SHOE STIFFENER MATERIALS

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Filed: Mar. 17, 1971
Appl. No.: 125,055

U.S. Cl.................. 117/68, 12/146 D, 36/68, 117/68.5, 117/76 A, 117/76 FB, 117/76 T, 117/122 H, 156/245, 161/82
Int. Cl................... B32b 27/12, A43d 31/00
Field of Search........... 117/76 T, 76 A, 122 H, 117/68.5, 161 K, 68; 260/78.3 R

References Cited
UNITED STATES PATENTS
2,840,492 6/1958 Emerson.................. 117/140 A
2,611,726 9/1952 Harrison.................. 117/76 T
2,962,524 11/1960 Hostetler et al........... 260/78.3 R
3,477,998 11/1969 Nakahara et al............ 260/78.3 R
3,627,567 12/1971 Tensho.................... 117/76 T
2,917,410 12/1959 Vitalis.................. 260/78.3 R X

FOREIGN PATENTS OR APPLICATIONS
977,230 12/1964 Great Britain.............. 260/78.3

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ABSTRACT

Improved shoe stiffener materials such as box toe blanks and counter blanks are formed of a base layer of an impregnated fabric carrying a polystyrene-type impregnant in incompletely coalesced particle form. At least one and preferably both sides of the base layer carries a polycapro lactone thermoplastic layer. The shoe stiffener material is solid and non-tacky at standard room temperature and has sufficient softness and flexibility to permit ease of use in conventional box toe and shoe back part forming apparatus. Heat is used to form a continuous thermoplastic film of the polymers in the shoe stiffener when formed into three-dimensional box toes and counters. The heat also acts to adhesively unite the stiffener with surrounding layers such as shoe uppers and shoe linings.

12 Claims, 5 Drawing Figures
SHOE STIFFENER MATERIALS

BACKGROUND OF THE INVENTION

A large variety of thermoplastic shoe stiffener materials have long been known in the shoe art for use as box toe blanks and counter blanks in conventional shoe molding and lasting procedures. A type of shoe stiffener material which has been highly successful and extensively used in recent years is described in U.S. Pat. No. 2,840,492. Such shoe stiffener materials are formed into a box toe blank or counter blank having a fibrous base impregnated with incompletely coalesced particles of polystyrene-type impregnant. The term "polystyrene-type" is used herein to mean conventional shoe stiffener polystyrene-containing thermoplastics which are preferably mixtures of styrene-butadiene copolymer and a styrene polymer wherein the ratio of total styrene to butadiene is between 75:25 and 95:5. Such shoe stiffeners as in the form of a box toe blank are used in accordance with conventional practice wherein a shoe upper and liner are sewn together, the box toe blank is softened by a liquid solvent and inserted between the liner and upper and the assembly applied to a last. The box toe blank remains pliable at least through the lasting operation. The liquid solvent acts to cause the impregnant to firmly adhere to the upper and liner while coalescing the impregnating particles to form a continuous film so that by the time the shoe is removed from the last, the liner, box toe blank and upper are integrated into a relatively rigid structure having high resistance to impact.

Such shoe stiffeners provide box toe and counter blanks which can be readily softened by application of selected solvents which are capable of adhesively integrating the upper and liner to provide a stiffened shoe structure having good impact resistance. The blanks are formed so that the plastic impregnants are incompletely coalesced and incompletely film formed in order to allow ease of handling and rapid solvent penetration.

Problems connected with the use of such shoe stiffeners include that of obtaining outstanding adhesion to liners and uppers which requires difficult to obtain ideal solvent activation conditions. Handling of solvent soaked blanks is messy and time consuming. The manufacturing time for forming the stiffeners in shoe making operations is usually long since often several hours are required for the solvent to evaporate. The timing in back part molding and lasting operations is critical since solvent activated shoe stiffeners must be molded while sufficient solvent is still present which requires juggling of solvent blends to fit particular sets of factory conditions. Moreover, use of the solvents can cause problems of toxicity and flammability normally associated with the handling of solvents.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a shoe stiffening material in sheet form which can be molded into three-dimensional box toes and shoe counters having good flexibility, stiffness and impact resistance with excellent adhesion to conventional shoe upper and shoe lining materials.

It is another object of this invention to provide a shoe stiffener material in accordance with the preceding object which comprises a thermoplastic impregnated fabric having at least one coating of polycaprolactone whereby the material can be molded within standard shoe making temperature limits to form a continuous film and adhesively unite with conventional shoe upper and shoe lining materials.

Still another object of this invention is to provide a shoe stiffener material which can be activated and molded by heat without the use of liquid solvents and which is economical to manufacture and use efficiently in shoe making procedures.

According to the invention a thermoplastic shoe stiffening material in sheet form comprises a base layer of an impregnated fabric carrying a thermoplastic impregnant in the form of incompletely coalesced particles. At least one outer layer comprises polycaprolactone. The material is capable of being heat treated at a temperature of from 140°F to 360°F and preferably 175°F to 250°F to form a continuous plastic film having adhesive properties.

Preferably the incompletely coalesced thermoplastic impregnant is of a styrene type preferably comprising a mixture of styrene-butadiene copolymer and a styrene polymer with the ratio of total styrene to butadiene being between 75:25 and 95:5. The polycaprolactone has a molding temperature between 140°F and 360°F and preferably 175°F to 250°F with a softening point of from about 140°F to 180°F. Preferably the polycaprolactone is applied to both sides of the impregnated fabric as a thin layer in a continuous film having a thickness of between 0.001 and 0.005 inch and the impregnated fabric has a thickness of from 0.020 to about 0.090 inch.

The polycaprolactone can be modified with suitable viscosity depressants which preferably do not affect the desired flexibility of the polycaprolactone. Such viscosity depressants include rosin derivatives, terpene phenolics and waxes. Conventional modifiers, fillers and the like can also be incorporated in the polycaprolactone.

In an alternate embodiment of this invention, the impregnated fabric coated on both sides with a polycaprolactone film has one of the polycaprolactone films further coated with a barrier layer. This embodiment can be used in unlined shoe manufacture where the barrier coating prevents adhesion of the polycaprolactone to lasts during formation of the shoe stiffeners into three-dimensional configurations.

In the method of using the shoe stiffeners of this invention, a shoe stiffener blank having an incompletely coalesced thermoplastic particle impregnated fabric with outer coatings of polycaprolactone, is preheated while pressed against a shoe upper and/or liner in a conventional shoe box toe of back part forming apparatus. Preferably a machine temperature of from 250°F to 350°F is used to obtain a blank temperature of 175°F to 250°F for from 5 to 20 seconds. The preheated blank is then placed in the box toe or heel seat lasting section. The blank is thus adhesively united with a shoe upper and/or lining while simultaneously forming the shoe stiffener blank into a continuous film. As soon as the laminate so formed is cooled to room temperature, a solid shoe part is obtained having the required stiffness.

It is a feature of this invention that adhesion to conventional shoe lining and shoe upper materials is extremely good and in fact far better than obtained by solvent activated materials under normal operating conditions. Shoe making operations are greatly simplified since manufacturing time is decreased by orders of
magnitude due to elimination of the time necessary for the solvent to evaporate. Critical timing in back part molding and lasting operations is not necessary since the materials of this invention are permanently remoldable at reasonable temperatures which can easily be attained by normal steaming operations. Problems of toxicity and flammability associated with handling of solvents are avoided. Firmness, i.e., the resistance to deformation of molded box toe and counter shapes, is greater for the material of this invention than with comparable solvent activated shoe stiffeners. Molded shoe counters or shoe box toes made from the material of this invention have good impact strength and high resistance to fracture. Use of polycaprolactone layers on both sides of the base fabric provides for moisture seals of the material which minimizes the softening effect of moisture if present.

While the exact mechanism that takes place during heating and molding of the shoe stiffener material of this invention is not fully understood, it is believed that the polycaprolactone acts as an adhesive to bond the shoe stiffeners to the upper and/or lining material of the shoe. In the molten state, the coating is believed to cause some activation of the polystyrene impregnant, i.e., it causes the impregnant to swell and coalesce at least partially into a continuous film. Moreover, the coating of polycaprolactone penetrates and flows into the impregnated fabric and around polystyrene particles which have not coalesced. Because polycaprolactone and polystyrene are quite compatible, it is believed that there is a dissolution of the polystyrene into the molten polycaprolactone. These actions bond the incompletely coalesced particles into a uniform continuous film. The result of molding in conventional box toe and counter apparatus is that the shoe stiffener material after molding is an essentially continuous resin film reinforced by a fabric which gives the necessary hardness and durability to the three-dimensional molded stiffeners.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and advantages of the present invention will be better understood from the following description when read in conjunction with the accompanying drawings in which:

FIG. 1 is a top plan view of a preferred embodiment of a shoe stiffener material of this invention in the form of a shoe counter;

FIG. 2 is a cross sectional view through line 2—2 thereof;

FIG. 3 is an alternate embodiment thereof in the form of a box toe blank;

FIG. 4 is a cross sectional view showing a step in the molding of the counter of FIG. 1 between a shoe upper and shoe lining; and

FIG. 5 is a cross sectional view through an alternate embodiment of a shoe stiffener material in accordance with this invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

With reference now to the drawings, the shoe stiffening material of this invention is illustrated in sheet form in the shape of a counter blank 10 in FIG. 1 and a box toe blank 20 in FIG. 3. The counter blanks and box toe blanks can be of any conventional shape and the shapes 10 and 20 are shown for illustrative purposes. The shoe stiffener materials will be referred to with reference to the counter blank 10, but, it should be understood that whether in a counter blank or box toe blank shape, the makeup of the shoe stiffener material is the same.

The counter blank 10 as shown in FIG. 2 is formed of a flat fibrous base 16 impregnated with polystyrene-type incompletely coalesced particles 15 to make up a base layer 12. Both the upper and lower surfaces of the base layer 12 are coated with a thin, continuous film 11, 13 of polycaprolactone adhered to the base layer. Preferably the base layer 12 has a thickness of from 0.020 to 0.090 and each film coating 11, 13 has a thickness of from 0.001 to 0.005 inch. However, the thickness of each layer can vary greatly depending upon particular materials used and particular results desired.

The counter blank 10, because of the polycaprolactone used is solid and non-tacky at standard room temperature of 70°F and remains non-tacky allowing storage at temperatures as high as at least 135°F.

The impregnated fiber base layer 12 is a conventional shoe stiffener sheet capable of being activated by a liquid solvent in conventional box toe and counter blank apparatus. Suitable base layers are described in U.S. Pat. No. 2,840,492 and are well-known in the art. As described in that patent, the fibrous material 16 is a textile material which can be knitted, woven, felted, needle punched, non-woven or the like from fibers of cotton, felt, jute or the like. The impregnant is preferably aresinous composition which is a thermoplastic styrene-type material preferably consisting essentially of a mixture of styrene-butadiene copolymer and a styrene polymer wherein the ratio of total styrene to butadiene is not less than approximately 75:25 and does not exceed approximately 95:5 with a preferred range being between 80:20 and 90:10. The impregnant can be a styrene copolymer alone or a styrene blend alone. Styrene copolymers and blends with natural and synthetic rubbers such as butadiene or with acrylates can be used. As known in the art, such base layers when used alone as box toe or counter blanks are formed by impregnation in a conventional manner so that the fibrous base picks up from approximately 200 percent to 500 percent or more of its weight of the resins composition (dry basis) to produce an impregnated sheet with a coating or surface of the resinous material which is incompletely coalesced and incompletely film formed. The terms “incompletely coalesced” and “incompletely film formed” are used to indicate that the resin is capable of substantial further coalescing and film forming as by solvent activation in conventional shoe molding procedures.

The impregnating composition is preferably a mixture of aqueous dispersions of the copolymer and styrene polymer containing suitable thickening agents which do not undergo bacterial decomposition and which are preferably relatively water resistant when dried out. The fabric material is passed through the aqueous dispersion and the base layer 12, then dried out in any suitable manner such as conventional oven drying or drying on textile cans at temperatures of approximately from 180°F to 280°F and preferably 180°F to 210°F. The time and temperature of drying is controlled as known in the art to avoid complete film forming and coalescing which would render the sheet too rigid for ease of handling in conventional molding.

The polystyrene thermoplastic impregnant can have suitable fillers and other compounding materials incorporated therein as known in the art.
It is conventional to use the base layer 12 as a box toe or counter blank directly as by soaking such blanks in a solvent and then molding. However, as pointed out above, several disadvantages ensue.

In the counter blank 10 of this invention, polycaprolactone film layers 11 and 13 are deposited on the upper and lower surfaces of the base layer 12 to form a bonded sheet. The formation of the film layers or coatings 11 and 13 can be carried out by conventional hot melt roller coating, extrusion and the like. Preferably the film layers 11 and 13 are formed as substantially uniform thickness layers using conventional hot melt, roller coating techniques at a temperature in the hot melt of about 360°F.

The polycaprolactone polymers of the layers 11 and 13 are known in the art to have the following structural formula:

\[
(\text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{CH}_2\text{O})_n
\]

where \(n\) preferably varies from 100 to at least 1,000. It has now been found that such polymers which are solid at room and normal storage temperatures are ideally suited for use in shoe stiffener materials to eliminate the need for solvent activation. Polycaprolactone has good compatibility with styrene-type polymers, good stiffness, flexibility and impact resistance and excellent adhesive properties to normal shoe upper and shoe lining materials. Moreover, at the temperatures at which polycaprolactones become adhesive and flow are ideally suitable for shoe making procedures since softening and flow can be obtained in a temperature range which is non-destructive to shoe uppers and high enough to prevent strike through of the thermoplastic through the shoe upper and lining materials.

Preferably the polycaprolactone polymers used have weight average molecular weights of at least 25,000 with a weight average molecular weight in the range of 25,000 to 50,000 being preferred. Such polycaprolactone polymers have excellent adhesive properties and eminently suitable molding temperatures in the range of from 140°F to 360°F and preferably 175°F to 250°F.

Typical molten viscosities for useful polycaprolactone polymers obtained by Brookfield Model LVT using spindle SC-34 at 0.6 rpm (Brookfield's Thermo-sel equipment) are given below:

| Polycaprolactone polymer weight average molecular weight 28,000 |
|---------------------|-----------------|------------------|
| 350°F               | 375°F           | 400°F            |
| 7750 cpsi           | 5000 cpsi       | 66,000 cpsi      |

Polycaprolactone polymer weight average molecular weight 40,000

<table>
<thead>
<tr>
<th>350°F</th>
<th>375°F</th>
<th>400°F</th>
</tr>
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<tbody>
<tr>
<td>66,000 cpsi</td>
<td>51,000 cpsi</td>
<td>61,000 cpsi</td>
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</table>

A preferred polycaprolactone polymer for use in this invention is available from Union Carbide Corporation of New York, N.Y. and designated PCL-700. This polymer has a weight average molecular weight of 40,000 with the viscosity noted above. Other properties of the polycaprolactone polymer are listed below and are described in Union Carbide Corporation product information sheets F-42501:

Chemical formula: \(\text{C}_4\text{H}_6\text{O}_3\)  
Structural formula: \(\bigg(\text{CH}_2\bigg)_{\infty}\)

where \(n\) preferably varies from 100 to at least 1,000.

<table>
<thead>
<tr>
<th>% secant modulus, p.s.i.</th>
<th>Yield stress, p.s.i.</th>
<th>Tensile strength, p.s.i. (based on initial cross sectional area)</th>
<th>Percent elongation</th>
<th>Melting point, °C</th>
<th>Glass transition temperature, °C</th>
<th>Density, g/cc. at 0°C</th>
<th>Density, g/cc. at 60°C</th>
</tr>
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<tbody>
<tr>
<td>30,000</td>
<td>1,400</td>
<td>3,000 to 4,000</td>
<td>500 to 1,000</td>
<td>60</td>
<td>-60</td>
<td>1.160</td>
<td>1.149</td>
</tr>
</tbody>
</table>

The PCL-700 polycaprolactone polymer has a viscosity which is too high to allow application as a thin coating of from 0.001 to 0.005 inch using conventional hot melt, roller coating techniques and it is therefore extrusion coated when the film layers 11 and 13 consist of this polymer. However, extrusion of the film coatings 11 and 13 can add cost to the shoe stiffener materials of this invention. Thus, it has been found that it is possible to modify the polycaprolactone polymers used with suitable viscosity depressants and preferably viscosity depressants which do not affect flexibility and are compatible with polycaprolactone. Such viscosity depressants can be blended with the polycaprolactone in conventional blending operations such as conventional blending in a hot melt. Preferably the film layers 11 and 13 comprise at least 60 percent by weight polycaprolactone polymer. Conventional modifiers, fillers and other additives can also be incorporated in the polycaprolactone as known in the art.

Useful viscosity depressants include rosin derivatives, waxes and terpene phenolics alone or in combination with each other. When terpene phenolics are used as viscosity depressants, a modifying polymeric material is also used to prevent the terpene phenolics from britting the polycaprolactone. Thus, such viscosity depressants do not change the flexibility of the polycaprolactone. The rosin derivatives are preferably used in amounts of from 10 to 40 percent by weight and can be rosin esters including but not limited to pentaerythritol esters of hydrogenated rosin, methyl esters of hydrogenated rosin, glycerol esters of polymerized rosin and glycerol esters of hydrogenated rosin. The waxes can be natural, microcrystalline and ester waxes having melting points above the melting point of the polycaprolactone polymer and preferably above 160°F. Such waxes are preferably used in amounts of from 1 to 5 percent by weight of blends useful in this invention. The waxes act to depress viscosity and also improve blocking characteristics thus preventing counter blanks and box toe blanks from sticking to one another when stacked for shipment and storage even though environmental temperatures may be high.

The terpene phenolics when used are preferably blended with polycaprolactone with or without rosin and waxes in preferred amounts of from 10 to 40 percent by weight of the blends. The terpene phenolics act...
as blocking agents as well as viscosity depressants as do the waxes. Since the terpene phenolics tend to embrittle polycaprolactone, when used, they are used in conjunction with a polymeric material such as ethylene vinyl acetate acting as a softening agent. Other acetates and vinyl materials can be used. Ethylene vinyl acetate does not appreciably affect the flexibility of blends of terpene phenolics and polycaprolactone. Such polymeric materials are preferably used in amounts of from 5 to 15 percent by weight of the blends.

The particular amount of the viscosity depressants and modifiers added to the polycaprolactone can vary depending upon the molecular weight of the polycaprolactone used and its initial viscosity. In most cases, it is preferred that the viscosity depressants and modifiers used be used in amounts of from 10 to 40 percent by weight of the blend with polycaprolactone. In all cases, the additives are compatible with polycaprolactone in that they do not significantly adversely affect the desirable properties of the polycaprolactone.

In the method of using the shoe stiffener material of this invention, as suggested in FIG. 4, a counter blank 10 is formed into a three-dimensional molded counter in a conventional shoe back part forming machine such as a United Shoe Machinery UBMA. Other conventional molding equipment such as International Shoe Machinery Corporation Model CHT with Model TA activator can be used. The counter blank 10 as shown in FIG. 4 is heated after positioning between a show upper layer 21 and shoe lining 22 for shaping, at conventional machine temperatures and times. For example, at 275°F cycle times are normally 12 to 20 seconds while at 350°F cycle times are normally 6 to 10 seconds. After heating, the laminated counter, shoe lining and shoe upper which are pulled down over a last as in conventional practice, are transferred to a second station and then allowed to cool. The counter 10 easily conforms to the shape of the last and is easily molded. During the molding operation, the counter blank 10 is formed into a continuous film throughout and adhesively unites to the leather upper and leather lining without strike through of the thermoplastic material to the outer surfaces of the lining 22 or upper 21. After molding, the shoe parts can be air-cooled or allowed to cool at room temperature so that a complete molded box toe structure or counter structure is rapidly formed and which maintains its shape well. This procedure avoids the long time periods ordinarily used to evaporate solvents after lasting.

FIG. 5 illustrates an alternate embodiment of this invention where the box toe blank 20 with layers 11, 12 and 13 as previously described is formed with an adherent layer 14 of a blocking film. The film 14 can for example be a film of styrene acrylonitrile applied to the lower layer 13. Thus, layer 11 can be applied to a shoe upper in a molding operation with layer 14 directly contacting the last. The layer 14 provides a barrier to prevent adhesive attachment of the blank to the last during the lasting operation while allowing adhesive attachment to the shoe upper.

In most cases, it is preferred to use the shoe blanks of this invention with dual coatings 11 and 13 as described in laminated constructions between a lining and shoe upper. Use of dual coating assures continuous film formation of the molded blank. However, in some cases, only one coating 11 or 13 need be used.

The shoe counter blanks 10 and box toe blanks 20 are compatible with a wide variety of conventional shoe uppers and linings. For example, the shoe upper can be leather, cloth, or other materials including synthetic polymeric materials such as porous micellar shoe upper materials, polyvinyl chloride coated fabrics, or polyurethane coated fabrics. The shoe linings can be conventional sheet or textile materials of cotton, jute, felt, leather, synthetic polymeric materials such as permeable materials, and the like. In all cases, the adhesive properties of polycaprolactone are outstanding.

Illustrative examples for preparing and using the shoe stiffener materials in accordance with the present invention are given below:

EXAMPLE 1

An aqueous dispersion of 88.5 parts of a 60-40 styrene-butadiene copolymer (Polycro 2415, a Borden Chemical Company product) is mixed with 144 parts an aqueous dispersion of polyisocyanate (Polycro 220NS, a Borden Chemical Company product) to produce a latex mixture having a total solids content of about 47 1/4 percent and a total styrene to butadiene ratio of about 3/17. A 25 percent ammonium hydroxide solution is then added in an amount sufficient to produce a pH of 10 to 11, followed by gentle heating to a temperature between 120° and 150°F, after which 1 percent thickening agent (Lytron 820, a styrene-maleic anhydride copolymer having an average molecular weight of 20,000 and an acid number of 180, a Monsanto Chemical Co. product), based on the weight of resin, is added and the mixture is stirred until a uniform dispersion is produced. The mixture is then cooled to room temperature (70°-90°F) and then run into the impregnating apparatus.

A double nap flannel, 4 1/4 ounce — 3/3 double nap, is then run through the treating composition, passed through squeeze rolls or between doctor blades to remove the excess, and dried at a temperature of 180° to 210°F, the pick-up of latex solids being 260 percent of the fabric base.

EXAMPLE 2

The same procedure as set forth in Example 1 was followed, except that 85 parts of the styrene-butadiene copolymer of 70-30 ratio (Polycro 2410, a Borden Chemical Company product), 125 parts of the polystyrene and 0.67 percent of the thickener were used to produce a 47.4 percent dispersion having a total styrene to butadiene ratio of 87:13 and the pick-up of latex solid was 250 percent of the fabric base.

EXAMPLE 3

A base layer as formed in Example 1 is coated with a uniform continuous film of polycaprolactone (PCL700) on each side with the film having a uniform thickness of 0.002 inches on each side of the base layer. The coating film is applied by conventional extrusion coating at 225°F and line speeds of 20 to 70 feet per minute and are allowed to cool to room temperature. The polycaprolactone film has a molten viscosity of 31,000 cps at 375°F.

EXAMPLE 4

Example 3 is repeated using the base layer formed in Example 2 rather than that formed in Example 1 and varying the extrusion conditions. Extrusion was carried
out at 200°F at line speeds of from 10 to 40 feet per minute. Both sides of the base layer are coated with a continuous film having uniform thickness of 0.004 inch.

EXAMPLE 5

The base layer formed in Example 1 is coated with a polycaprolactone mixture on both sides with each film having a thickness of 0.0035 inch. A coating mixture is formed by mixing together in a hot melt at 360°F, 65 percent by weight polycaprolactone (PCL-700), 21 percent by weight terpene phenolic resin (SP-560, a Schenectady Chemical, Inc., of Schenectady, New York product) having a melting point, (ball and ring ASTM E-28) of 150°C, an acid number of 65 and a specific gravity at 25°C of 1.10 with a viscosity of 0.48 at 0.25 grams per 100 ml toluene (Elvax 410, an E. I. Du- Pont de Nemours Co., Inc. product) and 4 percent by weight microcrystalline wax (Mobil Wax 2305, a Mobil Oil Corporation product) having a melting point, ASTM, of 178°F and a needle penetration ASTM at 77°F of 25/30 with a viscosity of 70–85 at 210°F, SUS. The coating is applied by conventional hot melt roller coating at 360°F using a line speed of the base layer of 20 to 120 feet per minute. The coating formed has a viscosity of 17,000 cps at 375°F.

EXAMPLE 6

Example 5 is repeated; however, the base layer used is that formed in Example 2. The terpene phenolic used is LTP-135, a product of Pennsylvania Industrial Chemical Corporation having a softening point (ring and ball) of 135 with a specific gravity of 1.03 and a 0 acid number. The resultant film coatings 11 and 13 have a molten viscosity of about 16,500 cps at 375°F.

EXAMPLE 7

Example 6 is repeated except that the coating hot melt is substituted with the following mixture: 65 percent by weight polycaprolactone (PCL-700), 21 percent by weight terpene phenolic (SP-560), 10 percent ethylene vinyl acetate (Elvax 410, a DuPont de Nemours & Co., Inc. product) and 4 percent by weight synthetic wax (Ross Wax 160, a Frank B. Ross Co. of Jersey City, N.J. product) which is an N-(dialkyl-4,4′ dianidophenylmethane). The coatings formed each have a thickness of 0.0035 inch and a molten viscosity of about 17,000 cps at 375°F.

EXAMPLE 8

Example 7 is repeated except that the coating hot melt is substituted with the following mixture: 65 percent polycaprolactone (PCL-700), 21 percent by weight of a glycerol ester of polymerized rosin (Poly-Pale ester 10, a product of Hercules Powder Co. of Wilmington, Del.), 10 percent by weight ethylene vinyl acetate (Elvax 410), and 4 percent by weight microcrystalline wax (Mobil Wax 2305). The coatings have a viscosity of 16,000 cps at 375°F.

EXAMPLE 9

Example 6 is repeated except that the following mixture is used for the coating hot melt: 72 percent by weight polycaprolactone (PCL-700), 25 percent by weight glycerol ester of polymerized rosin (Poly-Pale ester 10), and 3 percent by weight microcrystalline wax (Mobil Wax 2305). The film coatings 11 and 13 formed have a molten viscosity of 15,000 cps at 375°F.

EXAMPLE 10

Example 6 is repeated; however, the coating hot melt mixture is substituted with the following mixture: 72 percent by weight polycaprolactone (PCL-700), 25 percent by weight of a maleic modified pentaerythritol ester of rosin (Pentalyn G, a Hercules Powder Co. product) and 3 percent by weight microcrystalline wax (Mobil Wax 2305). The film coatings formed on either side of the base layer have a molten viscosity of 15,500 cps at 375°F.

EXAMPLE 11

Example 6 is repeated; however, the hot melt coating mixture is substituted with the following mixture: 72 percent by weight polycaprolactone (PCL-700), 25 percent by weight of a glycerol ester of hydrogenated rosin (Stabelyte Ester-10, a Hercules Powder Co. product) and 3 percent by weight microcrystalline wax (Mobil Wax 2305). The coating composition has a molten viscosity of about 14,500 cps at 375°F. The molten viscosities of the coatings of this invention are determined with the Brookfield technique described above with relation to PCL-700.

EXAMPLE 12

The shoe stiffener material produced in Example 11 is used. A counter in the sheet form 10 shown in FIG. 1 is cut from the shoe stiffener material of Example 11. The sheet center 10 is then positioned in contact with a calfskin shoe upper sheet and a leather shoe liner after which the assembly is pulled down over a wooden last with the sheets urged into pressing contact, and processed in a United Shoe Machinery UBMA back part forming machine using a machine temperature of 275°F and a machine time of 15 seconds. The resultant stiffened shoe part shows good adhesive lamination of the three layers with good bond strength, and excellent shape retention properties. When any of the shoe stiffener materials of Examples 3–10 are used in this process, similar results are obtained. Variations in temperature and time of from 275°F to 350°F and 6 to 20 seconds and higher give desirable results. The specific time and temperature varies depending upon the specific materials, thicknesses and the like as known in the art.

While specific embodiments of this invention have been shown and described, it should be understood that many variations are possible. In all cases, it is important that the layers 11 and 13 be formed of polycaprolactone having desirable adhesive properties and capable of forming three-dimensional molded configurations with desired stiffness and ease of handling without the use of conventional liquid solvents. The polycaprolactone in all cases functions as an adhesive and forms a continuous film of the shoe stiffener material. Preferably the polycaprolactone polymer or blend of this polymer with suitable modifiers has a molten viscosity (Brookfield technique as described above) of at least 7,000 centipoise (CPS). When the viscosity is below 7,000 cps, adhesive properties are adversely affected and strike through problems can occur.

What is claimed is:

1. A thermoplastic shoe stiffener sheet comprising,
a base layer of an impregnated fabric carrying an in-
completely coalesced thermoplastic polymer im-
pregnant and having first and second outer sur-
faces,
an outer layer adhered to a surface of said base layer
and consisting essentially of polycaprolactone.

2. A thermoplastic shoe stiffener sheet in accordance
with claim 1 and further comprising a second outer
layer adhered to a second surface of said base layer
and consisting essentially of polycaprolactone.

3. A thermoplastic shoe stiffener sheet in accordance
with claim 2 wherein said sheet is capable of being
reated with heat at a temperature of from 140°F to
360°F to activate said sheet to form a continuous film
thereof and render it adhesive.

4. A thermoplastic shoe stiffener sheet in accordance
with claim 3 wherein said thermoplastic polymer im-
pregnant comprises polystyrene.

5. A thermoplastic shoe stiffener sheet in accordance
with claim 4 wherein said thermoplastic polymer im-
pregnant consists essentially of a mixture of styrene-
butadiene copolymer and a styrene polymer wherein
the ratio of total styrene to butadiene is not less than
75:25 and does not exceed 95:5.

6. A thermoplastic shoe stiffener sheet in accordance
with claim 5 wherein said thermoplastic polymer im-
pregnant and said fabric are in the ratio of at least 2:1
by weight and said polycaprolactone has a molten vis-
cosity of at least 7,000 cps at 350°F.

7. A thermoplastic shoe stiffener sheet in accordance
with claim 6 wherein said polycaprolactone has a
weight average molecular weight of from 25,000 to
50,000.

8. A thermoplastic shoe stiffener sheet in accordance
with claim 7 wherein said polycaprolactone of said first
and second outer layers is blended with from 10 to 40
percent by weight of a viscosity depressant selected
from the group consisting of rosin derivatives, terpene
phenolics and waxes.

9. A thermoplastic shoe stiffener sheet in accordance
with claim 8 wherein said viscosity depressant is a ter-
pene phenolic in an amount of from 10 to 40 percent
by weight, and from 5 to 15 percent by weight of a
compatible polymeric material selected from poly-
meric acetates and vinyl materials is uniformly incor-
porated in said polycaprolactone to prevent embrittle-
ment by said terpene phenolic.

10. A thermoplastic shoe stiffener sheet in accord-
ance with claim 9 wherein said base layer has a thick-
ness of from 0.020 to 0.090 inch and said first and sec-
ond outer layers each have a thickness of from 0.001
to 0.005 inch.

11. A thermoplastic shoe stiffener sheet in accord-
ance with claim 1 wherein said thermoplastic polymer
impregnant consists essentially of a mixture of styrene-
butadiene copolymer and a styrene polymer wherein
the ratio of total styrene to butadiene is not less than
75:25 and does not exceed 95:5, and said sheet is capa-
ble of being treated with heat at a temperature of from
140°F to 360°F to activate said sheet to form a continu-
ous film thereof and render it adhesive.

12. A method of forming a shoe stiffening sheet for
use as shoe counter blanks and shoe box toe blanks,
said method comprising,
impregnating a fibrous material with an aqueous dis-
spersion of a mixture of a styrene-butadiene copoly-
mer and a styrene polymer wherein the ratio of total
styrene to butadiene is between 75:25 and
95:5 to form an impregnated base layer,
drying said base layer without causing complete co-
alescence of the polymers,
and applying an adherent film coating consisting es-
sentially of polycaprolactone on outer surfaces of
said base layer.

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