Patented Jan. 7, 1947

2,413,806

UNITED STATES PATENT OFFICE

2,413,806

METHOD OF MAKING WEAR-RESISTANT LEATHER

George Virtue, Boston, Mass.

No Drawing. Application March 18, 1943, Serial No. 479,591

3 Claims. (Cl. 12—146)

1

This invention pertains to wear-resistant tanned leather, more particularly to shoe soles and to shoes having soles made of such leather, and to a novel method of preparing such leather, soles and shoes.

Previous attempts have been made to make tanned leather, intended for shoe soles, more resistant to wear, but so far as is known to me, no such prior attempts have been attended with any real degree of success. Obviously, no treatment of leather intended for a shoe sole should lower the resistance of the leather to penetration by moisture, since the free entrance of moisture results in leaching out the tannin or other water-soluble constituents of the leather with resultant deterioration. Neither must the treatment of the sole substantially detract from those characteristics of conventionally tanned leather which are recognized as essential to its use in the manufacture of shoes, such, for instance, as durability, flexibility, strength and color; amenability to the usual operations involved in shoe making, for example retention of cements customarily employed; capability of receiving and retaining sewing stitches; workability in response to leveling pressure; edge trimming, edge setting; bottom finishing, etc., and such porosity as is requisite to foot comfort when worn. Manifestly, to be of any real value, the characteristics imparted by the wear-increasing treatment must be substantially permanent.

Prior proposed impregnation of the leather with oils, waxes, etc., or its treatment with various chemicals which alter the characteristics of the leather fiber have not met all of the above requirements, nor has the previously proposed impregnation of the leather with synthetic resins which become polymerized in situ by the application of heat adequately solved the problem, since any heat treatment necessary for such polymerization adversely affects the strength of the conventionally tanned leather fiber with the ultimate result of decreasing rather than prolonging the useful life of the material. As a matter of fact, most of the prior attempts at wear increase have been directed primarily to the exclusion of moisture from the leather, and with that object in view have resorted to the use of materials which reduced the natural porosity of the leather or its flexibility to a degree such as greatly to lessen its desirability for use in making shoe soles.

The principal object of the present invention is to provide tanned leather, for example shoe soles, possessing substantially all of the usual characteristics of conventionally tanned leather with respect to suitability for use in the manufacture and wear of shoe soles, by including within the

2

substance of the previously tanned leather a medium which itself is inherently resistant to wear and which increases the tensile strength, resistance to abrasion, resistance to wear and, preferably, resistance to penetration by moisture as compared with ordinary soles. A further object is to provide tanned leather having within its substance a permeating medium which tenaciously binds together the normal fibers of the leather, thereby increasing the resistance to wear of the leather itself.

A further object is to provide a tanned leather whose individual fibers retain their normal strength and other usual characteristics but having within its substance a tough continuum, network, or skeleton of abrasion-resistant, water-insoluble synthetic resin, increasing the weight of the leather by approximately 8% to 12%, but whose presence does not unduly lessen the normal porosity of the leather.

A further object is to provide a novel method of treating ordinary fully tanned leather, for instance shoe soles, and a novel method of making shoes thereby to impart to the leather, to the sole, and to the shoe increased wear resistance. Other and further objects and advantages of the invention will be pointed out in the following more detailed description.

In accordance with a preferred procedure, and assuming that the ultimate purpose is to provide shoes having wear-resistant soles, the leather (fully tanned and finished in accordance with usual and customary practice) is first cut into soles either by the cut-sole manufacturer or by the shoe manufacturer. The treatment of the cut-soles in accordance with the present invention, and which it is contemplated will usually be carried out by the shoe manufacturer, involves the immersion of the soles in a fluid-treating medium under such conditions and for so long a period of time as to insure their impregnation with the fluid.

The treating fluid in accordance with the present invention, comprises a synthetic resin which is water-insoluble but soluble in certain organic solvents, together with an appropriate plasticizer, dispersed in a suitable volatile solvent. It should be noted particularly that the resin has been polymerized to the extent that it is an abrasion-resistant solid, capable of forming a tough tenuous film on deposit from solution, and stable against spontaneous further polymerization, and that further polymerization of the resin in situ by the use of heat is neither requisite nor desirable.

Merely by way of specific examples of suitable treating media, but without intent to limit the invention to such specific examples, the following

formulae have been found to give the sought-for results:

(1)	Lewisol-2L (maleic resin)	pounds	120
	Abalyn	do	40
	Xylol	gallons	16
	Stoddard solvent (or 32 gal. aromatic petroleum solvent)	gallons	16
(2)	Lewisol No. 125 (modified phenolic resin)	pounds	100
	Blown castor oil	do	60
	Stoddard solvent	gallons	32

In the above formulae, the substance Lewisol-2L is a modified alkyd resin, to wit, a maleic acid, glycerol, rosin combination, this alkyd resin was at one time sold by J. D. Lewis, Inc., 68 Traverse Street, Providence, Rhode Island, but is now marketed by the Hercules Powder Co., of Wilmington, Delaware.

Abalyn (methyl abietate) is a viscous pale yellow liquid containing approximately 95% of a mixture of methyl esters of several isomeric forms of abietic acid; has the approximate chemical formula $C_{19}H_{29}COO.CH_3$; completely dissolves most synthetic resins now in use, and is miscible at room temperature with solutions of resins in practically all solvents, including alcohol and benzene; and is a product of the Hercules Powder Co., of Wilmington, Delaware.

Stoddard Solvent is the name used to designate a well-known type of petroleum base solvent; it may be purchased from Cities Service Corp., among others; it is sometimes called "White Spirits" or "Naphtha Safety" solvent; it is insoluble in water; has a sp. gr. of 0.78–0.79; a boiling point of 155–190° C.; and a flash point of 39° C.

Xylol is commercial xylene and is of the approximate formula $C_6H_4(CH_3)_2$.

Any single petroleum solvent which may be substituted for Stoddard solvent—xylol combination—should be high in aromatics; and should have approximately the same boiling range and solvent power as the Stoddard solvent—xylol combination.

Lewisol No. 125 is a phenolic resin modified by the addition of rosin and originally made and sold by J. D. Lewis, Inc., 68 Traverse Street, Providence, Rhode Island, but now marketed by the Hercules Powder Co., of Wilmington, Delaware.

Other resins suggested, merely by way of further example, are Hercules Polypale ester No. 1 (polymerized rosin and ethylene glycol) or Hercules Resin No. 2190–26 (alkyd terpene), both products of Hercules Powder Co., of Wilmington, Delaware. It may further be noted that if a resin be employed which has incorporated within its molecule a plasticizing element (as is common in the modified alkyd resin), no additional plasticizer may be necessary.

It is to be emphasized that whatever resin be selected, it should not require the application of heat for polymerizing it after its incorporation in the leather, since subjection of tanned leather to a temperature high enough to effect polymerization of synthetic resin would be injurious to the leather fiber. Moreover, it must be at a stage of polymerization, when applied, such that it will readily dissolve, in proportions substantially as above suggested, in the solvent selected so as to yield a solution of low viscosity which will readily penetrate the leather, preferably without recourse to the use of vacuum or pressure. A solution viscosity of 60.5 seconds, at 100° F., Saybolt is suggested as desirable. On the other hand, it must be sufficiently polymerized to be a solid; when properly plasticized it must be tough rather than brittle and highly resistant to abrasion when deposited from solution by evaporation of the solvent, and it must be stable against further spontaneous polymerization or oxidation.

In herein referring to "polymerization," it is thereby intended to designate any chemical reaction, for example esterification, which results in an increase in the size of the resin molecule with attendant changes in the physical properties of the resin such as change in melting point, solubility, tensile strength or resistance to abrasion.

Having prepared the selected impregnant fluid, it is conveniently applied by placing the fluid in an elongate open-topped tank or trough, the depth of the fluid being sufficient completely to immerse the leather which is to be placed in the trough or tank for treatment. If cut-soles are to be treated, they are preferably packed in an open-work basket and lowered into the fluid near one end of the tank. The basket is then moved toward the opposite end of the tank to make room for a second basket and so on until the first basket arrives at the further end of the tank when it is lifted out. A treating period of the order of 20 minutes, more or less, has been found sufficient to provide the desired result. After removal from the tank, the soles are allowed to drain and then removed from the basket and so stacked or otherwise arranged as to prevent free access of dry air and allowed to mull in moist condition for a period of two or three days, more or less, during which the treating medium becomes substantially uniformly distributed throughout the entire fibrous substance of the leather.

The soles (now containing within their fibrous interstices the substantially uniformly distributed plasticized and polymerized resin together with some solvent) are now ready for use in making shoes. However, they may, if preferred, be subjected to a drying operation at this point, as for example by passing them through a drying chamber or by blowing air over them, but care must be taken not to heat the soles, at any stage of the procedure, to a temperature substantially exceeding 120° F., for example, such as might substantially dehydrate or change the structure, strength or other characteristic of the leather or leather fiber.

Following usual practice, the soles are coated on the flesh side, preparatory to laying, with a suitable cement, the soles treated as above described being substantially as retentive of usual cements as are untreated soles. After sole laying, the shoe proceeds from one usual operation to another, and during this time the solvent, which originally represents from 50 to 60% by weight of the treating fluid, gradually evaporates until at the time the shoe is finished, substantially all of the volatile solvent has disappeared, the plasticized resin remaining apparently as a sort of continuum or network extending throughout the substance of the leather, embracing or encasing the individual fibers and bonding them together. This resinous material apparently forms an integral though open and tenuous skeleton, coextensive with the sole, which is itself tough and abrasion-resistant, thus adding its own strength and ability to resist wear to that of the original leather. Apparently the water-absorbent, non-fibrous, organic constituents of the tanned leather become permeated with the plasticized resin which acts as a size, mak-

ing such organic constituents highly water-resistant and binding them together so as to increase their resistance to wear and abrasion.

By following the above procedure, the weight of the treated leather, after evaporation of the solvent, is from 8 to 12% greater than before treatment. While the exact disposition of the added material within the structure of the tanned leather is not definitely known, it is believed, as above suggested, that it may be visualized as a sort of skeleton of resin, which coats the walls of the original pores, voids or interstices of the tanned leather, permeates the softer constituents of the leather and reduces the aggregate volume of such voids by not more than approximately one-half, and which is stable in composition and not subject to oxidation, further spontaneous polymerization, or other change during the wear of the sole. Since this skeleton of resin does not form an appreciable coating upon the outer surface of the leather (principally because during mulling they are not freely exposed to the air), nor apparently ever fills more than approximately one-half of the original voids in the leather, the treated leather is still porous to a degree such that it is cool, dry and comfortable to the wearer, while the texture of the leather is not detrimentally affected with respect to its working characteristics in shoe making.

The complete sole is thus flexible and its color is substantially the same as before treatment. On the other hand, the sole is resistant to penetration or saturation by moisture and greatly improved with respect to its resistance to wear. Thus, for example, in careful tests, wherein the treated soles have been compared with untreated soles by incorporating them in shoes and subjecting the shoes to actual wear, it has been found that the treated soles outwear the untreated soles by approximately 50%.

While a preferred mode of treating leather has hereinabove been specifically described by way of example, it is to be understood that the invention is not necessarily limited to this particular mode of treatment, but that any and all treatments for improving wear and moisture-resistance which fall within the terms of the appended claims are to be regarded as within the scope of the invention.

I claim:

1. Method of making leather shoe soles which are wear-resistant and in which the individual fibers of the leather retain their normal strength and substantially normal flexibility and other usual characteristics but wherein the leather has within its substance a tough continuous network of abrasion-resistant water-insoluble synthetic resin whose presence increases the weight of the leather by approximately 8 to 12% but which does not unduly lessen the normal porosity of the leather, which comprises as steps providing soles cut from leather previously tanned and finished, immersing the soles in a fluid bath having a solution viscosity of 60.5 seconds at 100° F., Saybolt, said bath comprising a soluble synthetic resin which has been polymerized to the solid state—a plasticizer and a volatile solvent; said media being in substantially the following proportions:

Resin	pounds	120
Plasticizer	do	40
Solvent	gallons	32

keeping the soles in the bath until they are impregnated with the fluid, removing them from the bath, allowing them to mull until the treating fluid is substantially uniformly distributed throughout the fibrous structure of the soles, and permitting the solvent to evaporate, and drying the soles by exposure to moving air the soles being kept at a temperature, not substantially exceeding 120° F., sufficiently low throughout the treatment to avoid any further polymerization of the resin or any injury to the leather fibers.

2. Method of making leather shoe soles which are wear-resistant and in which the individual fibers of the leather retain their normal strength and substantially normal flexibility and other usual characteristics but wherein the leather has within its substance a tough continuous network of abrasion-resistant water-insoluble synthetic resin whose presence increases the weight of the leather by approximately 8 to 12% but which does not unduly lessen the normal porosity of the leather, which comprises as steps providing a sole cut from leather previously fully tanned and finished, immersing the sole in a bath comprising synthetic resin of the modified alkyd class, polymerized to the solid state and which is tough and resistant to abrasion and stable against spontaneous further polymerization but which is soluble in volatile organic solvents, methyl abietate as a plasticizer, and a volatile solvent; said media being in substantially the following proportions:

Resin	pounds	120
Plasticizer	do	40
Solvent	gallons	32

keeping the sole in the bath until it is impregnated, removing the sole from the bath, and permitting the solvent to evaporate, all of the aforesaid steps being carried out at a temperature, not substantially exceeding 120° F., so low as to avoid further polymerization of the resin.

3. Method of making leather shoe soles which are wear-resistant and in which the individual fibers of the leather retain their normal strength and substantially normal flexibility and other usual characteristics but wherein the leather has within its substance a tough continuous network of abrasion-resistant water-insoluble synthetic resin whose presence increases the weight of the leather by approximately 8 to 12% but which does not unduly lessen the normal porosity of the leather, which comprises as steps providing a sole cut from leather previously fully tanned and finished, immersing the sole in a bath containing synthetic resin polymerized to the solid state and stable against spontaneous further polymerization but soluble in organic solvents, a plasticizer and a volatile solvent, said media being in substantially the following proportions:

Resin	pounds	120
Plasticizer	do	40
Solvent	gallons	32

immersing the leather in said bath and keeping it immersed for a period of approximately 20 minutes, removing it from the bath, allowing it to mull while protected from free contact with the air for a period of the order of 2 or 3 days and permitting the solvent to evaporate, the entire treatment being carried out at a temperature, not substantially exceeding 120° F., so low that the resin is not further polymerized and the leather is not dehydrated nor its fibers injured.

GEORGE VIRTUE.