Feb. 15, 1966 M. R. RADCLIFFE 3,234,668

LAMINATE ARTICLES USEFUL AS SHOE STIFFENERS

Filed Jan. 8, 1962

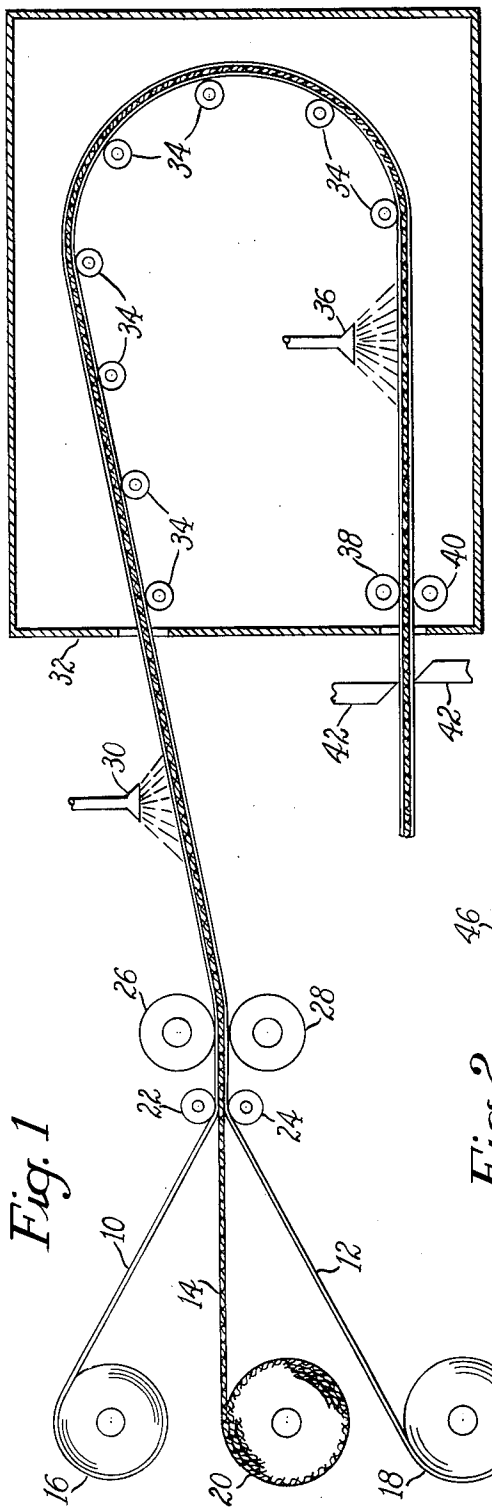


Fig. 1

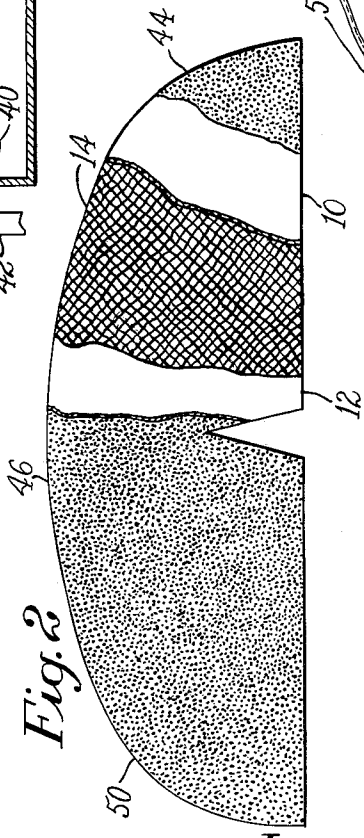


Fig. 2

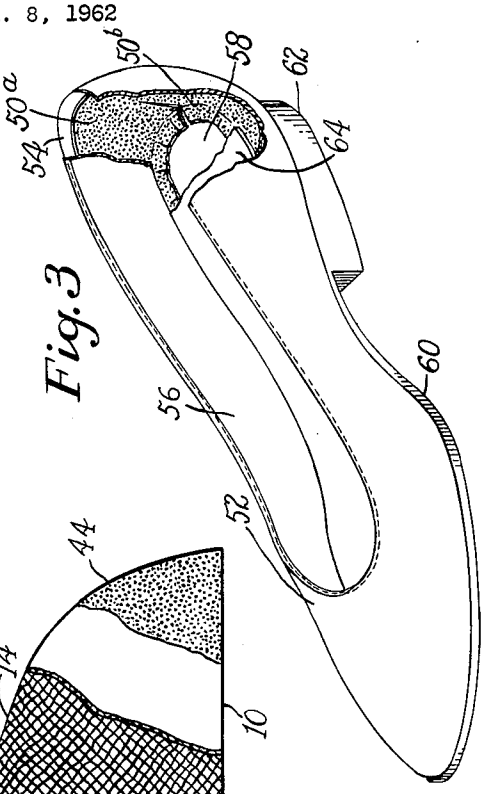


Fig. 3

Inventor
Milton R. Radcliffe
By his Attorney
Lawrence F. Cleary

United States Patent Office 3,234,668 Patented Feb. 15, 1966

3,234,668

LAMINATE ARTICLES USEFUL AS SHOE STIFFENERS

Milton R. Radcliffe, Marblehead, Mass., assignor to United Shoe Machinery Corporation, Boston, Mass., a corporation of New Jersey

Filed Jan. 8, 1962, Ser. No. 164,730
6 Claims. (Cl. 36—68)

The present invention relates to laminate articles and more particularly relates to articles of this type which are useful as shoe stiffeners.

The term shoe stiffener includes both counters and toe boxes. As indicated by the term, the stiffener is included in a shoe upper for the primary purpose of perpetuating the shape of the form or last, introduced into the upper by the forming or lasting operation. While a shoe stiffener must exhibit sufficient dimensional stability to maintain itself and the shoe upper in the three dimensional curved configuration so introduced, it should do so in a manner which affords comfort to the wearer. For this reason, except in specific instances where shoes are designed to give extreme protection, for example ski boots, combat boots, etc.; stiffeners made of hard and unyielding materials such as pyroxylin impregnated fabrics and the like are less than attractive, at least by present standards of shoe making. Rather in usual instances the stiffener should be stiff without being hard, or to state it differently, the stiffener should be sufficiently flexible to distort when pressure from the foot is applied to it and resilient enough to return to its assigned configuration when the pressure is removed. On this basis alone stiffeners made from a number of materials have been found to perform satisfactorily; these materials include leather, various composite materials, synthetic polymeric materials such as many of the thermosetting types, and, as well thermoplastic types exemplified by high density polyethylene, polypropylene, and the like. However, stiffeners made from these materials, in general mode of practice, are first molded to a shape anticipating that of the last, then included in a shoe upper assembly, and thereafter lasting is carried out.

In present day shoemaking, emphasis is being increasingly directed toward improving production rates. An expedient suggested for this purpose is a process in which shaping of the stiffener would be carried out on the last coincidental with lasting of the shoe upper. Successful practice of such a process calls for a shoe stiffener article which prior to lasting could be either introduced into the shoe upper assembly in a flaccid state, or once introduced be capable of easy conversion to a flaccid state, and which could then be shaped to the configuration of the last during the lasting operation. On removal from the last the shoe stiffener should retain the introduced configuration corresponding to the shape of the last in stiffened form, and exhibit resiliency and flexibility as previously described. The transition from flaccid to stiffened state in such a process should be capable of being effected within, or reasonably consonant with the time ordinarily required for lasting the shoe upper to shape. The usual time for shaping runs less than 60 seconds. However, suggesting such an expedient and effecting the same are different propositions, with the latter not as yet having been satisfactorily resolved.

A major difficulty which interferes with effecting the suggested process arises from the fact that the use of elevated temperatures, which could otherwise be used to expedite matters, is very much restricted. Exposure to temperatures above about 180° F. for periods greater than momentary has a deleterious effect on leather from which shoe uppers largely are made. This temperature

limitation then militates against the use of many of the known stiffeners in a process of the type proposed. An example of such stiffeners are those which depend upon thermosetting resins such as phenolics, etc. to contribute requisite stiffening. These resins generally require elevated temperatures or extended residence times in order for them to react to a final stiffened stage. Alternatively, while it is possible for them to be reacted quickly under relatively low ambient temperature conditions, to do so requires the use of catalysts, making them expensive to use, difficult to handle, the latter leading to erratic results.

Thermoplastic resins on the whole appear to be more attractive materials on which to rely in providing shoe stiffeners capable of performing in the suggested process. However, to arrive at a shoe stiffener which relies on a thermoplastic resin and which is capable of operating within the process limitations set forth above to exhibit in final stiffened form the properties of stiffness and resiliency with flexibility, is itself an extremely difficult task, and, past efforts to do so have been less than successful. Many otherwise suitable thermoplastic materials have thermoforming temperatures which are too high, or above the 180° F. indicated above as critical.

Another major reason for the difficulty surrounding the use of thermoplastic material arises from the fact that many when used alone, or with backing such as textile fabric or the like, evidence unfavorable flow properties; they flow excessively and unevenly at their thermoforming temperature. A shoe stiffener relying upon them, which must be exposed to this temperature in order to convert to a flaccid condition, will as a result exhibit loss of uniformity in thickness with associated loss of strength and stiffening capacity.

Another property which if shown by a shoe stiffener results in an improved final shoe construction, is the capacity to effect permanent unitization of the various shoe components. Taking a counter as an example, this property is shown in a counter which in addition to acting as a back part stiffener serves to unitize the shoe quarter to the quarter lining and the insole through to the lasting margin of the upper each through the agency of the stiffener. This property is made even more attractive if the unitization is capable of being effected coincidental with lasting, because of the improved production rate which may be obtained. Obtaining unitization of this nature in shoe stiffeners constituted of thermoplastic resins, polyethylene, etc. has been and remains a significant problem because of the difficulty in obtaining good adhesion between the thermoplastic material and the shoe parts either directly or through the use of adhesives.

Accordingly, it is an object of this invention to provide a laminate article which can be introduced into a shoe upper assembly prior to lasting and provided in a flaccid state by exposure to temperatures of less than 180° F. and which can then be subjected to a convenient forming operation, to obtain as a result of said operation a shoe stiffener resembling the three dimensional curved configuration of the last and which is resilient and flexible.

Another object of this invention is to provide a laminate article as described above which includes a thermoplastic polymeric material and which nevertheless when subjected to operating temperatures up to 180° F. and formed, results in a shoe stiffener which has essentially the same uniformity of thickness, strength, and stiffening capacity as were originally present in the said article.

Another object of this invention is to provide a laminate article as described above which when placed in a shoe upper assembly, made flaccid at a temperature not exceeding 180° F. and formed under convenient conditions results in a shoe stiffener which serves to unitize components of the shoe upper.

These and other objects of the invention are obtained in a laminate article adapted to be formed into a resilient shoe stiffener of three dimensional curved configuration and unitized with a shoe upper in a forming or lasting operation carried out under convenient temperature and time conditions, the said laminate article comprising sheets of thermoplastic polymeric material coalesced through a flexible open-mesh web interposed between the said sheets and having a coating of thermally active adhesive at the exterior surface of at least one of said sheets, the said sheet having a thermal forming temperature and the said coating having a thermal activating temperature each in the range of 140–180° F.

The sheets of thermoplastic polymeric material, on which the laminate article of the present invention relies, can be made from a synthetic polymeric resin composition which has as a first prerequisite a thermal forming temperature of 140–180° F. The lower thermal forming temperature limit of 140° F. is chosen from the standpoint of its being above the temperature the finished shoe will be exposed to during ordinary wearing, storage, etc. Thermal forming temperature refers to that temperature at which the polymeric material in sheet form, for instance up to 50 mils thick, can be contoured or shaped into a three dimensional curved configuration with the application of nominal pressure, for instance a pressure of 15 p.s.i. Synthetic polymeric materials which have a sharply defined thermal forming point are particularly desirable as facilitating improved production rates. Secondly, the polymeric material must be of such a nature that sheets of thicknesses ranging 2 to 50 mils, made from the same exhibit resiliency and flexibility at ordinary temperatures as differentiating from elasticity as exhibited by elastomeric materials. Then too the polymeric material should be such that it exhibits a minimum amount of flow when it is exposed to its thermoforming temperature, for instance 140–180° F. while nevertheless exhibiting sufficient flow at conveniently obtainable lamination temperatures, 250 to 350° F. in order that in the latter it can flow through the interstices of the web to be used in producing the laminate and facilitate coalescence of the sheets made from it during the said lamination. Thermoplastic materials which are particularly adapted for the present purpose are polyvinyl chloride homopolymers and copolymers of the same as exemplified by copolymers of vinyl chloride and vinyl acetate, the latter component constituting up to 15% in the copolymer as well as copolymers of vinyl chloride and vinylidene chloride, diethyl fumarate, etc. Also admixtures of polyvinyl chloride with other polymeric materials can be used to obtain sheets exhibiting good performance. As an instance, acrylic polymers and copolymers can be included for the purpose of contributing toughness to the resulting sheets. An example of such an admixture is one which contains in addition to the polyvinyl chloride, up to 20 weight percent on total of an acrylic polymer such as a homopolymer of an acrylate or methacrylate, and preferably a methacrylate, containing 1 to 4 carbon atoms in the alcohol residue or moiety of the same. A specific instance of such an acrylic polymer is a homopolymer of methylmethacrylate.

Because the thermoplastic sheets include polyvinyl chloride, it is recommended that a plasticizer compatible with polyvinyl chloride be present in the same. The amount of plasticizer will depend somewhat upon the particular polymeric composition and the plasticizer decided upon, as well as on the temperature and pressure conditions to which the thermoplastic sheets are to be exposed, particularly during lamination. Generally the plasticizers can be used in an amount ranging 10 to 20 weight percent of the polyvinyl chloride present. Illustrative of the plasticizers which can be used are: the halogen substituted hydrocarbons, such as chlorinated diphenyls; alicyclic ketones, such as camphor and pyrononeS; substituted aliphatic ketones, such as benzoyl acetone; alkyl esters of polybasic acids such as dioctyl adipate and dioctyl phthalate, diphenyl phthalate, and tri(paratertiarybutylphenyl) phosphate. Other plasticizers which can be used include: cyclohexyl p-toluene sulfonamide, ethyl o-toluene sulfonamide, ethyl p-toluene sulfonamide, chlorinated diphenyl, triethylene glycol di-2-ethyl butyrate, diglycol sebacate, ethyl o-benzoyl benzoate, diphenyl mono (o-chlorophenyl) phosphate, di(triglycol chlorhydrin) phthalate, di(butoxyethyl) phthalate, tricresyl phosphate, triphenyl phosphate, diphenyl butyl ketone, diphenyl mono (tertiarybutylphenyl) phosphate, diphenyl mono(chlorophenyl) phosphate, tri(p-tertiarybutylphenyl) phosphate, xylyl heptadecyl ketone, as well as mixtures of these and other plasticizers.

The thermoplastic polymeric material sheets can in many instances be made further attractive by the inclusion of other additives in the thermoplastic resin used in them. Particularly recommended are heat, light and oxygen stabilizers, such as the epoxy type stabilizers, hydroquinone, α,α-bis-(2-hydroxy-3,5-dimethylphenyl) butane, barium-cadmium alkylated phenoxide and lead silicate complex salts. Finally additives such as colorants, fillers and the like such as carbon black, iron oxides, clay, barytes, whiting, etc. can also be used.

The thermosplastic sheets can be of any thickness, provided that under convenient laminating procedures they can be coalesced through the open-meshed web which is interposed between them in a lamination process using convenient laminating temperatures and pressures. Sheets ranging 2 to 50 mils in thickness and more particularly 5 to 20 mils in thickness can be used to advantage with the web material which will be described in detail later in this paper.

In the laminate article of the present invention the sheets of thermoplastic polymeric resin are coalesced through a flexible open-meshed web. The web can be formed from fibers, filaments, and the like, which are at least essentially non-elastic in nature in order that upon being subjected to lasting pressure they will not stretch and vary the longitudinal and lateral dimensions of the laminate articles. Fibers and filaments of jute, sisal, cotton, glass metal as well as from various other natural and synthetic material sources, the latter exemplified by rayon, nylon and polyethylene terephthalate and combinations of the preceding fibers and filaments can be used to advantage from which to knit or weave a loose open-meshed web. Again, the web should be knitted or woven in a sufficiently open manner as to allow the web to be shaped into a three dimensional curved configuration during the lasting operation, while, nevertheless being able to at least essentially retain its longitudinal and latitudinal dimensions, under the conditions presented preliminary to and during lasting.

The web should be of sufficiently open-meshed nature to allow portions of the thermoplastic material of the sheets to flow therethrough and bring about coalescence of the sheets during production of the laminate article itself. In this regard, the lamination strength of the laminate article is dependent to a significant extent on the kind and amount of flow which takes place between the sheets of thermoplastic material during lamination of the laminate article. The large number of interstices present in the web, the greater number of sites available for coalescing to take place. Loosely woven textile material, and specifically burlaps and cheesecloth type materials, operate well as webs in providing the laminate articles of the present invention. Burlap materials which are 6 to 12 oz. weight and 2 to 20 mils fiber thickness are particularly well adapted to act as webs when the laminate article is intended for use as counters. In this latter regard it bears mentioning that the thickness of the article will to a large extent be governed by the thickness of the web; lesser thicknesses achieved in the web can lead to more attractive shoe stiffeners from the standpoint of wearer comfort. Then too minimum thicknesses can contribute to improved production rates, in

that the skiving operation, otherwise practiced, and directed to providing a feather edge on the top curved periphery of the laminate article designed to be used as a counter, can be eliminated.

The adhesive which is coated, filmed or otherwise deposited on the surface or surfaces of thermoplastic sheets of the laminate article is also thermoplastic in nature having a thermal activating temperature ranging 140°–180° F. This has an important double bearing on production rate. Initially, it allows for adhesion between the stiffener and the shoe upper parts to be effected during lasting. Secondly because the adhesive is fluid in nature, at this temperature range it is possible for the shoe upper to be moved relative to the stiffener if so desired, during lasting. Movement of this type is desirable in that it allows the operator to eliminate wrinkles, bagging and the like, which more often than not appear in the upper during the lasting or forming operation. To facilitate production of the laminate article itself the adhesive should be capable of being dissolved, suspended or emulsified into various liquid media, or liquidified or dispersed by some other convenient method for application to the surfaces of the thermoplastic sheets. Adhesives which on drying to a coating, present a non-tacky surface at room temperature are the more attractive as allowing for ease of handling, storing, etc.

Included among the adhesives which can be used in practice of the present invention are those which are predominantly a wax with a minor amount of rubbery component, and a minor quantity of a resinous modifier to act for example as a plasticizer.

The wax component can be a micro-crystalline paraffin wax having a melting point in the range of 160° F. to 185° F.; ordinary crystalline paraffin wax having a melting point in the range of 130° F. to 140° F.; also higher fatty acids, for example, stearic acid, oleic acid or hydrogenated fish oil fatty acids. Others are elastomeric film-forming waxy non-oil modified alkyd resins, such as are represented by Neolyn 23 (a tough elastomeric, grease-resistant non-migrating rosin-derived alkyd-type resin having a softening point of about 162° F. by the Hercules drop method and a softening point of 136° F. by the ASTM ring and ball softening point method).

The rubbery component can be chosen from various rubbery polymers of the nature of high molecular weight polyisobutylene, for example, butyl rubber (GR–10), milled natural unvulcanized rubber, and GR–S and GR–N synthetic rubbers. GR–S rubber is a copolymer of butadiene with styrene, and GR–N contains acrylonitrile in addition to butadiene.

The resinous modifier can be made up of a thermoplastic fusible resin, for example, polystyrene latices and resins, polyvinyl chloride homopolymer and copolymer resins, ethylene-vinyl acetate copolymers, and polyterpenes and bituminous resins. Representative resins include polymerized beta-pinene (Piccolyte) bituminous resin from Utah coal (RBH Resin 510L), and modified polystyrene resins.

The wax based adhesive compositions can be prepared for application by solvating in a volatile solvent. They can also be prepared by compounding at a temperature sufficient to allow for complete admixture and fluidity.

In one method for formulating the melted type of the adhesive, it is recommended that the rubbery component and the paraffin wax be mixed together in a mixer, and the resinous modifier be then added to the resultant batch. The mass then obtained is allowed to become melted together in a steam jacketed kettle and mixed until a homogeneous material is obtained.

The solvated type adhesive is formulated by solution of the components in a convenient solvent such as toluene, naphtha, etc. The mixture is simply agitated at room temperature or slightly elevated temperatures up to 140° F. Added refluxing of the solvent can be carried out if desired. When a homogeneous solution is obtained the adhesive composition is cooled to room temperature and can be applied directly to the laminate by dipping, spraying, knife coatings, and like procedures.

The thickness of the adhesive coating finally obtained in the laminate need only be sufficient to insure that as a result of subjecting to lasting pressure while in a fluid state a good adhesive bond is obtained between the laminate article and the various components of the shoe upper. Thicknesses ranging 0.5 to 5.0 mils operate well to obtain desired bonding or unitization.

The following drawings are included for the purpose of illustrating the invention in which:

FIG. 1 is a diagrammatic longitudinal section view showing production of laminate sheets from which laminate articles designed for use as shoe stiffeners can be died out;

FIG. 2 is an exaggerated diagrammatic view of a shoe stiffener in the form of a shoe counter blank having parts partially broken away to show successive laminae of the same.

FIG. 3 is a perspective view of a shoe upper having parts partially broken away to show the presence of a counter formed from the blank of FIG. 2.

Referring to the drawings, and first to FIG. 1, a pair of polymeric thermoplastic sheets **10** and **12**, together with open-mesh web **14** located intermediate of the said sheets are simultaneously reeled off rolls **16** and **18** and **20**, respectively, and directed between idler rolls **22** and **24** and then through heated pressure rolls **26** and **28**. The temperature and pressure under which pressure rolls **22** and **24** operate is sufficient to cause portions of polymeric material located at the facing surfaces of sheets **10** and **12** to flow through the voids or interstices of web **14** and to become coalesced at the interior of the web **14**.

The laminate member, constituting of sheets **10** and **12** coalesced through web **14**, which leaves pressure rolls **26**, **28**, is directed under nozzle **30** from which a spray of solvated thermosensitive adhesive is directed onto the top surface of the same. The laminate member is then introduced into oven **32**, where the solvent is volatilized off leaving an adhesive coating on the then top surface of the said member. A cascade of rollers **34** are provided within oven **32** over which the laminate member is routed for the purpose of inverting it during this drying and/or volatilization step. Because the laminate member exhibits stiffness, rollers **34** are positioned in an arcuate manner to ease turning of the said member and eliminate possibilities of its becoming cracked or checked. Following inverting, deposition of adhesive from spray nozzle **36** onto the second surface of the laminate member is carried out. In instances where the laminate article is designed for use as shoe stiffeners in shoe uppers which are unlined this second spraying operation is eliminated. The laminate member remains in the oven **32** long enough to volatilize the solvent vehicle of the adhesive applied to the second surface. Now coated at both sides with thermoplastic adhesive, the laminate member is drawn through pinch rolls **38** and **40** and leaves oven **32** to be cut into convenient handling lengths by shears **42**.

A laminate article **50** in the form of a shoe stiffener blank, and more specifically a shoe counter blank as shown in FIG. 2, if desired it could be a toe box, is died flat from the laminate member as obtained in FIG. 1. The laminae constituting the laminate article are successively: thermosensitive adhesive surface coating **44**, thermoplastic sheet **10**, web **12**, thermoplastic sheet **14** and thermosensitive adhesive surface coating **46**. If desired a skiving operation can be carried out on the counter blank to provide it with a feather edge around its upper curved periphery. This expedient however, is not shown because the laminate article of this invention can be made of sufficiently thin gauge as not to warrant skiving.

The laminate article of FIG. 2 can be utilized in lasting operations carried out in variety of fashions. In one such lasting operation, to which no illustrations are

specifically directed, the laminate article is positioned in a shoe upper and subjected to heating at a temperature of 140–180° F. until the laminate article becomes flaccid. The shoe upper assembly is then transferred to a lasting machine where the shoe upper is shaped over the last with the immediate result that the laminate article is (a) conformed to the shape of last and (b) becomes unitized with those parts of the assembly which are contacted by the same. On cooling, and while still on the last, the laminate article stiffens to provide a shoe stiffener having a three dimensional curved configuration as shown in FIG. 3.

In FIG. 3 a shoe upper **52**, after being lasted, has its quarter **54** stiffened and unitized to quarter lining **56** through the upright portion of shoe stiffener **50***a*. The lasting margin of quarter **54** which is located to the bottom of said quarter and turned inward thereof, is stiffened and unitized to insole **58** through the agency of bottom horizontal portion **50***b* of the said stiffener. The outsole **60** and heel **62** are attached to upper **52** after lasting to produce a finished shoe and a slip lining **64** is inserted within the said upper **52**.

The following example is included for the purpose of illustrating the invention.

EXAMPLE I

A pair of resilient thermoplastic sheets, each 10 mils in thickness, are sheeted out of thermoplastic resin having the following formulation:

Component:	Amount (p.p.w.)
Vinyl chloride-vinyl acetate copolymer (weight percent amount 88–12 respectively)	200
Acryloid KM227 (homopolymer methacrylate)	40
Dioctyl adipate	20
Harshaw 6V2 (barium-cadmium stabilizer)	5
Paraplex G–62 (epoxy type stabilizer)	10
Plumbosil C (lead-silicate stabilizer)	10

A web of 10 oz./yd.^{2} burlap is interposed between the thermosplastic sheets and the assembly is laminated by subjecting it to pressing at 250 p.s.i. and 350° F. for a period of 5 minutes in a hydraulic press. After cooling for 15 minutes the laminate is removed from the press. Each of the surfaces of the laminate is in turn spray coated with adhesive solution of the following formulation:

Component:	Amount (p.p.w.)
Neolyn 23 (resin derived alkyd type resin)	40
Butadiene acrylonitrile copolymer rubber	20
Vinyl chloride-vinyl acetate copolymer (88–12 weight percent respectively)	20
Butylbenzyl phthalate	20
Naphtha	90
Toluene	90

The coated laminate is hung in a circulating air oven, set at 250° F., for a period of 5 minutes allowing the solvent to evaporate. As a result an adhesive layer 1 mil thick having a melting point of 145° F., is obtained at each surface of the laminate article.

The laminate article has a total thickness on the order of 33 mils and is stiff, tough, and resilient while exhibiting a desired amount of flexibility as reflected by the following test indicia:

Table I

Stiffness/Tinius Olsen (1 x 6 inches sample 20% deflection and 1 lb. load)	46%.
Tensile strength	6140 p.s.i.
Tear strength	1500 p.p.i. thickness.
Flex fatigue (Ross flexer)	20,000 (cracked). 25,000 (broken).
Resilience (percent recovery from 180°) bend around 0.25 inch diameter mandrel (in 60 seconds)	70%.

Flat counter blanks having a thickness 33 ±2 mils over the entire area of any given blank, are died from the laminate article and inserted into ladies flat shoe uppers. The uppers are then exposed to a temperature of 150° F. on a steaming block for 15 seconds until the blanks become flaccid. The uppers are then transferred to a lasting machine, formed to shape, and provided with an outsole and heel. The time for forming is 15 seconds. When removed from the last, each of the shoes is noted to have a heel seat, or back part which is in excellent conformity with the heel configuration of the last. The back part is also stiff with flexibility and resiliency sufficient to insure extended and comfortable wearing. It can be flexed and subjected to deformation pressure exceeding that to which a foot will subject it during extreme wearing, and on removal of the pressure it returns immediately to the original three dimensional curved configuration introduced by the last to the counter and associated shoe upper components. In addition, unitization of the various shoe components in contact with the counter, to wit, quarter, quarter lining, insole and upper margins is observed to have taken place.

When the lining is peeled off the counter of the shoe it is noted that the counter has maintained the uniformity of thickness i.e. 33±2 mils, which it had as a blank when inserted in the assembly prior to lasting. It is also noted that there is no evidence of any delamination between the various lamina of the laminated article, now a shoe stiffener, having taken place. From these observations it can be concluded that with exposure to elevated temperature of the nature of that required to convert it to a flaccid state, and, later lasting, the thermoplastic sheet material has not undergone an undesirable amount of plastic flow.

It will thus be seen that the object set forth above, among those made apparent from the preceding description, are efficiently obtained and, since certain changes may be made in carrying out the above method and in the shoe stiffener article set forth without departing from the scope of the invention, it is intended that all matter contained in the above description including that shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

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

1. A shoe stiffener blank adapted to be formed into a resilient shoe stiffener of three dimensional curved configuration and unitized with a shoe upper in a forming operation, the said blank comprising continuous sheets of thermoplastic polymeric material coalesced through a flexible open-mesh web being interposed by said sheets and having a coating of thermally active adhesive at the exterior surface of at least one of said sheets, the said sheets having a thermal forming temperature and the said coating having a thermal activating temperature each in the range of 140–180° F.

2. A shoe stiffener blank according to claim **1** wherein the thermoplastic polymeric material is an admixture of vinyl chloride polymer and up to 20 weight percent on total polymer weight of an acrylic polymer selected from the class consisting of acrylates and methacrylates the alcohol residue of which contain 1 to 4 carbon atoms.

3. A shoe stiffener blank according to claim **2** wherein the vinyl chloride polymer contains up to 15 weight percent of vinyl acetate in copolymerized form.

4. A shoe stiffener blank according to claim **2** wherein the acrylic polymer is a homopolymer of methyl methacrylate.

5. A shoe stiffener blank according to claim **1** wherein the flexible open-mesh web is a loosely woven textile material.

6. A shoe stiffener blank according to claim **5** wherein

the flexible open mesh web has a fiber thickness of 2 to 20 mils.

References Cited by the Examiner

UNITED STATES PATENTS

2,569,764	10/1951	Jonas	36—68
2,572,184	10/1951	Newton	36—68
2,611,195	9/1952	Brophy et al.	36—68
2,611,726	9/1952	Harrison	36—68 X
2,619,441	11/1952	Levy	36—68 X
2,690,769	10/1954	Brown	161—95 X
2,721,819	10/1955	Munro	154—
2,734,289	2/1956	Heaton et al.	36—68
2,787,570	4/1957	Lott et al.	161—95 X
2,812,570	11/1957	Petersilie et al.	161—95 X

FRANK J. COHEN, *Primary Examiner.*

EDWARD V. BENHAM, *Examiner.*