case, the coating line is about 0.5 in. wide and the amount of solution used is that calculated to obtain a deposit of elastomer 10 mils in thickness after the solvent becomes volatilized. The coated shoe components are dried at room temperatures for about 30 minutes to allow the coatings to become clear tack-less films, the latter property allowing the shoe outsoles to be stacked if so desired. Additionally, the deposited films of polyesterurethane are resistant to being peeled off the outsole, indicating that some portion of the same have become intermingled with surface portions of the outsoles.

The shoe components are placed in a heater in the manner previously described for a period of 30 seconds allowing them to reach an adhesive surface temperature (on the surface of the deposited elastomer) of about 60° and causing the same to become adhesively activated. The elastomer deposits are mobile, tacky and pressure sensitive. Assembly, followed by pressure attaching under conventional conditions of 200 p.s.i. mechanical pressure for 10 seconds of the various shoe parts is then carried out as described previously to obtain welded shoes in which the outsoles are strongly and permanently attached to the shoe uppers as reflected by the following test results:

(B) *Adhesive bond testing.*—The bond strength obtained between shoe components is assessed by a number of known test methods. The following are descriptions of test methods used by applicants' assignor, B. B. Chemical Co.

Initial Bond Strength Testing is carried out immediately upon removal from the last. This is a particularly critical time in that the adhesive bond has not had time to set fully and the resilient outsole, which has become contoured to the bottom of the shoe upper through lasting, exerts a considerable stress on the adhesive bond in attempting to return to the alinement previously molded in it. In this test the force required to separate the components can be obtained directly from tensile testing apparatus readily available and adapted for this type of testing.

Dead load testing is carried out three days after sole attaching has been carried out. This allows ample time for (*a*) the adhesive to set and (*b*) migration of plasticizer, in the polyvinyl chloride outsole, if it is to take place, to manifest itself. A period of three days is more than sufficient to satisfy both of the preceding conditions. Actually, setting of the adhesive takes place within a short time, on the order of one hour, and the extended period of three days concerns the plasticizer migration. For this test a circulating air oven capable of being set at moderately elevated temperature is used. After the shoe components have arrived at equilibrium temperature, a weight is hung from the sole for a period of 60 minutes. This test is so designed as to allow a reasonably accurate insight into the performance which can be expected from the bond over extended wear under ordinary stress and temperature conditions.

Aged Bond Testing is also carried out three days after sole attaching has been carried out. The procedure used relies upon tensile testing apparatus, and otherwise is essentially that used in the initial bond strength test. The force required to separate the components is again indicative of bond strength performance.

When subjected to the testing procedures set forth above, adhesive bonds obtained by the sole attaching process of the present invention exhibit greater than acceptable strength, with the majority of the bonds exhibiting strength greater than those generally accepted as excellent.

As can be seen from the above, the method here prescribed for attaching outsoles of plasticized polyvinyl chloride to shoe uppers in the manufacture of welded shoes provides an adhesive bond between these components which is convenient to obtain and which exhibits both initial and permanent strength while, nevertheless, relying upon a thermoplastic material as the adhesive.

It will thus be seen that the objects set forth previously, among those made apparent from the preceding description and drawings, are efficiently obtained, and, since certain changes can be made in carrying out the method, materials and apparatus used in the manufacture described above without departing from the scope of the invention, it is proposed that all matter contained in the description and drawings shall be interpreted as illustrative and not in a limiting sense.

Having described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. In a method for adhesively attaching a shoe upper to an outsole constituted of a plasticized synthetic polymeric material selected from the class consisting of homopolymers of polyvinyl chloride, copolymers of polyvinyl chloride, vinyl acetate and mixtures of the same, which method includes the steps of (*a*) applying a solvent-type adhesive to said outsole (*b*) evaporating solvent from the said adhesive outsole (*c*) heat-activating the adhesive remaining on said outsole and (*d*) contacting the activated adhesive on said outsole with a heat-activated coating of the adhesive on said shoe upper, the improvement which comprises using as said solvent-type adhesive a solution of an essentially aliphatic hydrocarbon solvent-insoluble, linear polyesterurethane elastomer in a volatilizable, normally liquid, organic solvent selected from the class consisting of tetrahydrofuran, dimethylformamide and mixtures of the same containing up to 35 weight percent of methyl ethyl ketone based on the weight of solvent and capable of solvating both the said elastomer and the said polymeric material, the said elastomer being soluble in organic solvents selected from the class consisting of tetrahydrofuran, dimethylformamide, dioxan, cyclohexanone and methyl ethyl ketone, the said solution compris-

ing about 5.0% to about 30.0% by weight of said polyesterurethane based on the weight of the solution and having a viscosity of about 50 to 50,000 centipoises.

2. The improved method according to claim 1 wherein the synthetic polymeric material of said outsole is a homopolymer of polyvinyl chloride.

3. The improved method according to claim 1 wherein the synthetic polymeric material of said outsole is a copolymer of polyvinyl chloride containing up to 15% by weight of a copolymerized vinyl acetate.

4. The improved method according to claim 1 wherein the synthetic polymeric material of said outsole is a copolymer of polyvinyl chloride containing 4% by weight of copolymerized vinyl acetate.

5. The improved method according to claim 1 wherein the plasticizer is di-octyl phthalate.

6. The improved method according to claim 1 wherein the plasticized synthetic polymeric material contains as a plasticizer di-2-ethyl hexyl phthalate.

7. The improved method according to claim 1 wherein the solvent is tetrahydrofuran.

8. The improved method according to claim 1 wherein the solvent contains 10 to 20 percent by weight of linear polyesterurethane elastomer based on the total weight of solution.

9. The improved method according to claim 1 wherein the solution has a viscosity of 500–2,500 centipoises.

10. An outsole adapted to be thermally adhered to a shoe upper comprising in combination an outsole supporting an adhesive, the said outsole comprising a plasticized synthetic polymeric material selected from the class consisting of homopolymers of polyvinyl chloride, copolymers of polyvinyl chloride, vinyl acetate and mixtures of the same, the said adhesive comprising an essentially linear polyesterurethane elastomer being obtained by reacting 1.0 mol of a linear hydroxyl-terminated polyester having a molecular weight of from 600 to 1200 and an acid number of less than 10 with about 1.1 to 3.1 mols of a diphenyl diisocyanate and the said polyester being obtained by reacting an aliphatic dibasic acid with a glycol in mol ratio of greater than 1.0 mol of glycol per 110 mol of the dibasic acid, the said elastomer applied to said outsole as a solution in which the solvent is selected from the class consisting of tetrahydrofuran, dimethylformamide and mixtures of the same containing up to 35 percent by weight of methyl ethyl ketone based on the weight of the solvent, the said elastomer being soluble in organic solvents selected from the class consisting of tetrahydrofuran, dimethylformamide, dioxan, cyclohexanone and methyl ethyl ketone, the said solvent being evaporated after application to said outsole.

11. The improved method according to claim 1 wherein the solution contains polyvinyl chloride.

References Cited by the Examiner

UNITED STATES PATENTS

2,965,615	12/60	Tess	260—77.5
2,995,840	8/61	Greenbaum	36—14 X
3,021,543	2/62	Crowley	12—142

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