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THERMOPLASTIC STIFFENER

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This invention relates to thermoplastic compositions and to flexible, fibrous sheets impregnated therewith. It relates particularly to such impregnated sheets adapted to be used in making box toes or other shaped articles.

A wide variety of substances have been proposed and used to impregnate the felt, paper, or cloth from which box toe stiffeners and like articles are prepared. The substances employed have been classified into at least three general groups, depending on which of the common classes of box toe blanks is to be prepared. Thus, a "water box toe" is heavily coated with glue, dextrine, or like water-swellable adhesive. To use a water box toe, the coated blank is soaked in water until the coating has swelled and is soft and sticky enough to adhere to the upper leather and the cloth lining of a shoe.

A "solvent box toe" is made from a fibrous sheet material coated with a liquid cellulose ester composition such as a solution comprising cellulose nitrate or cellulose acetate. In order to use this type of impregnated material in making box toes, it must be soaked in a solvent to soften the cellulose ester composition with which the blank is impregnated, since the blank will not adhere to leather or cloth if the solvent is not present. Furthermore, the solvent must be uniformly distributed throughout the cellulose ester impregnating material and for this reason solvent box toe blanks must be stored in closed containers in contact with the required solvent. The softened blank, still containing volatile solvent, is forced into shape and adheres to adjoining lining and upper because of the tacky nature of the solvent-softened surface. A necessary limitation and disadvantage of the solvent box toe is that all of the shoe manufacturing operations must be completed before the solvent evaporates. Furthermore, simply dipping such cellulose derivative coated fabrics in a solvent does not soften them throughout, which is a condition necessary to increase their plasticity at working temperatures and to render them adhesive. Hence, it has been the practice to furnish such box toes in cans so that they are pre-conditioned in contact with solvent vapors and are more readily rendered adhesive by dipping in solvent prior to use. The use of the "solvent" or "canned" box toes is further hazardous to health of operators because of the toxic nature of solvent vapors and because of the flammability of the solvents used.

The third class of box toe, known as the "thermoplastic box toe", has heretofore comprised a fibrous base, usually felt or paper, impregnated with black asphalt. The cellulose esters are not sufficiently adhesive at their softening points, or have too high softening points to be employed in thermoplastic box toes without injuring the leather unless solvents are used. The black asphalt usually employed in this type of toe-forming materials stains everything with which it comes in contact, especially when heated, and therefore cannot be employed in the manufacture of the better quality light-colored or white shoes.

Refined rosin and other resinous or waxy materials have been suggested and tried as the indurative for thermoplastic box toe forms. The recognized shortcoming of these agents alone is that, like asphalt, they have too low a viscosity when hot, and when cooled they are too brittle, tending to powder and separate from the felt or paper support when the latter is flexed.

From practical considerations, the thermoplastic material with which the fibrous base is impreganated should be capable of being applied in a liquid condition without solvents. It should be tough, flexible, and not sticky when cold. It should not crack, powder, or break on continued flexing. It should have a softening point sufficiently high to stand up under temperatures which shoes may encounter in use or when on display, and sufficiently low to adhere readily without solvents at a temperature which will not injure leather. It must soften and become adhesive at temperatures easily attainable in shoe machinery but must not have so low a viscosity that it is easily displaced or squeezed from the base during the pull-over and bed-lasting operations. The impregnating material must further be as light colored as possible and should not stain leather or fabric.

It is, accordingly, among the objects of the invention to provide a composition of matter suitable as an indurative for flexible fibrous materials used in box toe manufacture, which is capable of being applied as a melt at moderate temperatures. It is a further object to provide such a composition which will not stain leather or fabric, and which will adhere readily thereto when softened by heat without the use of solvents. It is another object to provide a flexible fibrous sheet material impregnated with a composition as aforesaid, the article being tough enough to withstand the pull-over operation in making shoe toes, characterized by its strong adherence to leather and cloth at the working

temperatures available in customary bed-lasting operations, and capable of being readily skived. A further object is to provide a box toe blank capable of maintaining its adherence to leather and cloth when cold and withstanding continued flexing without cracking, powdering, or breaking under temperatures normally met with in shoe wear. It is a particular object to provide a box toe blank of suitable stiffness and resilience, comprising a textile fabric impregnated with the new composition and which will have the aforesaid desired characteristics.

According to the present invention, the foregoing and related objects are attained through the employment as the thermoplastic adhesive in box toe manufacture of a particular type of composition comprising a major proportion of a relatively low melting resin and minor proportions of cellulose ethers and plasticizers. The said composition, to be more fully described hereinafter, is employed as a molten composition to impregnate a flexible base which is preferably a woven fabric such as cotton flannel, or it may be a self-supporting felted flexible fibrous sheet such as felt or paper. The flexible supporting base is impregnated by immersion in the heated liquefied thermoplastic and the fabric, or other fibrous base, is removed from the impregnating bath, doctored, or passed between rollers to provide a uniform weight of impregnating thermoplastic to a given area of fibrous base, suitably 8–16 ounces per square yard. The impregnated fabric is then cooled away from contact with outside surfaces until the plastic composition has set, and subsequently cut and shaped into the desired form and size. Box toe blanks cut from the so-impregnated fibrous sheet can be applied to shoes at moderate temperatures, e. g. 180°–250° F., without the use of volatile solvents in the customary pull-over or bed-lasting operations in shoe manufacture to form a stiff, resilient, non-staining adherent toe stiffener.

Of the fibrous base materials available for use in making box toes, it has long been recognized that a woven fabric such as cotton flannel would be preferable to the felted fibrous materials, such as felt or paper, which are commonly used in this art. Cotton flannel has not been used as a base for impregnation with melted rosin or asphalt because the impregnated flannel could not be satisfactorily skived. The art was thus left to use a fibrous base having little mechanical strength and an impregnant which became so fluid at elevated temperatures that it did not improve the tear strength of the fibrous base. This factor is important because the box toe material is subjected to the severest strains when it has the least mechanical strength, namely in the pulling-over and bed-lasting operations when the box toe is soft and adhesive from the applications of heat.

The preferred combination of a woven fabric which has high mechanical strength and a resinous impregnating material which has high viscosity at elevated temperatures by virtue of its cellulose ether content is a great improvement over the prior art thermoplastic toe in which the indurative becomes so fluid under shoe making conditions that it has no cementing action on the fibers of the base material, even if the two articles are considered from the standpoint of strength alone. The high viscosity of the cellulose ether-resin indurative of the present invention, when hot, prevents the thermoplastic adhesive from squeezing out at the points of pressure in the pulling-over and bed-lasting operations. Further, the cellulose ether-resin indurative is tough enough when cold to permit the box toe to be skived readily.

Although canton flannel or like absorptive woven fabric is preferred as a base for impregnation with the new composition to yield a thermoplastic box toe of greatly improved properties, felt or absorbent paper may be employed as the fibrous base. When impregnated with the resin-cellulose ether compositions described herein, the reduced flow of the said compositions increases the strength of these fibrous bases at working temperatures to such an extent that a marked decrease in spoilage from tearing and mechanical failure of the box toe is obtained.

The resins which constitute the major proportion of the compositions of the present invention and which are suitable for use therein, are those commonly employed in the lacquer and varnish trade, which melt at temperatures below 160° C. and preferably those which melt between 115° and 150° C. The resins employed may be either synthetic or natural, provided that on continued heating at temperatures up to about 150° C. in the presence of a cellulose ether they are not converted into higher melting or infusible products. Among the resins which have been found satisfactory are rosin, dammar, "run" natural resins, the rosin esters such as ester gum, lower alkyl rosin esters and the like, phenol-modified copals, non-thermosetting phenol-formaldehyde resins, cumarone-indene resins and their phenol-modified products, and the like. The natural resins and their chemically modified derivatives are preferred.

The cellulose ethers which may be employed in the preparation of the thermoplastic adhesives include ethyl cellulose, benzyl cellulose, ethyl lauryl cellulose, butyl cellulose, and like alkyl, aralkyl, and mixed alkyl-aralkyl ethers of cellulose. It is a preferred limitation that the cellulose ether soften without decomposition at temperatures at or below 150° C., and that it be miscible with the resin employed. The cellulose ether may preferably be further characterized by having a relatively low intrinsic viscosity, and there is used especially advantageously an ethyl cellulose, the viscosity of which, in 5 per cent solution in 80:20 toluene:ethanol, is below 30 centipoises. Even small amounts of a low viscosity cellulose ether materially increase the viscosity of a resin melt.

In order to prepare the thermoplastic compositions without having to employ volatile solvents which would be inconvenient and undesirable to handle in an application of this type, the cellulose ether may first be plasticized by intimately mixing the same with up to an equal weight of a softening plasticizer for cellulose ethers such as castor oil, dibutyl phthalate, tricresyl phosphate, diphenyl-monoortho-xenyl phosphate, ethyl phthalyl ethyl glycolate or the like. The plasticized cellulose ether may then be stirred into the molten resin. Another method of making the composition comprises heating the resin to a temperature of about 250° C., for example, then adding the cellulose ether, stirring for a few minutes until the cellulose ether dissolves, then chilling back toward 150° C. by the addition of cold plasticizer. The preferred amount of cellulose ether in the compositions is about 10 to 30 parts for each 90 to 70 parts, respectively, of the resin employed. The amount of plasticizer may vary from 3 to 18 parts for each

10 to 30 parts of cellulose ether. Expressed in terms of per cent composition, there may be used from 8.5 to 30 per cent of cellulose ether, from 60 to 87.5 per cent of resin, and from 3 to 18.5 per cent of plasticizer.

A preferred composition comprises: ethyl cellulose, 17.5 per cent; a meltable resin, 75 per cent; and softening plasticizer, 7.5 per cent. Small amounts of pigments or fillers may be added to the composition if desired.

Each of the following examples illustrate a composition which has been employed satisfactorily in the preparation of box toes. The composition in each instance was prepared by melting the resin in a saturation tank while heating until the temperature was approximately 150° C. To the melted resin was added a plasticized cellulose ether. The mixture was thoroughly stirred until a uniform melt was obtained. A sheet of cotton flannel, felt, or paper was then passed into and through the solution, being conveyed therethrough in a manner such that the sheet became completely impregnated. The impregnated sheet was withdrawn from the bath, passed between heated rollers or heated scraping knives to remove excess composition, and then conveyed with cooling out of contact with other surfaces for at least 10 feet until the indurative composition was no longer tacky. It was then cut, shaped, and built into a shoe in the customary manner.

Example 1

	Per cent
Wax-free dammar	75
Standard ethoxy, low viscosity, ethyl cellulose	17.5
Castor oil	7.5

Example 2

	Per cent
Elemi	73
Ethyl cellulose	18
Diphenyl mono-ortho-xenyl phosphate	9

Example 3

	Per cent
Rosin	75
Ethyl cellulose	17.5
Dibutyl phthalate	7.5

Example 4

	Per cent
Wood rosin	74.6
Benzyl cellulose, medium viscosity	12.7
Dibutyl phthalate	12.7

Example 5

	Per cent
Wood rosin	76
Ethyl cellulose (standard ethoxy, 10 centipoise)	15
Dibutyl phthalate	7.5
Titanium oxide	1.5

When fibrous materials, such as canton flannel, were impregnated with the above compositions and molded, or otherwise shaped for use as box toes, the formed product was stiff enough to retain its shape under severe service conditions, yet flexible enough to be adapted to use in the better class "dressy" shoes as well as in "service" or "work" shoes. The thermoplastic impregnated fabric did not crack or break when flexed and the indurative composition showed no tendency to powder or crumble.

The inherent softness of benzyl cellulose imparted to the composition of Example 4 a resilience and an adhesive quality unexpectedly superior to like properties of the heretofore employed compositions. For all-around practicability, the odorless, non-staining, substantially colorless ethyl cellulose compositions of the other examples are to be preferred in thermoplastic box toes.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the materials or method employed, or the article thereby produced, provided the materials, method or article set forth in the following claims or the equivalent of such stated materials, method or article be employed or obtained.

I therefore particularly point out and distinctly claim as my invention:

1. A thermoplastic sheet suitable for making box toes and the like consisting essentially of an absorbent flexible fibrous base and, as an indurative therefor, a composition fusible below 150° C. which is viscous and highly adhesive when warm, and tough, non-tacky and substantially non-powdering at room temperature, the said indurative consisting essentially of between about 8.5 and 30 per cent of a cellulose ether, between 3 and 18.5 per cent of a softening plasticizer for the cellulose ether and from 60 to 87.5 per cent by weight of a fusible non-setting resin compatible in the molten state with the cellulose ether, the said resin being selected from the group consisting of the natural resins and their chemically modified resinous derivatives.

2. A thermoplastic sheet suitable for making box toes and the like consisting essentially of an absorbent flexible fibrous base and, as an indurative therefor, a composition fusible below 150° C. which is viscous and highly adhesive when warm, and tough, non-tacky and substantially non-powdering at room temperature, the said indurative consisting essentially of between about 8.5 and 30 per cent of a cellulose ether, between 3 and 18.5 per cent of a softening plasticizer for the cellulose ether and from 60 to 87.5 per cent by weight of rosin.

3. A thermoplastic sheet suitable for making box toes and the like consisting essentially of an absorbent flexible fibrous base and, as an indurative therefor, a composition fusible below 150° C. which is viscous and highly adhesive when warm, and tough, non-tacky and substantially non-powdering at room temperature, the said indurative consisting essentially of between about 8.5 and 30 per cent of ethyl cellulose, between 3 and 18.5 per cent of a softening plasticizer for the ethyl cellulose, and from 60 to 87.5 per cent by weight of a fusible non-setting natural resin compatible in the molten state with the ethyl cellulose.

4. A thermoplastic sheet suitable for making box toes and the like consisting essentially of an absorbent flexible fibrous base and, as an indurative therefor, a composition fusible below 150° C. which is viscous and highly adhesive when warm, and tough, non-tacky and substantially non-powdering at room temperature, the said indurative consisting essentially of between about 8.5 and 30 per cent of ethyl cellulose, between 3 and 18.5 per cent of a softening plasticizer for the ethyl cellulose, and from 60 to 87.5 per cent by weight of rosin.

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