Oct. 23, 1951 C. G. NEWTON, JR 2,572,184

UNSUPPORTED BOX TOE AND COUNTER MATERIALS

Filed Feb. 24, 1949

Fig. 2

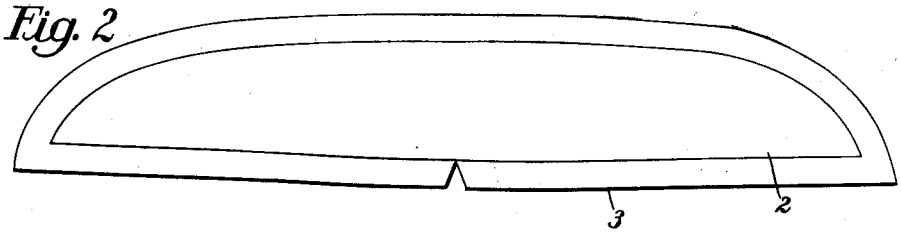


Fig. 1

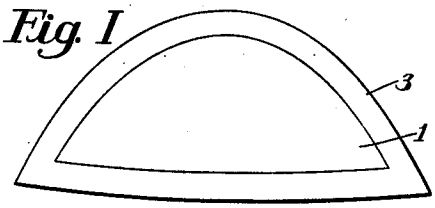


Fig. 4

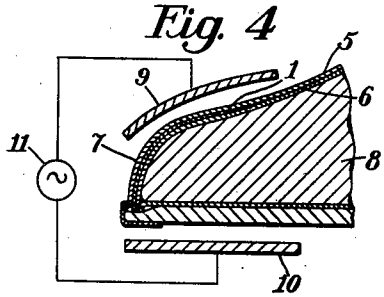


Fig. 3

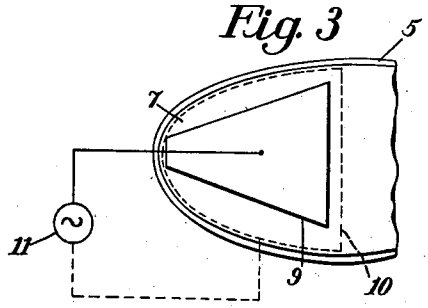


Fig. 6

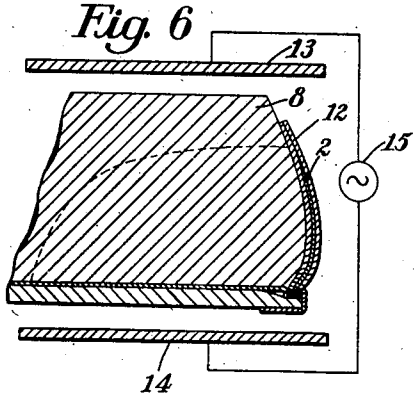
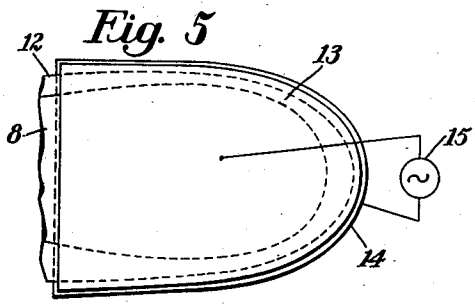


Fig. 5



Inventor

Charles G. Newton, Jr.

By his Attorney

Patented Oct. 23, 1951

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UNITED STATES PATENT OFFICE

2,572,184

UNSUPPORTED BOX TOE AND COUNTER MATERIALS

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Application February 24, 1949, Serial No. 78,148

13 Claims. (Cl. 36—68)

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This invention relates to stiffening selected portions of the uppers of shoes and to a new stiffening material.

It has heretofore been proposed (see the application of John J. Brophy and Charles G. Newton, Jr., Serial No. 714,812, filed December 7, 1946 and now abandoned) to provide a limp and stretchable stiffener blank comprising a thermoplastic resin and a polymerizable compound which, in its untreated state acts as a plasticizer but is capable upon being treated, for example by heat, of converting the whole mass to a non-plastic, non-tacky, less soluble condition wherein it is hard and resilient. Stiffener blanks made in accordance with the teachings of that application have been found to give highly satisfactory stiffening of portions of shoe uppers such as toes and counters, the stiffened portions being strong, resilient and resistant to permaent deformation.

It is a feature of the present invention to provide a new, relatively inexpensive composition comprising a mixture of a thermoplastic resin, relatively long fibrous filler and a polymerizable material which, in its monomeric form, acts as a plasticizer but is capable of being polymerized, for example by heat, to convert the mass to a non-plastic, strong, resilient condition. The composition also includes catalysts.

According to another feature of the invention, the novel, limp, stretchable stiffener blank is incorporated in a selected portion of the upper of a shoe, conformed to a last, and, while it is so held, treated with heat to render it hard and resilient.

These and other features of the invention, including certain details of composition and procedure, will be set forth in the specification in connection with examples of the stiffener blank and method of using it as pointed out in the appended claims.

Reference is made to the patent to John J. Brophy, No. 2,406,738, granted September 3, 1946, which is directed to an apparatus, and to the copending application of John J. Brophy, Serial No. 564,605, filed November 22, 1944, which has materialized into Patent No. 2,492,413, granted December 27, 1949, and the copending application of John J. Brophy and Charles G. Newton, Jr., Serial No. 714,812, filed December 7, 1946, which are directed to blanks and methods for stiffening portions of the uppers of shoes, making use of a high-frequency field.

Referring now to the accompanying drawings,

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Fig. 1 is a plan of a toe stiffener blank according to the present invention;

Fig. 2 is a similar view of a counter stiffener blank;

Fig. 3 is a diagrammatic plan view of an apparatus for subjecting the front portion of the upper of a lasted shoe to the heating effect of a high-frequency field, a shoe being shown in place;

Fig. 4 is a diagrammatic, vertical longitudinal section, taken on the line IV—IV of Fig. 3;

Fig. 5 is a diagrammatic plan view of an apparatus for subjecting the rear portion of the upper of a lasted shoe to the heating effect of a high-frequency field, a shoe being shown in place; and

Fig. 6 is a diagrammatic, vertical longitudinal section, taken on the line VI—VI of Fig. 5.

The stiffener blanks 1 and 2 (see Figs. 1 and 2) of the present invention comprise thin flexible sheets of an intimate mixture comprising a copolymer of styrene with isobutylene, a thermoplastic resin of relatively low molecular weight which may be a coumarone-indene resin or similar inexpensive compatible resin such as the terpene resins or rosin derivatives having a softening point R. B. of from 75° to 125° F., a substantial proportion of relatively long fiber filler and a polymerizable material which, in unpolymerized state, serves to soften and plasticize the composition, and which is polymerizable, for example by heat, to a stiff condition which hardens the entire composition. Also, the composition includes a catalyst for the polymerizable material.

I have found that when these components are assembled within certain ranges of proportions there is obtained an inexpensive material which is soft and limp at normal atmospheric temperatures and which will retain its softness and limpness for extended periods. It appears that the fiber, when dispersed throughout the composition, in some way reduces the tendency of the polymerizable material to undergo polymerization. The mode of its functioning is not understood but it has been found that compositions containing the fiber will remain soft and limp for at least 50% longer than compositions not containing this type of fiber. Also the fiber appears to improve the ability of the composition to be activated by high-frequency treatment.

The copolymer of styrene with isobutylene employed in the composition of the present invention may comprise from 40 to 80% of styrene. High molecular weight copolymers are preferred,

and the materials known as polymer S50 and polymer S60, obtained from the Enjay company, which comprise, respectively 50% and 60% of styrene with from 50% to 40% of isobutylene, have been found very satisfactory.

With the copolymer materials, there will be employed from 25 to 100 parts of a light colored compatible thermoplastic hydrocarbon resin or certain rosin derivatives. Resins for use in the present composition will have color not exceeding "8" as determined by comparison with the colorimetric standard solutions of the manufacturers, e. g., of the Barrett Division of Allied Chemical and Dye Corporation or of the Neville Co. Preferred resins are the light colored coumarone-indene resins since these resins cooperate with the other components of the mixture to give a stiffener having excellent mechanical properties. For some reason which has not as yet been determined, the darker colored resins interfere, to a limited extent, with the rapid polymerization of the polymerizable component. Other light colored resins which have been found acceptable are the terpene resins known as Piccolite S115 and S85, and Piccolastic having a melting point of 100° F. or better. Rosin derivatives which can be used include a 50% hydrogenated rosin product known as Stabelite, a dimer of rosin known as Poly Pale resin and esters of these resins.

Fillers which have been employed in the composition include cellulosic fibers including a wood cellulose fiber, known as alpha flock, and cotton linters, and other relatively long fibrous materials such as asbestos. To obtain the advantages of the present invention, the average length of the fibers should be at least 40 microns. Fibers as long as six inches may be used. Materials in which the fibers have been broken up or shortened, such as wood flour, have not been found satisfactory in the present composition. With 100 parts by weight of the styrene isobutylene copolymer there are employed from 25 parts to 300 parts by weight of the fibrous material.

The polymerizable ingredient of the composition, which is convertible to a condition in which the entire mixture stiffens to a strong resilient condition, is preferably a compound having a relatively low vapor pressure. Such a compound in unpolymerized state is compatible with and softens the mixture so that it can be readily mixed and sheeted, but may be polymerized or hardened by the action of heat, light, or other treatments. From about 15 parts to about 100 parts of this polymerizable ingredient will be employed in combination with 100 parts of the copolymer of styrene and isobutylene. Suitable compounds are those containing the polymerizable group $=C=CH_2$ and at least one other polymerizable olefinic group separated therefrom by at least one intervening atom so that the double bonds do not form a conjugated system. Polymerizable constituents which have been found highly satisfactory for use in combination with the styrene isobutylene polymer and resin include the liquid dimethacrylic acid esters of polyethylene glycols. A particularly suitable polymerizable constituent is polyethylene glycol 200 dimethacrylate, which is a mixture of monomeric esters which may be prepared by the esterification of methacrylic acid with polyethylene glycol 200, which is a mixture of various glycols, said mixture having an average molecular weight of 200±15. This is a material obtained from Carbide and Carbon Chemicals Corporation under this name and is described by them in their chart of "Useful Data on Important Organic Chemicals" (copyright 1946), at page 5, under "Polyethylene Glycols," as having the chemical formula $HO(C_2H_2O)xH$, a specific gravity at 20/20° C. of 1½, an approximate flash point of 350° F., and an infinite solubility in water. A distillation analysis of this material gave the following results:

Weight Percent	Material	Molecular Weight
2.78	Monoethylene glycol	62
5.6	Diethylene glycol	106
18.47	Triethylene glycol	150
18.1	Tetraethylene glycol	194
12.25	Pentaethylene glycol	238
4.6	Pexaethylene glycol	282

The distillation anlysis was stopped with 36.5% higher boiling glycols left in the residue. The average molecular weight of the analyzed material was 205.5.

Other available polymerizable ingredients are diallyl phthalate, diallyl maleate, tetraethylene glycol dimethacrylate, pentaethylene glycol dimethacrylate and divinyl benzene. Mixtures of two or more polymerizable compounds are as suitable for use as the polymerizable ingredient in this invention as is a single compound.

As hardening catalysts where heat is used to harden the compound, organic peroxides such as benzoyl peroxide, or di-t-butyl peroxide in amount from about 0.4% to about 2.5% by weight of the hardenable plasticizer have been found suitable. Other catalysts may be used where other hardening treatments are used.

The composition for use in stiffening portions of the uppers of shoes may be formed into a sheet of from about 0.020 to about 0.040 inch in thickness, for women's box toe stiffeners, and from about 0.045 to about 0.120 inch in thickness for men's box toes.

The sheet material is limp and stretchable so that it can be made to conform to the shape of portions of a shoe having complicated three-dimensional curves therein.

For stiffening toes and counters of shoe uppers, limp stretchable stiffener blanks, for example, a toe stiffener blank 1 (Fig. 1), and a counter stiffener blank 2 (Fig. 2), are cut from the sheeted material. If desired, the edges of these blanks may be skived to provide tapering edges 3 for the stiffener. These blanks may be incorporated in the upper of a shoe at any suitable stage in the manufacture of the shoe. Conveniently, the blanks may be incorporated in and become part of the upper during the assembling of parts of the upper in the stitching room. It has been found that a stiffener blank may be adhered to a portion of the shoe upper 5, for example, a tip doubler 6 or the tip or toe portion 7, by applying an adhesive, e. g., a 20% solution of "Acryloid B-7," an acrylic resin made by Resinous Products and Chemical Corporation, of Philadelphia, Pa., dissolved in ethylene dichloride, to the stiffener blank and portion of the shoe upper.

Where complete freedom to stretch is not necessary, the stiffener material may be calendered on cloth or other fabric including felt, and this material used for stiffening toes and counters.

According to another method, the blanks 1 and 2 may be positioned on the proper portions of the upper 5 of a shoe and may be bonded thereto by applying a controlled heat and pressure at selected points on the stiffeners and shoe portions to effect a bond without causing the stiffener

blanks to be converted to their final, stiff, resilient condition. If desired, a tapering edge or scarf 3 may be formed along any desired edges, for example, along the edge of a toe stiffener blank 1 remote from the toe of the shoe by heating and pressing the edge between platens shaped to provide the desired taper. Heating and pressing to effect bonding and/or tapering may be effected between electrodes connected to a high-frequency power source.

With the stiffener blanks 1 and 2 in position, the upper 5 may then go through the regular shoe manufacturing operations, including being mounted upon and conformed to a last 8. The shoe upper 5 may be subjected to heat or to other treatment to harden the blanks at any time after the lasting has been completed while the portions of the shoe upper to be stiffened are maintained in the desired shape by the last.

Apparatus for high-frequency heating of the assembled shoe upper 5 is shown diagrammatically in Figs. 3 to 6. Figs. 3 and 4 illustrate the toe portion 7 of a lasted shoe upper 5 disposed between and in spaced relation to an upper electrode 9 and a lower electrode 10, the electrodes 9 and 10 being connected to a high-frequency source of power 11. As shown in Figs. 3 and 4, the electrode 9 disposed adjacent the top of the toe portion 7 may be curved to correspond generally with the curvature of the lasted toe; while the electrode 10 adjacent the bottom of the toe portion may be flat. The electrode 9 adjacent the top and the electrode 10 adjacent the bottom of the lasted toe have such dimensions in relation to the size and shape of the lasted toe as to insure a substantially uniform heating effect in the stiffener blank 1 in the lasted toe.

Figs. 5 and 6 show the counter portion 12 of a lasted shoe upper 5 disposed between an upper electrode 13 and a lower electrode 14, the electrodes being connected to a high-frequency power source 15. The upper and lower electrodes 13 and 14 are shaped to provide a substantially uniform heating effect throughout the stiffener blank 2.

To produce the desired heating in order to convert the stiffener blank to its hardened condition, it has been found that a heating period of the order of about 10 seconds may be effective where the frequency of the field is from about 75 to about 250 megacycles or higher and the voltage is from about 3 to about 4 kilovolts. Lower frequencies and lower voltages may be employed but they have been found to be less efficient and less satisfactory, generally, than the values noted above.

The following examples of compositions from which the new stiffener blanks may be cut are given as illustrative only, to aid in understanding the invention. It is to be understood that the invention is not limited to the constituents or proportions of the compositions of the examples.

Example I

	Parts by weight
Coumarone-indene resin (Neville R15)	75
Styrene isobutylene copolymer containing 50% styrene (S50 polymer resin)	100
Cellulosic fiber—cotton linters	100
Polyethylene glycol 200 dimethacrylate	60
Benzoyl peroxide	1.3

The mixture of the above ingredients, after milling and mixing on rolls, was sheeted to a thickness of .035 to .040 inch and toe stiffener blanks were cut from the milled mixture. These stiffener blanks were disposed between the liner and the doubler of a shoe and the shoe was subjected to lasting. The lasted shoes with the stiffener blanks therein were placed in operative relationship to the electrodes, as shown in Figs. 3 and 4, and were subjected for a period of 12 seconds to the heating action of a field created by applying two kilovolts at a frequency of 130 megacycles to the electrodes. Power was cut off from the electrodes and the lasted shoes were permitted to cool. When the lasts were removed after cooling of the shoes, it was found that the toes were stiff and strong and resiliently resistant to deformation.

Example II

	Parts by weight
Styrene isobutylene copolymer containing 60% styrene (S–60 polymer resin)	100
Rosin dimer (Polypale resin)	25
Wood cellulose fiber (alpha flock)	125
Polyethylene glycol 200 dimethacrylate	20
Benzoyl peroxide	0.3

The mixture of the above ingredients was milled on mixing rolls and was sheeted to a thickness of 0.035 to 0.040 inch. The resultant flexible sheet was cut to form a toe stiffener blank. The stiffener blank was disposed between the liner and the doubler of a shoe and the shoe was shaped on a last. The shoe, while held in shaped relation to the last was subjected for a period of 14 seconds to the heating action of a high-frequency electric field established between an electrode system similar to that shown in Figs. 3 and 4. A voltage of two kilovolts and a frequency of 130 megacycles was employed at the electrodes. The shoe was permitted to cool, the last was removed from the shoe, and the resultant toe was stiff and strong and resiliently resistant to deformation.

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

1. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% of styrene, from 25 to 300 parts by weight of fibers having a length of at least 40 microns and from 15 to 100 parts by weight of a polymerizable ingredient which contains the polymerizable group $=C=CH_2$ and at least one other polymerizable olefinic group separated therefrom by at least one intervening atom so that the double bonds do not form a conjugated system.

2. As an article of manufacture, a limp, stretchable stiffner blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% styrene, 25 to 100 parts by weight of a compatible light colored thermoplastic resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulosic fibers having a length of at least 40 microns and from 15 to 100 parts by weight of a polymerizable ingredient which contains the polymerizable group $=C=CH_2$ and at

least one other polymerizable olefinic group separated therefrom by at least one intervening atom so that the double bonds do not form a conjugated system.

3. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% of styrene, from 25 to 100 parts of a light colored coumarone-indene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulosic fibers having a length of at least 40 microns and from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate.

4. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% of styrene, from 25 to 100 parts of a light colored rosin derivative having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulosic fibers having a length of at least 40 microns and from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate.

5. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% of styrene, from 25 to 100 parts of a light colored terpene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulosic fibers having a length of at least 40 microns and from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate.

6. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, 25 to 100 parts by weight of a light colored coumarone-indene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of wood cellulose fibers having a length of at least 40 microns, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4% to 2.5% of a polymerization catalyst.

7. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, 25 to 100 parts by weight of a light colored coumarone-indene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cotton linters, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4% to 2.5% of a polymerization catalyst.

8. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, from 25 to 100 parts by weight of a light colored rosin dimer having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of wood cellulose fibers having a length of at least 40 microns, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4 to 2.5% by weight of a polymerization catalyst.

9. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, from 25 to 100 parts by weight of a light colored rosin dimer having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cotton linters, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4 to 2.5% by weight of a polymerization catalyst.

10. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, from 25 to 100 parts by weight of a light colored terpene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of wood cellulose fibers having a length of at least 40 microns, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4 to 2.5% of a polymerization catalyst.

11. As an article of manufacture, a limp, stretchable stiffener blank adapted to be incorporated in an end portion of the upper of a shoe and to be conformed to a last, said blank comprising a thin, flexible sheet having an outline shaped to correspond to the shape of said end portion, said sheet being composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, from 25 to 100 parts by weight of a light colored terpene resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cotton linters, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4 to 2.5% of a polymerization catalyst.

12. In a method of producing a stiffening portion in a shoe the steps comprising incorporating in a selected portion of the upper a stiffener blank comprising a thin flexible sheet composed of an intimate mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 40% to 80% styrene, 25 to 100 parts by weight of a compatible light colored thermoplas-

tic resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulosic fibers having a length of at least 40 microns and from 15 to 100 parts by weight of a polymerizable ingredient which contains the polymerizable group $=C=CH_2$, and at least one other polymerizable olefinic group separated therefrom by at least one intervening atom so that the double bonds do not form a conjugated system, conforming the upper to a last, and thereafter, while holding the upper so conformed, subjecting the selected portion to heat to fuse the mixture and bond the mixture to the upper, and continuing the heat to convert the polymerizable ingredient to a condition in which it hardens the mixture to a stiff-resilient condition capable of retaining the upper in its lasted form when the last is removed.

13. In a method of producing a stiffening portion in a shoe, the steps comprising incorporating in a selected portion of the upper a stiffener blank comprising a thin flexible sheet composed of a milled mixture of 100 parts by weight of a copolymer of styrene and isobutylene containing from 50 to 60% styrene, 25 to 100 parts by weight of a light colored thermoplastic resin having a melting point of from 75° to 250° F., from 25 to 300 parts by weight of cellulose fibers having a length of at least 40 microns, from 15 to 100 parts by weight of polyethylene glycol 200 dimethacrylate and from 0.4 to 2.5% of a polymerization catalyst, conforming the upper to a last, and thereafter, while holding the upper so conformed, subjecting the selected portion to the heating effect of a high-frequency electric field to fuse the milled mixture and bond it to the upper and to convert the polyethylene glycol 200 dimethacrylate to a condition in which it hardens the mixture to a stiff resilient condition capable of retaining the upper in lasted shape when the last is removed.

CHARLES G. NEWTON, JR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,155,590	Garvey	Apr. 25, 1939
2,274,749	Smyers	Mar. 3, 1942
2,406,738	Brophy	Sept. 3, 1946
2,418,978	Mertens	Apr. 15, 1947
2,468,094	Marks	Apr. 26, 1949
2,468,534	Young	Apr. 26, 1949