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SHOE STIFFENER AND METHOD OF MAKING SAME

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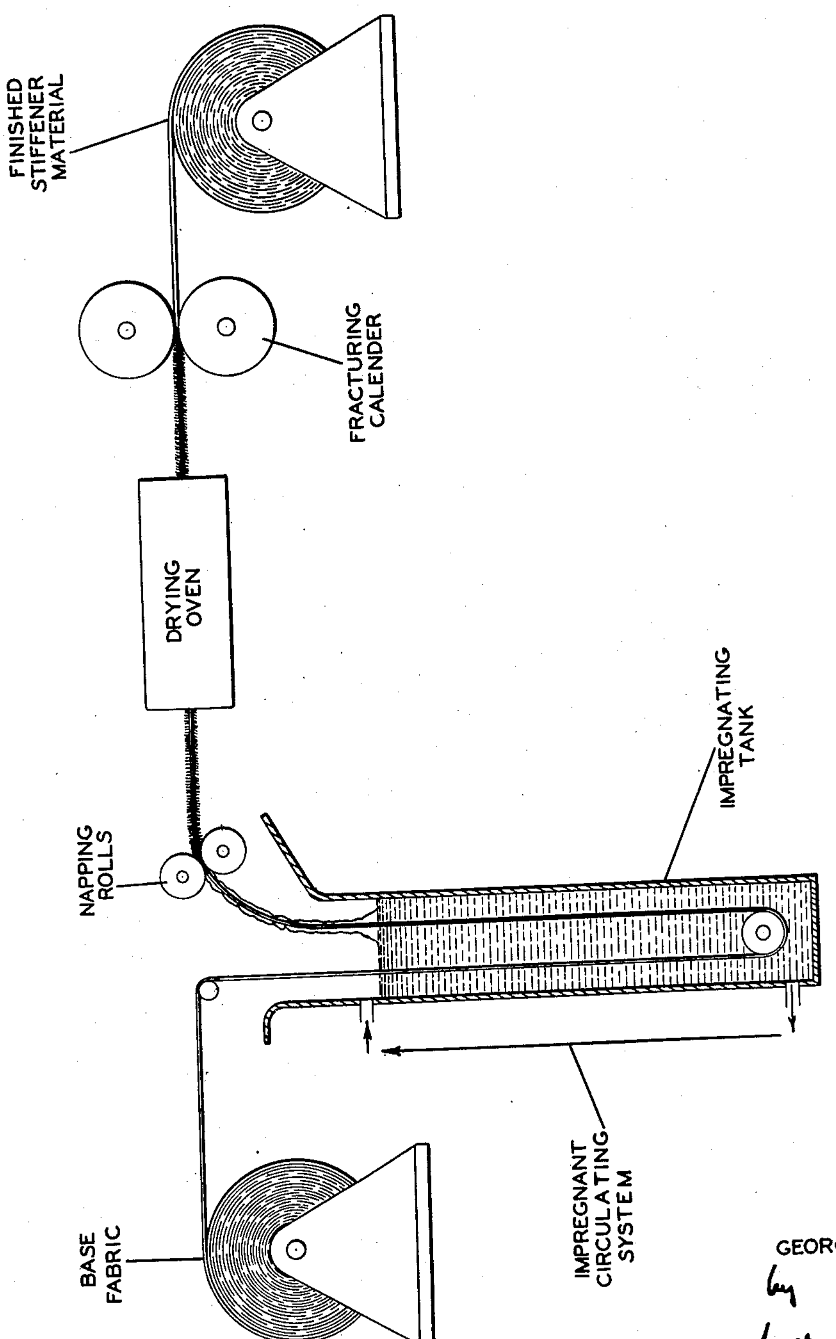

Inventor
GEORGE E. EHLE
by
Walter & Kaufman
Attorney

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SHOE STIFFENER AND METHOD OF MAKING SAME

George E. Ehle, Lancaster Township, Lancaster County, Pa., assignor to Armstrong Cork Company, Lancaster, Pa., a corporation of Pennsylvania

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This invention relates to a shoe stiffener and method of making the same and is concerned particularly with water-soluble resin impregnated stiffeners such as those fabricated with a water-soluble aminoplast impregnant.

It has been proposed in Almy Patent 2,277,941 to form a shoe stiffener by saturating a fibrous web such as double napped cotton flannel with a mixture of urea-formaldehyde resin and rubber latex carrying a porous filler such as diatomaceous earth. The saturated web is dried and then cut into stiffener blanks such as box toes. The urea-formaldehyde resin is in a low stage of condensation and is water-soluble. The resin is stabilized and is capable of being activated (converted to a hard, water-insoluble condition) upon treatment with phosphoric acid or ammonium phosphate. Shoe stiffeners of this type are supplied to the shoe manufacturer as cut blanks in a dry, stiff condition and are immersed in an activating solution at the shoe factory immediately prior to the insertion of the stiffener into the shoe. The solution renders the blank soft and flaccid so that proper lasting may be effected, and, since the solution contains an activator, the blank is rendered hard and water-insoluble upon drying and setting.

It is desirable in shoe manufacture to use a stiffener which may be made soft and lastable in a relatively short period of time. Generally, the stiffener is dipped into the softening solution and is then withdrawn and permitted to "mull" to thus effect the desired softening of the blank for proper lasting in the shoe. With the urea-formaldehyde type of stiffener, using a diatomaceous earth filler, mulling requires in the order of 30 seconds to two minutes. The use of a diatomaceous earth filler in water-soluble resin impregnated stiffeners has a desirable effect upon the rate of mulling, for the diatomaceous earth is naturally porous and thus aids in getting moisture within the blank and in contact with the resin, but the quantity of diatomaceous earth which can be incorporated is limited because of the shape and character of the particles; they have a great tendency to filter out on impregnation of the fabric foundation and thus do not properly penetrate throughout the thickness thereof. Another objectionable characteristic of the diatomaceous earth is its siliceous nature; it is extremely hard and tends to rapidly dull the knives employed in the skiving of the stiffener blanks.

Another problem involved in the use of water-soluble resin impregnated stiffeners is the sus-

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ceptibility of the stiffener to change upon the absorption of moisture. The material has a tendency to absorb moisture from the atmosphere, particularly during warm, humid, summer days, and, since the sheet material must, in most instances, be skived subsequent to dieing out into the appropriate shape, the absorption of water by the blank renders it sticky or tacky and very difficult to skive.

There is also the problem of dehydration of the impregnant in the stiffener material under low humidity conditions, as in the winter months, and this results in a reduction in solubility, lengthening the time for softening.

A further problem is encountered with the water-soluble resin impregnants heretofore used and this is the tendency for filler particles to settle out in the impregnant, thus making it difficult to secure a uniform impregnation of the base or foundation fabric for the stiffener, with the filler particles properly dispersed throughout the mixture.

Urea-formaldehyde resin saturants previously suggested possess substantially no natural porosity as finally dried, and softening is effected practically entirely by the solvent action of the water in the activator upon the thin films of urea resin which surround the fibers and are disposed therebetween; this requires a substantial mulling period prior to lasting.

An object of my invention is to provide a water-soluble resin impregnated shoe stiffener which may be softened and rendered flaccid substantially instantaneously upon immersion in a water solution of an activator for the resin, requiring no "mulling."

Another object of my invention is to provide a water-soluble resin impregnated shoe stiffener which is resistant to the deleterious action induced by the absorption of moisture from the atmosphere, and which will not excessively dehydrate under low humidity conditions.

A further object of my invention is to provide a water-soluble resin impregnated shoe stiffener in which the resin is in a porous condition to facilitate softening.

An additional object of my invention is to provide a method of making shoe stiffener material which will be extremely porous, the porosity at least in part resulting from fracture of the impregnating resin after deposition and drying on the fibers of the supporting base of the stiffener.

In order to attain the foregoing objects, the impregnant is rendered porous so that, instead of the water of the activating solution working on continuous films of resin on the fibers of the base fabric, it will act on discontinuous films which may be quickly penetrated throughout their extent. This porosity is preferably achieved by incorporating an agent into the resin solution which will cause it to dry as a discontinuous, porous film.

Preferably, the material is also "opened" mechanically, and this may be accomplished by napping the fabric while wetted with the impregnant and subsequently drying the fabric in distended condition. The agent employed for forming a discontinuous film may also serve the additional function of imparting a high apparent viscosity to the impregnating solution to facilitate the napping operation.

A further increase in the speed of softening may be accomplished and thus the objects of the invention attained by mechanically fracturing the dried resin on the fibers, and this is facilitated, of course, by the napping of the resin impregnated fabric and drying in distended condition. This fracturing may be accomplished by passing the napped and dried resin impregnated fabric through a pair of relatively closely set calender rolls.

By rendering the resin impregnant porous, by mechanically opening the fibrous structure, and by fracturing the resin, the speed of softening is so increased that naturally porous fillers such as diatomaceous earth may be dispensed with, but, more important, this combination also renders it feasible to incorporate large quantities of finely divided fillers which, when disposed througout the fabric, serve both to render the stiffener resistant to deleterious action from moisture absorbed from the atmosphere or lost to the atmosphere and to further enhance the speed of softening by increasing the surface area of the dried, porous resin available for contact with the water of the activating solution, eliminating the necessity for "mulling."

In order that the invention may be readily understood, a preferred embodiment thereof will be described in conjunction with the attached drawing in which the single view is a diagrammatic illustration of equipment useful in carrying out my process to which appropriate descriptive designations of the various parts have been applied.

In my preferred practice, I prepare an impregnating bath by mixing together the following ingredients in the proportions given, all parts being by weight:

150 urea-formaldehyde syrup (70% solids-water-soluble resin)	60% solids
80 water	
4 dispersing agent	
100 ground screened talc	
10 wetting agent (30% solution in water)	
25 latex (polychloroprene-50% solids)	
10 thickener (15% solution in water)	
5 glycerine	

In the above example, the urea-formaldehyde resin constitutes the base for the saturant or impregnant, and it is diluted with water to the desired solids content, is stabilized in its water-soluble, partially condensed condition, and is capable of being rendered insoluble or set upon activation with phosphoric acid, for example. The urea-formaldehyde resin of the Almy patent will serve very well in the practice of my invention.

While I prefer to use a urea-formaldehyde resin, other water-soluble aminoplast resins of a similar nature may be employed such as the thiourea aldehyde resin, urea aldehyde derivative type of resin, melamine aldehyde resin, or mixtures thereof. The urea-formaldehyde resin disclosed in Almy Patent 2,277,941 may be used with excellent results and is preferred.

A dispersing agent is included in the mixture to aid in the proper distribution of the various components of the mixture, particularly the filler. Any of the well-known dispersing agents may be used, although I prefer to use the alkyl aryl sulfonate type.

The ground screened talc is a relatively soft filler material and is preferably of a fineness of 300 mesh, U. S. standard, or finer.

In place of the talcs, other acid resistant fillers such as micas, clays, or other inorganic materials of a similar nature may be substituted. Organic fillers such as walnut shell flour or insolubilized starch may also be used. These are all acid resistant fillers in the sense that they are substantially inert toward the acid used in the conditioning solution such as a water solution of ammonium phosphate. The quantity of filler employed will vary but will generally be in the range between 80% and 120% based upon the dry weight of the resin of the impregnant, 100% being preferred.

The wetting agent is employed to facilitate the impregnation of the resin solution into the base fabric. I prefer to use one of the proprietary wetting agents of which many are currently available.

The latex serves a dual function; primarily, it adds adhesiveness to the impregnating mixture so that proper and effective bonding of the stiffener to the shoe parts may be obtained; and, incidentally, it serves as a plasticizer for the resin. I prefer to use a latex such as polychloroprene (neoprene).

In some stiffeners, the rubber latex may be eliminated, but, for most purposes, the incorporation of this material is desirable. In place of polychloroprene, other synthetic rubber latexes may be employed or natural rubber latex may be used. Synthetic resin plasticizers and adhesives may also be incorporated either alone or in substitution for a part of the natural or synthetic rubber latex. Preferably, the plasticizer is incorporated in an amount equal to about 10% to 20% of the weight of the resin.

The thickener is preferably sodium polyacrylate, and it serves to increase what is generally termed the apparent viscosity of the impregnating composition for the purpose of facilitating the napping operation and rendering the dried impregnant porous, both of which will be more fully hereinafter described, while at the same time avoiding any substantial increase in the solids content of the impregnating solution. It also serves to maintain the filler particles in proper suspension in the impregnant, avoiding settling and segregation.

In place of the sodium polyacrylate, other thickeners such as carboxymethylcellulose, derivatives of polyacrylic acids, bentonite, silica gel, gum arabic, or gum tragacanth may be employed. These are all gel type thickeners which are inert toward the other impregnating ingredients, particularly the resin constituent thereof.

The small quantity of glycerine employed serves to maintain a small but effective quantity of moisture in the finished material, particularly in winter weather when low humidities are encountered. Other humectants may be substituted for the glycerine.

In order to secure the desired physical characteristics and qualities in the lasted stiffener such as hardness, waterproofness, resilience, etc., and the optimum porosity and other qualities of the stiffener blank, the base fabric should preferably carry and have impregnated into it between 200% and 300% impregnant, based upon the dry weight of the base fabric and the dry weight of the impregnant. In the specific example given above where the base fabric is a cotton flannel weighing ½ pound per square yard, the dry weight of the impregnant in and on the fabric should be between 1 and 1½ pounds per square yard. The range for optimum results is narrower and falls within 230% to 250% of the base fabric weight. It is difficult to consistently get into the web with a continuous impregnation process quantities substantially above 250% to 300% of the fabric weight, and, below 200%, the quantity of impregnant is insufficient for general stiffener uses.

The porosity of the dried impregnant depends to a considerable measure upon the solids content of the impregnating bath. The solids content should be in the neighborhood of 55% to 65%, and, for optimum results, should be about 60%. If the solids content is higher than 65%, the binder tends to coalesce on the fibers of the base fabric, and the desired porosity is not obtained. If less than 55% of solids are present, it is difficult to obtain the desired percentage of impregnant in the finished product as discussed above. By the present invention, it is possible to have a relatively low solids content impregnant and obtain the necessary porosity and distension of the fibers in the napping operation by the use of a thickening agent which is of a thixotropic nature. While the term "thixotropic" is used in the specification to indicate an increase in the fluidity of the impregnant upon the application of shearing forces, I do not wish to be limited to the particular theory which thixotropy involves. From actual work, however, it has been learned that the impregnant becomes more fluid upon working by the circulating pump diagrammatically shown in the drawing and that the impregnant becomes thicker as the fabric with the impregnant carried on it leaves the impregnating bath and also apparently increases in thickness upon entrance of the impregnated fabric into the drying oven and upon the application of heat thereto. This may also be termed a desirable "consistency" and may be said to be determined at least in part by thixotropy, viscous flow, apparent viscosity, etc.

In order to obtain proper distension of the fibers during the napping operation using the equipment referred to above and diagrammatically illustrated in the drawing, the saturant should have a relatively high apparent viscosity. It is not possible to accurately determine the apparent viscosity of materials such as the impregnant given above, for, as pointed out, it is of a thixotropic nature, and the viscosity changes as the impregnant is subjected to hearing forces, as are necessary in viscosity determinations.

The quantity of thickener employed will depend to some extent at least upon the type of thickener, the nature of the saturating resin solution, the kind of base fabric employed, the quantity of plasticizer employed, and other variable factors. Generally, when 1% to 5% of thickener (dry weight) is incorporated, based upon the dry

weight of the resin in the mixture, the desired apparent viscosity will be obtained. Such quantities of thickener have no deleterious action on the final stiffener. The water resistance of the finished product is not materially changed, and the resistance of the material to the absorption of moisture from the atmosphere is not adversely affected. The thickener does have the very salutary effect, however, of providing a porous body of impregnant on the fibers. Instead of having a continuous film over each of the individual fibers, the film is discontinuous and porous, the pores being of very small size. Such porosity is not achieved in the absence of the thickener. The thickeners referred to exert their effects through physical action and have no chemical reaction with the resin or other constituents of the saturating solution.

By providing a porous binder for the base fabric, the incorporation of large quantities of filler is made possible. The use of such quantities serves a dual function. In the first place, the fillers render the product more resistant to change upon the imbibition of moisture from the atmosphere. Stiffener blanks made in accordance with this invention may be readily cut and skived even under relatively high humidity conditions encountered in the summer months in many shoe manufacturing areas. Even more important, however, is the action of the filler as a distender rendering the films of saturant more absorbent upon contact with water, due to the enormous increase in surface area for contact with moisture.

In the manufacture of the stiffening material, the impregnant is first prepared by mixing the ingredients given above to form a composition in which the various ingredients are properly mixed and the filler particles are properly dispersed and suspended. This impregnant is deposited in a tank, as shown in the drawing, and a web of base fabric which is preferably a double napped cotton flannel or sheeting weighing approximately ½ pound per square yard is fed from a roll into and through the impregnating tank. The speed of movement of the material through the tank is such that the flannel is substantially completely impregnated. As the web is withdrawn from the impregnating bath, it is contacted on its opposite flat faces by a pair of smooth steel rolls which may be chromium plated. Both of these rolls travel at substantially the same rate of speed and are disposed about 18 inches above the level of the bath of impregnant. As the material is withdrawn from the impregnating bath, the appearance of the sheet changes slightly, indicating that during this interval a portion of the water in the saturant is imbibed by the fibrous base fabric and the thickening agent is effective for causing a substantial increase in the apparent viscosity of the impregnating solution which is carried by the base fabric, evidenced by a change in the physical appearance of the surface of the web as it moves from the impregnating solution to the rolls. As the material passes between the rolls, a substantial quantity of the impregnating solution is expressed from the base fabric and the fibers in the flannel are fluffed up on opposite sides of the sheet, and, due to the apparent viscosity of the impregnant, the napped fibers remain in distended position. I believe that the impregnating solution has some measure of tackiness which causes it to adhere to the smooth napping rolls, and this tends to distend the fibers generally normal to the plane of the fabric as the fabric is moved between the rolls.

The impregnant with the thickening agent as given in the illustrative example above is thixotropic in character and exhibits a substantial fluidity when subjected to shearing forces. In the drawing, such working is diagrammatically illustrated by the circulating system for the impregnant. This is preferably a continuously operating pump. The reduction in apparent viscosity by such shearing action renders the impregnant sufficiently fluid to permit the controlled impregnation of the cotton flannel. There is, however, a sharp increase in body or apparent viscosity as soon as the impregnant is "at rest," evidenced by the change in appearance mentioned above, and a marked change in physical appearance is noted in the drier to which the material is delivered from the napping rolls.

With a double napped flannel of the type recited above, I have obtained excellent results with the napping rolls spaced apart about .045 inch. As the material leaves the napping rolls, the fibers are distended so that the napped fabric as it emerges from the rolls has a total thickness of about .135 inch, substantially three times the normal distance between the napping rolls.

Subsequent to napping, the sheet is fed into a drying oven or chamber which is effective for removing the water from the web. Care must be exercised in the drying operation in order to avoid premature activation of the urea-formaldehyde resin. This type of water-soluble impregnant is capable of being insolubilized by the application of heat. With the impregnating solution of the above example, drying may be accomplished in about 10 minutes in a drying oven heated to a temperature of about 240° F. This will render the sheet substantially dry in the sense that it will not contain more than about 2% of moisture. The sheet could be rendered bone dry if the drying were carefully accomplished, but, since there is no substantial advantage in so doing, I prefer to permit between 1% and 5% of moisture to remain in the sheet and thus avoid the problem of premature activation of the resin which might result from attempts to reach a bone dry condition.

Upon drying, the stiffener material is found to be relatively hard and stiff with the napped fibers remaining in a distended condition. The dried residue of the impregnating solution is microporous, and the filler particles are distributed substantially uniformly throughout the total extent of the thickness of the web, there being substantially no tendency for the fine filler particles to be filtered out during the impregnating step. The relatively large quantity of filler particles materially increases the surface area of the resin impregnating material and thus there are enormous exposed areas for contact with the activating solution to rapidly effect softening. The presence of the thickening agent in the impregnant and the presence of substantial quantities of water combine to render the impregnant porous, and this facilitates the rapid penetration of the activating solution throughout the extent of the stiffener, enhancing softening.

Improved softening can be obtained if the impregnant which is of a relatively brittle nature is actually fractured on and in between the fibers. This can be effected by calendering the material subsequent to drying and while the fibers are in a distended condition. The binder is hard and friable only if it is substantially dry, and, therefore, the preferred practice is to accomplish the fracturing operation substantially immediately upon withdrawal of the material from the drying oven and while the material contains not more than 5% of moisture. If the quantity of moisture is substantially greater than 5%, the extent of the fracturing of the resin will be limited because of a lack of friability. Also, the impregnating resin being water-soluble is softened by the imbibition of moisture from the air, and, when quantities of moisture substantially in excess of 5% are present in the stiffener material, the calendering is not only ineffective to obtain the desired fracturing, but there is a tendency to form the impregnant at the surfaces in contact with the calender rolls into continuous films which are not readily permeable.

In the fracturing operation, a pair of calender rolls having smooth, polished surfaces are preferably employed, the rolls operating at the same surface speeds. These rolls may be set about .040 of an inch apart, and, with the sheet referred to above having a distended thickness of .135 of an inch, a final finished stiffener web having a thickness of .045 to .050 of an inch will result. There is some tendency for the material to recover slightly after the fracturing operation which accounts for the increase in thickness from the .040 of an inch setting between the rolls to the .045 to .050 of an inch thickness of the finished material. The material, when examined under a microscope, shows that the resin on the fibers and in between the fibers is fractured at a great many points. This fracturing increases the absorptive characteristics of the material and facilitates softening. The fracturing operation, when effected by means of calender rolls, also reduces the sheet to a substantially uniform thickness for subsequent cutting into the stiffener blanks and skiving, where required. The pressure applied by the rolls may be in the order of 100 to 400 pounds per inch of line contact at the nip between the rolls. This is not a critical factor and will vary to a considerable extent, depending upon the thickness of the sheet and other variable factors. The rolls are preferably cold, but, if desired, they may be warmed or heated to a mild degree.

The stiffener material of this invention may be activated with the solutions referred to in the Almy patent, such as ammonium phosphate or phosphoric acid. The retarders mentioned in that patent such as the higher alcohols may be incorporated with good results. With the present invention, however, the material will become flaccid substantially instantaneously upon contact with the activator solution which contains water. As pointed out in the Almy patent, too rapid activation must be avoided in order to prevent the precipitation of the resin as discrete particles rather than as continuous films. Blanks dipped into the treating solution for a period of less than one second are substantially completely softened and ready for immediate insertion into a shoe. With high speed shoe manufacture, such rapid softening is an important factor. The "mulling" heretofore required is now unnecessary.

While I have illustrated and described a preferred embodiment of my invention, it will be understood that the same may be otherwise embodiment and practiced within the scope of the following claims.

I claim:

1. In a method of making a shoe stiffener material the steps comprising: (*a*) impregnating a fibrous base of napped fabric with an aqueous mixture of a reactive water-soluble urea-formaldehyde resin stabilized in partially condensed

condition, sufficient inert thixotropic thickening gel, between about 1% and 5% based on the dry weight of the resin, to cause said resin to dry in discontinuous porous films, and 80% to 120% of finely divided acid-resistant filler based on the dry weight of the resin, said mixture containing between 55% and 65% of solids; (b) subjecting said impregnated fabric to a napping operation to distend the fibers of the fabric and to meter the quantity of impregnant in and on the fabric to provide a matrix containing when dry between 200% and 300% of the weight of the fabric; (c) heating said mixture on and within said fabric, while said fibers are maintained in distended condition by the thixotropic action of said gel, until at least about 95% of the moisture is removed from said aqueous mixture and a dried, porous matrix is formed on said distended fibers and within the body of the fabric; and (d) pressing said fabric in such dried condition and while it contains not more than 5% of water to fracture said porous matrix on said distended fibers and within the body of the fabric at a multiplicity of points throughout its extent to form a stiffener material which may be rendered soft and flaccid substantially instantaneously upon immersion in water.

2. In a method of making a shoe stiffener material the steps comprising: (a) impregnating a fibrous base of napped cotton flannel with an aqueous mixture of a reactive water-soluble urea-formaldehyde resin stabilized in partially condensed condition, sufficient inert thixotropic thickening gel, between about 1% and 5% based on the dry weight of the resin, to cause said resin to dry in discontinuous porous films, and 80% to 120% of finely divided acid-resistant filler based on the dry weight of the resin, said mixture containing between 55% and 65% of solids; (b) subjecting said impregnated flannel to a napping operation to distend the fibers of the flannel and to meter the quantity of impregnant in and on the flannel to provide a matrix containing when dry between 200% and 300% of the weight of the flannel; (c) heating said mixture on and within said flannel, while said fibers are maintained in distended condition by the thixotropic action of said gel, until at least about 95% of the moisture is removed from said aqueous mixture and a dried, porous matrix is formed on said distended fibers and within the body of the flannel; and (d) calendering said napped flannel in such dried condition and while it contains not more than 5% of water to fracture said porous matrix on said distended fibers and within the body of the flannel at a multiplicity of points throughout its extent to form a stiffener material which may be rendered soft and flaccid substan-

tially instantaneously upon immersion in water.

3. In a method of making a shoe stiffener material the steps comprising: (a) impregnating a fibrous base of napped cotton flannel with an aqueous mixture of a reactive water-soluble urea-formaldehyde resin stabilized in partially condensed condition, sufficient inert thixotropic thickening gel, between about 1% and 5% based on the dry weight of the resin, to cause said resin to dry in discontinuous porous films, and 80% to 120% of finely divided acid-resistant filler based on the dry weight of the resin and consisting essentially of talc, said mixture containing between 55% and 65% of solids; (b) subjecting said impregnated flannel to a napping operation to distend the fibers of the flannel and to meter the quantity of impregnant in and on the flannel to provide a matrix containing when dry between 200% and 300% of the weight of the flannel; (c) heating said mixture on and within said flannel, while said fibers are maintained in distended condition by the thixotropic action of said gel, until at least about 95% of the moisture is removed from said aqueous mixture and a dried, porous matrix is formed on said distended fibers and within the body of the flannel; and (d) calendering said napped flannel in such dried condition and while it contains not more than 5% of water to fracture said porous matrix on said distended fibers and within the body of the flannel at a multiplicity of points throughout its extent to form a stiffener material which may be rendered soft and flaccid substantially instantaneously upon immersion in water.

4. A shoe stiffener material made in accordance with the method of claim 1.

5. A shoe stiffener material made in accordance with the method of claim 2.

6. A shoe stiffener material made in accordance with the method of claim 3.

GEORGE E. EHLE.

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