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MANUFACTURE OF IMPREGNATED FIBROUS BASE FOR SHOE STIFFENER PARTS OR THE LIKE

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This invention relates to the manufacture of an impregnated fibrous base such as is serviceable to good advantage in making shoe stiffener parts of the character of box toes or counters. It embraces also the preparation of the composition that is introduced as an impregnant into the fibrous base and that imparts to the impregnated base qualities that are highly desired in shoe stiffener parts.

For a good many years, the shoe-making industry has been using as the box toe stiffener a blank of fibrous material impregnated with thermoplastic substances which lend to the blank the property of becoming limp and moldable under the application of moderate heat such as does no damage to the shoe upper and which keep the blank at the desired stiffness and resiliency at room temperature conditions. In shoe-making practice, such a stiffener is steamed or otherwise heated until it can be readily molded, whereupon it is assembled with the shoe upper and the assembly conformed to the shape of the last during the pulling-over and bed-lasting operations. The stiffener thus conformed to the desired shape sets in such shape as the thermoplastic substances lose their plasticity or congeal.

A serious fault with a stiffener of the foregoing so-called thermoplastic type is that the thermoplastic stiffening imprgenant heretofore used therein was of a friable nature and, accordingly, that it tended to release such impregnant as dust not only during the cutting and skiving of the stiffener blank but during its service in the shoe wherein it undergoes repeated shocks incident to wear. Thus, ordinary rosin or colophony, which has heretofore been used extensively as a component of the stiffening impregnant by reason of its low cost, is faulty not only in the foregoing respect but further in that the stiffener in which it is present is lacking in the desired flexibility tending to crack or break open when flexed over a sharp angle.

Another well known type of shoe stiffener consists of a fibrous base impregnated with cellulose esters of the character of nitrocellulose and cellulose acetate. In shoe-making practice, this type of stiffener is dipped into a suitable volatile organic solvent that quickly gelatinizes the cellulose ester impregnant and thus renders the stiffener easily conformable to the shape of the last during the shoe-making operations, the stiffener setting or hardening in its conformed condition as the organic solvent evaporates. This type of shoe stiffener is valued because it is non-dusty and because it has high resiliency and flexibility, but it gives rise to the nuisance and serious fire hazard occasioned by the use of volatile organic solvents. Again, in effecting an impregnation of the fibrous base with the cellulose ester, it is necessary to work with solutions of the cellulose ester in volatile organic solvents thereby not only exposing the shoe stiffener factory to nuisance and fire hazard, but necessitating the installation of expensive solvent-recovery equipment or leading to a loss of such expensive solvent.

In accordance with the present invention, I produce shoe stiffener material and more particularly a box toe stiffener that partakes of the desirable characteristics of both types of prior art stiffeners hereinbefore described and that is without the disadvantages or faults of either type, because, not only is the stiffener of the present invention possessed of high resiliency or snappiness, flexibility, and non-dustiness, comparing favorably in these respects with the type of shoe stiffener containing nitrocellulose or cellulose acetate as the stiffening impregnant, but it is thermoplastic, that is, can be rendered limp and moldable for conformation to the last under temperature conditions non-injurious to the shoe upper.

In producing the shoe stiffener of the present invention, I use as the thermoplastic impregnant a mixture comprising ordinary rosin or colophony and polyvinyl ester of the nature of polyvinyl acetate and/or polyvinyl chloride and/or polyvinyl chlor-acetate, the rosin or colophony preferably preponderating in amount by weight over the polyvinyl ester. It is known that polyvinyl esters and rosin can be dissolved together in such organic solvents as alcohol and benzol and that a solution of both these materials can be introduced into a fibrous base and the base then dried to produce shoe stiffener material. In such case, however, one runs into the serious disadvantages already mentioned as being consequent to the use of volatile organic solvents. In an effort to do away with the use of volatile organic solvents, I mixed the polyvinyl acetate of commerce with the ordinary rosin or colophony of commerce and attempted to fuse or melt the mixture to produce a homogeneous liquid or solution that could be introduced as an impregnant into a fibrous base. These attempts proved futile, as the polyvinyl acetate did not dissolve in significant amount in the molten or heat-liquefied rosin. On the contrary, the crystals or lumps of polyvinyl acetate

tended to aggregate or coalesce into a gummy mass that settled out as an insoluble residue and that remained as such no matter how long heating was continued. While I cannot account with precision for these unsatisfactory results, nevertheless, it appears that the rosin, which has a melting point of about 175° to 180° F., is first fused and that the resulting highly fluid liquid does not dissolve the crystals or lumps of polyvinyl acetate with sufficient rapidity, in consequence of which the polyvinyl acetate, under the influence of the heat of the molten rosin, undergoes further polymerization to a state where it is insoluble in the molten rosin and accordingly tends to settle out as a gummy mass. In this connection, it is perhaps apposite to observe that the polyvinyl ester and more particularly the polyvinyl acetate that I use has a melting point distinctly higher than that of the rosin. When polyvinyl acetate having a softening point of about 300° F. is heated to a temperature sufficiently high to cause its fusion, it does not tend to become fluid but is merely transformed to a plastic state which persists even though the temperature to which it is heated is much higher than its softening point; and if such heating is continued for a considerable period of time, serious decomposition of the plastic mass ensues, and is evidenced by localized charring or blackening of the mass. Of course, when a mixture of polyvinyl acetate and rosin is being heated with a view toward realizing a homogeneous liquid or solution designed to enter as an impregnant into a fibrous base composed of cellulose and/or wool fibers, such solution must be attained at temperatures that will not cause scorching and embrittlement of the fibrous base; and the solution must have the proper degree of fluidity at such temperatures to enter uniformly into and throughout the fibrous base in a comparatively short period of time.

I have discovered that it is possible to bring about a complete fusion of polyvinvy acetate or other polyvinyl ester and ordinary rosin or colophony and to produce a homogeneous liquid solution at temperatures below those injurious to fibrous bases made up of vegetable and/or animal fibers of the nature of cotton and wool and further that the resulting liquid solution is of sufficiently high fluidity to penetrate quickly into and throughout the fibrous base, provided that both the polyvinyl ester and the rosin are each brought to a finely subdivided state, then intimately mixed, and the mixture subjected to sufficient heat to become liquefied. While I am uncertain as to the mechanism underlying the results that I secure by the foregoing practice, nevertheless, it would appear that by bringing together the polyvinyl ester and the rosin intimately and in a fine state of subdivision, the fine particles of polyvinyl ester are dissolved so rapidly in the heat-liquefied rosin that they do not have an opportunity of becoming transformed in substantial amount to the insoluble polymerized state. In other words, the rosin apparently performs the role of a flux, bringing about the fusion or melting of the polyvinyl ester particles at a lower temperature than the softening or melting point of the polyvinyl ester itself. Once the polyvinyl ester has been fluxed by and dissolved in the heat-liquefied rosin, there is evidently no longer any tendency for the polyvinyl ester to polymerize to an insoluble state, for I have observed that it is possible to maintain the solution for a long period of time at temperatures of about 340° to 350° F. with no observable separation of the polyvinyl ester. At these temperatures, the solution is highly fluid and a fibrous base made up of vegetable and/or animal fibers may be run therethrough and quickly and uniformly impregnated with the solution with no damage whatever to the base to produce the desired kind of impregnated product.

The following table shows the fluxing action of rosin having a melting point of about 175° F. upon polyvinyl acetate having a softening point of about 350° F., rosin-polyvinyl acetate mixtures containing from 2% to 30% polyvinyl acetate being given in the first column and their melting points being given in the second column:—

Polyvinyl acetate content (percent)	Melting point (°F.)
2	186
4	188
6	190
8	198
10	214
30	232

Once the mixture is melted into a liquid solution by following the principles of the present invention and the solution is allowed to cool and solidify, a solid mass of uniform color, consistency, and other characteristics is realized. This indicates either that the liquid solution is transformed to a solid solution or that the rosin and polyvinyl acetate have become chemically combined, particularly as it is possible to re-melt the solid mass to reproduce the liquid solution. Liquid solutions prepared in accordance with my invention from each of the foregoing mixtures give the desired uniformity of impregnation of fibrous bases at about 340° to 350° F.

I shall now indicate typical preferred practices that may be performed in accordance with my invention. Ordinary rosin or colophony of commerce made up of lumps of a wide variety of sizes is passed through a suitable pulverizing machine, for instance, a ball mill, hammer mill, stamp mill, or the like. The resulting powder is passed through a sieve, whose openings are of a size not exceeding about 100 mesh and preferably of a fineness of about 200 or finer mesh. Polyvinyl acetate of commerce having a softening point of, say, about 300° F. and made up of crystals varying widely in size is also reduced to a similar state of subdivision. The powdered rosin and polyvinyl acetate are then mixed or blended in the desired proportions, the rosin preferably preponderating over the polyvinyl acetate. This blending or mixing is preferably done by first intimately mixing the two powdered materials by mere stirring and then running the mixture one or more times through the disintegrating or pulverizing machine so as to ensure as uniform or perfect a mixture as possible. The uniform mixture or blend is then charged into a melting vat or kettle and is brought to a temperature of about 350° to 400° F., the particular temperature depending upon the proportion of polyvinyl acetate that is present in the blend, whereupon the molten mixture may be allowed to cool to a temperature of about 340° to 350° F., at which temperature impregnation of the fibrous base may be satisfactory performed, as hereinbefore stated. Ordinarily, it is desired to use at least about 10% to 15% of polyvinyl acetate in the molten blend,

as such a composition when introduced as an impregnant into a fibrous base conduces to a product of the desired characteristics. In some instances, however, a smaller proportion of polyvinyl acetate may be used, although, in such case, one does not arrive at the same quality of product as when a higher proportion of polyvinyl acetate is employed. On the other hand, one may increase the proportion of polyvinyl acetate to, say, about 30%, in which case, it is possible to realize a product which closely resembles the sort of product containing nitrocellulose, cellulose acetate, or similar cellulose esters as the impregnant. An important feature of the present invention, however, is that with only about 10% to 15% of polyvinyl acetate in the molten blend, it is possible to arrive at an impregnated product whose characteristics are vastly superior to those of the so-called thermoplastic stiffeners of the prior art. From a commercial standpoint, this feature is perhaps the most significant one, inasmuch as rosin is far less expensive at the present time than is polyvinyl acetate; and inasmuch as rosin can be used far in excess of the polyvinyl acetate while at the same time arriving at a decidedly improved product, the cost of manufacturing such improved product is not materially in excess of the thermoplastic stiffeners of the prior art.

A fibrous base that undergoes impregnation in accordance with my invention may be any one of those heretofore used for this purpose. Thus, I may use as the base a canton flannel or other woven fabric, a wool felt, or a waterlaid felt, such as is produced on a paper-making machine from rag half-stuff, wood pulp, cotton fibers, wool, jute, or mixtures of such fibrous materials. Any one of these fibrous bases may be run through a bath of the molten blend of the present invention to produce a uniformly impregnated sheet which may be squeezed to produce an impregnant to fiber ratio of, say 1 to 1, 1.5 to 1, more or less. The fibrous base may be run progressively through the bath of the melted mixture, progressively squeezed to the desired impregnant content, and run over cooling drums or festooning rolls so as to cause the impregnant to congeal in the sheet before the sheet is cut into the desired lengths or convoluted into rolls for storage and/or shipment.

The impregnated sheet material may then be cut or died out into box toe blanks or other shoe stiffener parts, although it is not necessarily limited to such uses. The box toe blanks or other shoe stiffener parts may be skived as ordinarily at their marginal portions. As already indicated, a box toe blank thus made is of the thermoplastic type and may be conditioned for use in the shoe factory by the usual steam or heat treatment which transforms it to a limp and moldable condition at temperatures that are non-injurious to the shoe upper.

While I have dealt with the use of stiffening impregnant made up of polyvinyl ester and rosin for the reason that these two materials constitute the essential components of the impregnant, nevertheless, it is possible to modify such impregnant in one or more respects by adding thereto such plasticizing agents as castor oil, dibutyl phthalate, or one or more other thermoplastic agents such as bitumen or wax to replace part of the rosin. These modifying agents are preferably added to an already prepared molten blend of the polyvinyl ester and rosin.

I claim:—

1. A process which comprises bringing rosin and polyvinyl ester together as a substantially uniform mixture of solids of such fine particle size that it can be fused under heat alone into a molten liquid solution substantially free from undissolved particles, and heating the mixture to cause its fusion into such molten liquid solution capable of congealing to a solid state.

2. A process which comprises bringing polyvinyl acetate and a preponderating proportion of rosin together as a substantially uniform mixture of solids of such fine particle size that it can be fused under heat alone into a molten liquid solution substantially free from undissolved particles, and heating the mixture to cause its fusion into such molten liquid solution capable of congealing to a solid state.

3. A process which comprises bringing polyvinyl acetate and a preponderating proportion of rosin together as a substantially uniform mixture of solids of such fine particle size that it can be fused under heat alone into a molten liquid solution substantially free from undissolved particles, heating the mixture to cause its fusion into such molten liquid solution capable of congealing to a solid state, and impregnating a fibrous base with such liquid solution.

4. A process which comprises bringing rosin and polyvinyl ester together as a substantially uniform mixture of solid particles of a size not exceeding about 100 mesh, and heating such mixture to fuse it into a molten liquid solution substantially free from undissolved particles and capable of congealing to a solid state.

5. A process which comprises bringing polyvinyl acetate and a preponderating amount of rosin together as a substantially uniform mixture of solid particles of a size not exceeding about 100 mesh, and heating such mixture to fuse it into a molten liquid solution substantially free from undissolved particles and capable of congealing to a solid state.

6. A process which comprises bringing polyvinyl acetate and a preponderating amount of rosin together as a substantially uniform mixture of solid particles of a size not exceeding about 100 mesh, heating such mixture to fuse it into a molten liquid solution substantially free from undissolved particles and capable of congealing to a solid state, and impregnating a fibrous base with such solution.

7. A process which comprises bringing polyvinyl acetate having a melting point of about 300° F. and a preponderating amount of rosin together as a substantially uniform mixture of solid particles of a size not exceeding about 100 mesh, heating such mixture to fuse it into a molten liquid solution capable of congealing to a solid state but substantially free from undissolved particles and having a temperature of about 340° to 350° F., impregnating a fibrous base with such solution, and causing the solution to set in the impregnated base.

8. A process which comprises bringing polyvinyl acetate having a melting point of about 300° F. and a preponderating amount of rosin together as a substantially uniform mixture of solid particles of a size not exceeding about 100 mesh, heating such mixture to fuse it into a molten liquid solution capable of congealing to a solid state but substantially free from undissolved particles and having a temperature of about 340° to 350° F., dipping a fibrous base into such solution to cause such solution to enter as an impregnant into the base, squeezing the base to the desired

impregnant content, and causing the impregnant to set in the base.

9. A process which comprises reducing rosin and polyvinyl ester to a powdered state, uniformly mixing the powders, and heating the mixture to cause its fusion by such heat alone into a substantially homogeneous molten liquid solution capable of congealing to a solid state.

10. A process which comprises reducing rosin and polyvinyl ester to particles of a size not exceeding about 100 mesh, uniformly mixing such particles, and heating the mixture to cause its fusion by such heat alone into a substantially homogeneous molten liquid solution capable of congealing to a solid state.

11. A process which comprises reducing rosin and polyvinyl acetate to particles of a size not exceeding about 100 mesh, uniformly mixing such particles with the rosin preponderating in amount, and heating the mixture to cause its fusion by such heat alone into a substantially homogeneous molten liquid solution capable of congealing to a solid state.

12. A process which comprises reducing rosin and polyvinyl acetate to particles of a size not exceeding about 100 mesh, uniformly mixing such particles with the rosin preponderating in amount, heating the mixture to cause its fusion by such heat alone into a substantially homogeneous molten liquid solution capable of congealing to a solid state, and impregnating a fibrous base with such solution.

13. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl ester, said blend being of substantially uniform color, consistency, and other characteristics.

14. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl ester, the rosin being present in said blend in amount preponderating over said polyvinyl ester and said blend being of substantially uniform color, consistency, and other characteristics.

15. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl acetate, said blend being of substantially uniform color, consistency, and other characteristics.

16. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl acetate, the rosin being present in said blend in amount preponderating over the polyvinyl acetate and said blend being of substantially uniform color, consistency, and other characteristics.

17. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl acetate, said polyvinyl acetate having a softening point of about 300° F. and said blend being of substantially uniform color, consistency, and other characteristics.

18. As a new article of manufacture, sheet material especially adapted for use in thermoplastic shoe stiffener parts comprising a fibrous base impregnated with a physically homogeneous heat-fused blend of rosin and polyvinyl acetate, said polyvinyl acetate having a softening point of about 300° F., said rosin being present in said blend in amount preponderating over said polyvinyl acetate, and said blend being of substantially uniform color, consistency, and other characteristics.

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