UNITED STATES PATENT OFFICE.

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WATERPROOF SUBSTITUTE FOR LEATHER AND THE LIKE.

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To all whom it may concern:

Be it known that I, HERBERT F. KENWORTHY, a citizen of the United States, residing at Stoughton, in the county of Norfolk and State of Massachusetts, have invented new and useful Improvements in Waterproof Substitutes for Leather and the like, of which the following is a specification.

This invention relates to processes and products for waterproof leather substitutes. It is an object of the invention to provide a material which may have suitable thickness and characteristics for the outer soles of shoes; and which in general will be workable like leather, with customary tools, methods and machinery for working leather; be waterproof; be flexible, and retain this flexibility throughout its life; be durable; be a non-conductor of heat; be resilient; have non-slip characteristics; and also will have advantages over the waterproof materials such as rubber as well as in general be cheaper than leather, and more useful than leather in various other respects. While soles of shoes are here described as an illustrative example, the uses of the products and processes are not limited to that.

The process which I have found successful provides a tough, thick substance, having a fibrous skeleton, in which the fibers, preferably of animal origin, such as wool, are embedded in and held by a filmy binder which supplements their strength and elasticity. The spaces between them are more or less filled, partly by said film, partly by small solid mineral particles embedded therein, and partly by a material which remains soft and semi-liquid or waxy, non-drying. Preferably, however, this non-drying filler contains a suitable proportion of a hard drying ingredient, *i. e.*, one which dries into a hard, tough film on exposure to atmosphere. The result is a composition that is flexible, owing to the flexibility of its fibers and filmy structure and the liquid and lubricating character of the mixture filling its interstices, and is waterproof because those interstices are filled with a viscous or colloidal substance impervious to water; and at the same time the liquid filling is permanently contained because such part of the filler as is exposed to air at the surface of the composition hardens and makes a skin which holds the rest of the filler in place and which prevents access of air to it. Whenever the outer surface is ground away by abrasion, a new skin forms immediately, recurring automatically and performing the same function as to all of the filling which remains.

For the said recurring skin it is preferred to use a wax, such as carnauba wax, which dries into a hard tough film on exposure to atmosphere, coupled with heavy blown oil and japan; for the viscous filling, non-drying jellies or waxes or petroleum products such as paraffin wax or petroleum; and for the porous, fibrous, filmy structure it is preferred to use blown oil, japan, and turpentine coupled with wool felt and comminuted mineral solids such as oxid of zinc or carbonate of lead. The structure may be made by mechanically combining the fibers with the other materials, liquids being first thinned with a volatile diluent such as naphtha, and by raising their temperature so that as a thin liquid they penetrate among the fibers, carrying also the pulverized solids in among them. The subsequent evaporation of the naphtha leaves a porous structure in which air is accessible to the remaining liquids all through the mass, so that they dry into the elastic filmy condition. Color can be added, either in the filling or in the initial liquid; and the product can be finished mechanically by sand papering, by embossing or by other suitable methods.

The filler may be introduced by immersing the porous, filmy, fibrous product in a bath thereof, heated enough to reduce its viscosity and yet not enough to injure the physical structure of the fibers. If the entrance of such liquid through both sides of a sheet of material leaves any of the air imprisoned in its pores, this air may be driven out and at the same time the structure of the whole rendered homogeneous as to tenacity and distribution, by passing the product between the rollers of a hot steam mangle.

For explanation of the process and product more in detail, the following illustrative example is given: Take 3 parts of fluffy oxid of zinc made by the so-called French

or German process; 1 part of carbonate of lead; 3 parts of blown oil; 1 part of japan; and 1 part of turpentine; and mix them thoroughly so that the solids are suspended and uniformly distributed through the liquid. Pigment may be introduced to give desired color. When ready to use, add naphtha varying in amount according to weather conditions. The amounts may be in the vicinity of about 50 per cent. by volume, making the liquid of a specific gravity of about 1.100. This gives a consistency much like that of olive oil. The precise proportions of ingredients above described may be varied. And in fact it has been found well in some cases to add about 10 per cent. of blown oil and about 30 per cent. of drier. The whole being well stirred in a tank, the sheets of filmy fabric, which may be of wool felt are immersed therein until the liquid and its suspended solids have entered thoroughly into them. If the felt be $\frac{1}{8}$ of an inch thick several hours of such immersion has been found sufficient, the liquid being well stirred. If the felt be moved through the liquid in strip form, moving around rollers, with bends and angles therein, a few minutes suffices. If the felt be thicker, a longer time is requisite. The combined liquid, solid and fibrous material then is dried, preferably in a room having a temperature in the vicinity of 160° Fahrenheit through which room air is blown, passing over and around the sheet material with its liquid contents. During this the naphtha is withdrawn by evaporation, and so is recovered; and the liquid material dries by a process of oxidation into tough, filmy form, incasing and gripping in its film the fibers and the solid particles, and leaving pores. Thereafter the material is cooled, with the drying process still continuing slowly to a more perfect stage, which is conveniently done by simply turning off the heat and allowing the blowing of air to continue at atmospheric temperature.

The material thus made, finished, if desired by sand papering or otherwise, has many of the characteristics of leather as regards utilities, and has many that are superior or additional to those of leather. It is porous, permitting passage of air, and not absolutely waterproof.

In order to make it permanently waterproof, and wear-resisting as well as flexible, suitable for outer soles of shoes, sheets of it of suitable thickness may be cut into shape for the shoe soles, and their pores filled with a fluid composition whose ingredients may be about as follows: 30 pounds of paraffin wax, 15 pounds of petrolatum or vaseline jelly; one pound of carnauba wax; 15 gallons of heavy blown oil; and $3\frac{1}{2}$ gallons of japan. To the above any desired color may be added as, for example, lamp black, or burnt sienna, or other pigment, the same being ground in finely. The above composition at ordinary atmospheric temperature is a heavy wax like substance which when heated to 150° Fahrenheit, resembles olive oil in smoothness and consistency. Immersion of the soles in it at this temperature for ten minutes or thereabouts has been found sufficient, if they are inserted edgewise, in which case the air bubbles out from pores freely. On being taken out, the soles may be run between steam heated pressing rollers, like the rollers of a mangle, at about the same temperature. Rollers of six inches diameter, operating on the material at the rate of ten linear feet a minute under considerable pressure have been found suitable. This takes off the surplus wax, possibly forcing some of it inward; seals the open pores on the surface; and distributes the filler uniformly through the mass. If the material coming from the last mentioned immersion has any air remaining in the interstices in its middle, to which the waxy liquid has not penetrated fully, that is crowded out by the compression which the material undergoes, passing out through the surrounding liquid because of its gasity. The filler which has already entered part way from both sides of the sheet is forced farther in, and in fact is uniformly distributed, because the addition of heat contributed from the rolls reliquefies any whose fluidity may have become too much reduced. The distribution of filler thus becomes, and remains, homogeneous, because when the material tends to expand, after passing the extreme compression of the rolls, the middle pores have already been filled with the fluid so that there are no openings to which air can return. Any pressure of exterior air, acting upon it after its release from the squeezing rolls, merely tends to keep or to force the filler more securely into the inner pores. The material issuing from the rolls is limp, soft and pliable. The product may be allowed to cool for a couple of days, during which the wax of the interior hardens to the state of viscosity which is normal for it at ordinary temperature. The surface may be finished as desired or left without further finish.

This product is waterproof, and is air tight, because of the complete filling of its pores by the said material. At the same time it is flexible, because the said filler permanently retains its softness and fluidity. Combined with this flexibility is the characteristic that there is a hard skin which forms an elastic, tough, superficial coating for resistance against abrasion, for binding the fibers, and for preventing the access of air to the parts of the filler which are within. As rapidly as this skin is worn away by use, it is replaced by a drying of that part

of the filler which was exposed by its being worn away. For these reasons the filler has the characteristic that it is fluid in form and effect, so far as the mass of it is concerned, and yet dries into a thin, tough, hard film at the surface of the sole. The oil, wax, or jelly, which is of non-drying characteristic, and which retains its softness at all ordinary temperatures, keeps the whole sole flexible and bendable, being capable of exuding and shifting in such minor directions as necessary in the interstices among the fibers. And it serves as a vehicle or carrier for the drying wax, drying oil and driers, holding them always in readiness to perform their function, the production of a superficial tough skin, whenever they get access to the atmosphere by abrasion of the existing skin. It is evident that other material may be used having these qualities. For the blown oil, oil of the flaxseed is preferred, though doubtless oil of other origin can be used; and carnauba wax or its equivalent on account of its very drying qualities. These two ingredients or their equivalents, with the aid of a suitable drier, make a surface of the composition that is hard, firm, and clean, and neither oily nor sticky.

The said product may be used for various purposes, one of which, for illustration, is as outer soles for shoes. When so used it has the following advantages as compared with leather: It is waterproof; it is a non-conductor of heat; it is permanently flexible and resilient, owing to the elasticity of the fibers, the film, and the skin and the freedom from stiffness maintained by the filler; it has a fibrous surface which does not acquire the smoothness of leather or rubber under abrasion, and, for that reason, and because of the material in the superficial skin produced by the drying, does not slip on pavement. In addition it has all of the qualities of the unfilled material, (except that its pores are filled), in that it neither shrinks nor swells, as leather does under changes of moisture; it is fast in color; it is of uniform flexibility, whereas the flexibility of leather varies in different hides and in different parts of the same hide; it will not check nor crack as leather does; it is cheaper than leather; and there are further economies resulting incidentally such as the saving of time and labor of mulling, involving a saving of expense; the elimination of the sorting operation, and the freedom of the stock from culls.

Oil from the flaxseed or the cotton seed, or China wood oil or other oil may be substituted as equivalents for the drying oil herein mentioned. For the non-drying oil petroleum products have advantages in availability, cost, freedom from odor, etc., but, doubtless, wax or jelly like products of fish oil, degras or other materials may be substituted. And obviously other fibrous material, or fibers arranged otherwise, might be substituted for the wool felt. The initial combination of liquid and fibers followed by the drying of the liquid into film form, pulls the fibers together and binds them firmly; the pulverized mineral solids add strength by filling in interstices to some degree and thus making the bond of fibers to each other stronger, with the drying oil acting as a binder. Insertion of the described filler into the interstices of the product makes the product waterproof and stiffer or less crushable, keeps its interior soft, and flexible in a way which, as compared with rubber, does not deteriorate with lapse of time, and provides it with a continuous, self-renewing, hard, dry, elastic surface. The suitability of such a material for shoe soles will be understood when one considers that the act of walking tends to produce a suction in the sole, because the convex bending of the sole at each step stretches open the superficial pores. In the case of leather this automatically draws into the sole any moisture which is on the surface of the pavement, by suction as well as by capillary action. In the product of the invention the result cannot follow because the pores are already full. It is therefore an important feature that the filling is mobile; that the structure as a whole is elastic, so that the pores can change shape; and that the filling can change its position accordingly and keep them filled when the sole is bent as in walking. An important feature in the attainment of the desired qualities is the elimination of rosin from among the ingredients, this being a material that has often been proposed for use for leather substitutes, and also the elimination of other stiff ingredients such as a shellac and glue, which either will stiffen permanently, or will not penetrate properly before they set, or which unless protected by other chemicals are liable to soften under exposure to water. Without saying that these ingredients must be absolutely excluded, experience has shown that a better product is produced without them.

The durability under wear depends in part on the persistence with which the fibers retain their positions. This may be improved by using a woven fabric, arranged centrally with fibers attached to both sides of it by felting. Such a web eliminates stretching when the product is used for such purposes as power transmission belts, and contributes to the strength. For shoe soles strong and coarse woolen fibers are preferably used. When the product is to be used for trunks and bags or other purposes requiring it, it may be finished by an enamel coating and by embossing. In the process

of manufacture the proportion of blown oil may be increased with respect to the proportion of drier in cases where more flexibility of the product is desired, and of course changes may be made in other respects according to needs. Naphtha, for example, is a type of what is referred to in the claims as "fugitive oil," meaning a liquid which is introduced and remains only temporarily, being readily evaporative at ordinary temperatures or at the temperature to which the mixture is subsequently subjected. The naphtha may be aided in its function of reducing the viscosity of the liquid by adding heat to the mixture, although if this increases the wastage of naphtha it may be preferred to omit the heating at this stage, unless this step is carried out in a closed space. In the drying which immediately follows, it is preferable to arrange the sheets in parallelism in a closed space, and then to force a blast of heated air through the passages between the sheets, as by power fans. By suitably confining the air, which thus becomes laden with naphtha, the naphtha may be recovered for repeated use. A temperature of 100° more or less above the atmosphere increases the speed of evaporation and also increases the speed and completeness with which the process of oxidation of the drying oils goes forward. When the drying oil composition is made of the particular ingredients and proportions mentioned, its elasticity after the oxidation process is noticeable, resembling that of rubber. This coupled with the inherent elasticity of the fibers makes the completed product both flexible and elastic.

For some uses the carnauba wax or other ingredient which dries into a hard tough film on exposure to atmosphere may not be needed in the filler. In that case the filler can more easily be made to exude, but so long as it remains in place, where it is held by atmospheric pressure, the waterproof and other qualities which it imparts continues.

What is claim is:—

1. A process of making resistant sheet material comprising the preparation of a mixture of intensely-drying oil, fugitive oil and pulverized solids; thoroughly impregnating a fibrous fabric therewith; drying the impregnated fabric by exposure to air; and further impregating with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant having jelly-like consistency, and containing hard drying wax, which on oxposure oxidizes into a superficial film.

2. A process of making resistant sheet material comprising the preparation of a mixture of intensely-drying oil, fugitive oil and pulverized solids; thoroughly impregnating a fibrous fabric therewith; drying the impregnated fabric by exposure to air; and further impregnating with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a mineral jelly, and containing hard drying wax, which on exposure oxidizes into a superficial film.

3. A process of making resistant sheet material comprising the preparation of a mixture of intensely-drying oil, fugitive oil and pulverized solids; thoroughly impregnating a fibrous fabric therewith; drying the impregnated fabric by exposure to air; and further impregnating with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant having jelly-like consistency, and containing hard drying vegetable wax, which on exposure oxidizes into a superficial film.

4. A process of making resistant sheet material comprising the preparation of a mixture of intensely-drying oil, fugitive oil and pulverized solids; thoroughly impregnating a fibrous fabric therewith; drying the impregnated fabric by exposure to air; and further impregnating with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of mineral jelly and containing carnauba wax.

5. A process of making a resistant sheet material comprising the preparation of an elastic, fibrous and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant and containing a small proportion of hard drying wax which on exposure oxidizes into a superficial, elastic film.

6. A process of making a resistant sheet material comprising the preparation of an elastic, fibrous and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant and containing a small proportion of hard drying wax which on exposure oxidizes into a superficial, elastic film, the said impregnation being accomplished by reducing the viscosity of the said material temporarily.

7. A process of making a resistant sheet material comprising the preparation of an elastic, fibrous and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant and containing a small proportion of hard drying wax which on exposure oxidizes into a superficial, elastic film; the said impregnation being accomplished by heating the said impregnating material thereby reducing its viscosity and immersing the said porous fabric therein.

8. A process of making a resistant sheet

material comprising the preparation of an elastic, fibrous and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant and containing a small proportion of hard drying wax which on exposure oxidizes into a superficial, elastic film; the said impregnation being accomplished by heating the said impregnating material thereby reducing its viscosity and immersing the said porous fabric therein; and subsequently compressing the impregnated fabric between hot rollers.

9. A process of making a resistant sheet material comprising the preparation of an elastic, fibrous, and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant and containing a small proportion of hard drying wax which on exposure oxidizes into a superficial, elastic film; the whole being substantially free from ingredients which become stiff and brittle at ordinary low atmospheric temperatures.

10. A fibrous and filmy fabric having pores filled with a viscous lubricant in which the film portion of the material surrounds and binds together the individual fibers, there being pulverized solids present among the fibers and likewise bound in the fabric; said filmy portion being composed of oxidized drying oils and said lubricant having within it a small proportion of hard drying wax.

11. A fibrous and filmy fabric having pores filled with a viscous lubricant having mixed with it a small proportion of hard drying wax, sufficient in quantity to produce an elastic film by oxidation when exposed at the surface.

12. A fibrous and filmy fabric having pores filled with a viscous lubricant having mixed with it a small proportion of carnauba wax, sufficient in quantity to produce an elastic film by oxidation when exposed at the surface.

13. A fibrous and filmy fabric having pores filled with a viscous lubricant, in which the filmy portion of the material surrounds and binds together the individual fibers, there being pulverized solids present among the fibers and likewise bound in the fabric; said filmy portion being composed of oxidized drying oils and said lubricant having an ingredient which produces an elastic film when exposed at the surface.

14. A fibrous and filmy fabric having pores filled with a viscous lubricant, in which the filmy portion of the material surrounds and binds together the individual fibers, there being pulverized solids present among the fibers and likewise bound in the fabric; said filmy portion being composed of oxidized drying oils.

15. A process of making a resistant sheet material comprising the preparation of an elastic, fibrous and filmy porous fabric and impregnating the same with a material which at ordinary temperatures is a fluid of high viscosity composed mainly of a non-drying lubricant.

Signed by me at Boston, Mass., this 25th day of September, 1916.

HERBERT F. KENWORTHY.

Witnesses:
EVERETT E. KENT,
CHARLES A. DE COURCEY.