

2,824,816

METHOD FOR TREATING LEATHER

Ian C. Somerville, Willow Grove, and Richard F. M. Fisher, Jenkintown, Pa., assignors to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware

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This application is concerned with improved methods for the impregnation of leather, and is particularly concerned with an improved method for imparting water-repellent properties to leather and especially without objectionably decreasing the permeability of the leather to water vapor.

Up to very recent times, the most common method of making leather resistant to water consisted in "stuffing," i. e., drumming emulsions of wax or grease into the tanned skins prior to drying down. When this is utilized in making shoe upper leather, it is found that although this shows good repellency to water in a static test, serious leakage takes place soon after the leather is flexed repeatedly such as in the flexing that occurs across the vamp in walking. Moreover, the presence of the wax or grease in the interstices between the fibers seriously reduced the water vapor permeability of this leather, making the shoes uncomfortable in warm weather, while solidification at low temperatures makes these shoes stiff and less flexible under winter conditions.

A considerable improvement was effected recently when oil-in-water emulsions of various water-insoluble organic polymers were applied to partially fatliquored shoe upper leather, and then broken by change in pH value, brought about either by reaction with the leather itself or by the addition of an organic acid or by a combination of these factors. This also resulted in deposition of the polymer largely in the spaces between the fibers, but in this case it has been claimed that 50% of the original water-vapor permeability is retained while the water repellency under dynamic conditions is greatly improved over that for the customary stuffed shoe leather. Parallel experiments on glove leather have been stated to produce comparable results on chrome tanned horse fronts.

The introduction of water-insoluble compounds into leather by dissolving them in a suitable non-aqueous solvent has been known for a considerable period. In this way better penetration is frequently effected and the organic materials tend to coat the surface of the fibers rather than be deposited in the interstices between the fibers. Probably one of the main reasons why it has not been more widely used in commercial practice is an economic one; namely, that it is much more expensive to use organic solvents than it is to operate in an aqueous medium. One of the factors in this higher cost is that high concentrations of the impregnant have to be used. Most of the impregnant remains behind in the large excess of solvent in which it is readily soluble, because it has little affinity in this medium for the leather fibers with which it is in contact.

In accordance with the present invention, a hydrophobic impregnant, preferably of a waxy or resinous material of viscous or plastic character, is dissolved in a hydrophobic organic solvent selected from the class of hydrocarbon and chlorinated hydrocarbon solvents, and the leather is agitated within the solution until an equilibrium condition of distribution of the impregnant between

the solvent and the leather is substantially obtained. A hydrophilic water-soluble solvent having some miscibility with the initial hydrophobic solvent and which reduces the solubility of the impregnant in the solvent system is then added gradually or in periodically repeated doses to favor the deposition of the impregnant within the leather and the leather is further agitated to exhaust the impregnant from the solution. The hydrophilic solvent comprises at least a predominant proportion of organic solvent material and may contain water. The hydrophilic solvent must have some miscibility with the hydrophobic solvent and the impregnant must have much less solubility in the hydrophilic solvent than in the initial hydrophobic solvent. It has been found that this system of operation thoroughly impregnates the leather and distributes the impregnant substantially uniformly on the fibers of the leather without objectionably decreasing the permeability of the leather to moisture vapor. After sufficient exhaustion in this manner, the leather is removed from the solution, drained, and dried.

In practice, the procedure of the present invention is performed upon a tanned leather in air-dry condition after dyeing and fatliquoring, but preferably after only a portion of the normal fatliquor that is customarily given. After the treatment with the impregnant, the leather may be subjected to a prolonged treatment at elevated temperatures for the purpose of curing the impregnant if it is of a nature to be further polymerized, condensed or both polymerized and condensed to an insoluble and/or infusible condition. The leather may also be subjected to the usual subsequent treatment of lacquering or finishing in other ways depending upon the purpose for which the leather is intended. In most cases, however, the treatment with the water-repellent impregnant is the final treatment of the leather. If there is no objection to water vapor impermeability in the leather because of the use to which it is intended to be put, the leather which is to be impregnated in accordance with the present invention may have been previously treated by a so-called stuffing procedure. However, the present invention is primarily directed to the making of leathers which are intended for use as gloves, shoes, garments, and the like water-repellent without objectionable loss in water-vapor permeability and stuffing or equivalent processes are not contemplated in these cases.

The first step in the process of the invention involves the preparation of a solution of the hydrophobic impregnant or water-repellent material in the hydrophobic solvent. The volatile solvent used may be of aromatic, naphthenic or aliphatic hydrocarbon type, such as benzene, toluene, xylene, cyclohexane, tetrahydronaphthalene, decahydronaphthalene, turpentine, solvent naphthas, mineral thinners, high flash point naphthas that are frequently referred to as safety solvents, light kerosene, or chlorinated hydrocarbons, such as ethylene dichloride, chloroform or carbon tetrachloride. The solvent may be a mixture of several of the above mentioned solvents. The concentration of the impregnant within the solution may be from 1% to 15% by weight and it may even approach the saturation limit at the temperature of operation. In some cases, the viscosity of the resulting solution may require the concentration to be kept within the lower part of the range specified above, but even at the lower concentrations the method of the present invention effects a thorough impregnation and substantially uniform distribution of the impregnant within the leather structure. The amount of the impregnant used in the bath or solution which is applied to the leather may amount to from 1% to 60% by weight of the leather, and for most practical purposes the preferred amount is from 5% to 20% by weight of the leather. The bath ratio, by which is meant the ratio of the weight of the solution to the weight

of the dry leather, may be from 2:1 to 10:1 and it is preferred that this bath ratio be from 4:1 to 6:1.

The leather is agitated within the solution of the impregnant at any temperature from room temperature up to about 65° C. The temperature of operation should be appreciably below the boiling point of the solvents used. Generally, it is preferred to operate at temperatures from room temperature to 50° C. The agitation of the leather within the solution may be effected in the type of drums customarily used in tannery practice for tanning or fat-liquoring in which the drums are rotated to effect tumbling of the leather within the solution. Of course, any other equipment that will effect agitation of the leather within the solution without harming the leather may be employed. For example, this agitation may be effected by repeated dipping of the leather into the impregnating bath. The agitation or tumbling of the leather within the solution is carried on for a period of time which is sufficient to effect thorough impregnation and distribution. This time may vary from about one-half to three or four hours in order to bring the system substantially to an equilibrium condition of distribution of the impregnant between the solution and the leather fibers. The particular time employed may vary in dependence upon the particular leather, its ease of penetration and thickness.

After, as a result of the agitation of the leather within the solution, the distribution of impregnant has come to substantial equilibrium, the hydrophilic solvent is added gradually or in portions at successive intervals. As stated previously, the hydrophilic solvent must have some miscibility with the initial hydrophobic solvent and the impregnant should be substantially insoluble in the hydrophilic solvent or it must have much less solubility therein than in the initial solvent. Sufficient hydrophilic solvent is added to markedly reduce the solubility of the impregnant in the resulting solvent medium, and the amount of hydrophilic solvent required to bring about this condition may be from 3% to 150% by weight of the initial solvent; preferably from 20% to 50% on the weight of the initial solvent is added. The amount depends on the particular hydrophobic solvent and the particular hydrophilic solvent that are mixed as well as on the particular impregnant dissolved in the initial solvent. The addition of water to the hydrophilic solvent even more effectively decreases the solubility of the impregnant in the solvent system. Thereby a deposition of the impregnant on the leather fibers is favored and this is effected without bringing about a precipitation of the impregnant within the solvent medium. In the preferred operation, sufficient of the hydrophilic solvent is added to separate the system into two liquid layers or phases, one of which is primarily a hydrophobic layer and the other is primarily a hydrophilic layer. The hydrophilic solvent employed may be a lower alcohol, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, or isobutyl alcohol, ethylene glycol, diethylene glycol, the methyl or ethyl monoethers of ethylene glycol or diethylene glycol, acetone, dioxane, methyl ethyl ketone, methyl acetate, ethyl acetate, or a mixture of two or more of these individual solvents, including particularly a mixture of one or more of these organic solvents with water.

The hydrophilic solvent employed in any particular instance depends upon the particular impregnant used therein and its solubility characteristics. Generally, a hydrophilic solvent is selected in which the impregnant has markedly lower solubility than in the hydrophobic solvent initially used. In addition, water can be added to a hydrophilic organic solvent or a mixture thereof to provide a mixed hydrophilic solvent in which the impregnant has even lower solubility than in the straight organic hydrophilic solvent. For example, when the simple monohydric alcohols mentioned hereinbefore are used with the preferred acrylic polymer impregnants described hereinafter, it is generally preferred to add water in an amount of at least about 3% by weight based on the

total weight of the mixed hydrophilic solvent to reduce the solubility of the impregnant in the resulting solvent system. Further improvement is generally obtained as the water is increased in proportion up to about 25% to 30% by weight and in some instances to even higher proportions. Even in those systems in which the impregnant is of reduced solubility in an individual hydrophilic organic solvent, water may be present in amounts of 3% by weight or more with somewhat improved deposition of the impregnant on the leather and corresponding better exhaustion of the impregnating system. As pointed out above, in preferred instances, sufficient hydrophilic solvent is added to effect a separation into two liquid layers which facilitates the recovery of impregnant and/or solvents from the spent liquor system. Those systems in which at least 3% of water is present in the hydrophilic solvent frequently produce a separation into two liquid layers or phases and they are accordingly preferred for this additional reason. However, such separation also occurs even with other hydrophilic solvent systems which do not contain water when the hydrophilic solvent is used in an amount which exceeds its limit of miscibility in the hydrophobic solvent.

During the addition of the hydrophilic solvent, or after each addition of a portion thereof, the agitation of the leather is continued within the liquid system. After the completion of the addition of the hydrophilic solvent or after each addition when several are made, the agitation is effected for a period of time sufficient to bring the system to a new equilibrium condition in respect to the distribution of the impregnant between the leather and either the solvent system or the hydrophobic layer of the solvent system, if two layers or liquid phases form. This may involve continued agitation for a period of about one-half to three hours total time after the start of the addition of the hydrophilic solvent to the system.

After completion of the agitation within the liquid system, the leather is removed from the liquid, drained and dried. When the impregnant is of a thermosetting character, the drying may serve to cure the impregnant to its final condition of polymerization or condensation, or, if desired, continued heating may be carried out beyond the completion of drying to bring about the final condition of polymerization or condensation of the impregnant within the leather.

The impregnant that may be applied to leather for effecting the treatment may be any hydrophobic material which, in its final condition in the leather imparts to the leather an essentially flexible character at room temperature and at all other normal conditions of use. For this purpose, waxy or resinous materials of hydrophobic character are useful. For example, the waxes consisting of long-chain saturated hydrocarbons having from 14 to 30 carbon atoms, such as paraffin waxes, may be used. Waxy materials of ester types, such as the esters of natural or synthetic origin of long-chain saturated aliphatic acids and/or of saturated aliphatic alcohols having from 8 to 30 carbon atoms are also included. Examples of such esters are beeswax, carnauba wax, tallow, montan wax, wool fat, stearyl acetate, ethylene glycol stearate. Similarly, waxy esters of polyhydric alcohols other than glycerol may be used. Examples are the esters of erythritol, hexitans or hexides which are substantially completely esterified with saturated fatty acids, e. g., sorbide distearate, sorbitan tetrapalmitate, mannidedipalmitate, and so forth. Similar waxy esters of aliphatic dicarboxylic acids with long-chain alcohols containing 8 to 18 and up to 30 or more carbon atoms are useful. Examples are di-n-hexadecyl succinate, di-n-dodecyl succinate, di-n-octadecyl succinate, diesters of n-octanol, n-decanol, n-dodecanol, n-hexadecanol, and n-octadecanol with n-hexylsuccinic acid, n-heptylsuccinic acid, n-octylsuccinic acid, adipic acid, and glutaric acid.

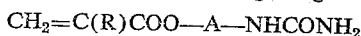
Another type of hydrophobic water-repellent comprises the long-chain isocyanates having from 8 to 30 carbon

atoms, such as octyl isocyanate, decyl isocyanate, dodecyl isocyanate, undecyl isocyanate, hexadecyl isocyanate, octadecyl isocyanate, montanyl isocyanate.

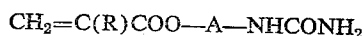
Another type of hydrophobic impregnant includes the long-chain ketenes such as dodecyl ketene, hexadecyl ketene, and octadecyl ketene. Similarly, long-chain ketones, such as dodecylmethyl ketone and di-dodecyl ketone may be used. Long-chain amides, such as stearamide, may be employed.

Various polymeric resinous materials may be applied to leather by the procedure of the present invention, such as various types of silicones, including the organo-poly-siloxanes, such as the methyl polysiloxane resin intermediate, methyl-phenyl poly-siloxane resin intermediate, or ethylphenyl polysiloxane intermediate of Examples 1 to 6 of U. S. Patent 2,389,477.

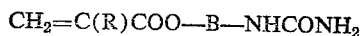
Other hydrophobic polymeric resinous materials that may be used include the water-insoluble polymers obtained by the polymerization of one or more monoethylenically unsaturated materials, such as ethylene, vinyl chloride, vinyl bromide, vinyl fluoride, vinyl esters of long-chain fatty acids, such as lauric, myristic, palmitic, and stearic acids; homopolymers of ureido esters of acrylic and methacrylic acids having the general formula



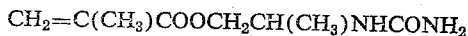
where R is methyl or hydrogen and A is an alkylene group having from 5 to 14 carbon atoms; esters of acrylic, methacrylic, or itaconic acids with long-chain alcohols, e. g., octyl, decyl, undecyl, lauryl, myristyl, hexadecyl, and octadecyl alcohols including (a) copolymers thereof with 2% to 95% of other monoethylenically unsaturated copolymerizable materials which alone would produce hydrophobic homopolymers, such as styrene, vinyl acetate, and esters of acrylic, methacrylic or itaconic acids with lower alcohols having from 1 to 7 carbon atoms, especially the methyl, ethyl, isopropyl, and butyl esters of acrylic, methacrylic and itaconic acids, and ureido esters of acrylic and methacrylic acids having the general formula



where R is methyl or hydrogen and A is an alkylene group having from 5 to 14 carbon atoms and (b) copolymers thereof with 1% to 15% of other monoethylenically unsaturated copolymerizable monomers which alone would produce hydrophilic homopolymers such as acrylic acid, methacrylic acid, itaconic acid, and ureido esters of acrylic and methacrylic acids having the general formula



where R is methyl or hydrogen and B is alkylene group having from 2 to 4 carbon atoms, such as β -ureidoethyl methacrylate, β -ureidoethyl acrylate,



and $\text{CH}_2=\text{CHCOOCH}_2\text{CH}(\text{CH}_3)\text{NHCONH}_2$.

Water-insoluble polymers of monoethylenically unsaturated molecules comprising at least 50% by weight of at least one ester of acrylic, methacrylic, or itaconic acids with higher saturated fatty alcohols having 8 to 18 carbon atoms are preferred impregnants because of their high degree of hydrophobicity, their flexibility at low temperatures, such as are encountered in Arctic regions, as well as at temperatures normally encountered elsewhere, their resistance to migration and consequent permanence in the leather under both static and dynamic conditions, and their quality of imparting water-repellency to the leather with a minimum loss of not over about 15% of its initial permeability to water-vapor.

When polymeric materials are employed, it is preferred that their degree of polymerization should not be so high as to render solutions of the desired concentration in hydrophobic solvents so viscous as to hinder or prevent

the penetration of the leather structure by the solution. Generally, the degree of polymerization should not be so high that solutions of 30% of the polymer in the selected hydrophobic solvent, such as toluene, are over 1000 centistokes at 100° F.

The procedure of the invention may be applied to all types of leather intended for all sorts of uses. It is particularly important for garment leathers that are intended to be used as wearing apparel, such as shoes, gloves, caps and jackets. The leather treated by the present invention is outstanding in respect to its combined properties of being highly water-repellent, and at the same time highly permeable to water vapor. Because of these characteristics, gloves, shoes, and the like can be worn without discomfort since their vapor permeability allows them to "breathe" while their water-repellency hinders the transmission of liquid water there-through. In addition, the procedure of the present invention is so effective in uniformly and thoroughly distributing the water-repellent materials within the fibers of the leather structure that the impregnated leathers retain their water-repellency through long periods of normal flexure. The leather treated by the present invention also shows good scuff-resistance and general wearing qualities.

The procedure of the present invention is applicable to leathers that have been tanned in any way whatsoever, such as by a chrome tannage, an alum tannage, vegetable tannage, a zirconium tannage, a synthetic tannage as well as to leathers which have been retanned.

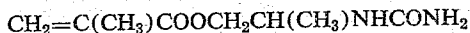
In the examples which follow and are illustrative of the invention, the flexing test for measurement of water-repellency under dynamic testing conditions is a modification of that developed by Maeser as adopted as the Federal Specification for estimation of water penetration designated KK-L-311a; methods 8021 and 8031. This test method was modified in that a leather sample having a size of 4 3/8" by 4 1/4" was used and in that, instead of the chamois wick, pieces of weighed cotton were placed in the trough after initial penetration of water had occurred, and these pieces were changed at 250, 500, 750, 1000 and 2000 flexes and the sum of the gain in weight taken as Water Transmitted. At the end, the increase in weight of the leather sample, after wiping off excess surface water, was taken as Water Absorbed, the Total Water being that absorbed plus that transmitted.

Example 1

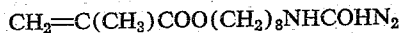
(a) Twenty pounds of a copolymer (obtained by the polymerization of a mixture of about 1 part by weight of cetyl methacrylate and about 2 parts by weight of stearyl methacrylate and having a viscosity of 520 centistokes in toluene at 30% concentration and at 100° F.) were dissolved in 400 pounds of a mineral thinner (essentially an aliphatic hydrocarbon mixture of boiling point range from 300 to 390° F.). Chrome-tanned horse fronts (100 pounds), which had been given 10%, that is one-half the normal amount, of fatliquor for glove leather, were taken in the dry condition after staking and drummed in the mineral thinner solution. After three hours tumbling in the drum, 10% by volume (based on the initial solvent) of isopropyl alcohol (containing 10 parts water by volume per 100 parts) was added and the tumbling in the drum was continued for one-half hour. Two further similar additions were then made at one-half hour intervals, drumming being continued throughout and for one-half hour after the last addition, the skins were removed, allowed to drain and then hung in a warm room (110-120° F.) for 48 hours. After cooling to room temperature and taking out, the dry leather was found to have a soft, mellow feel. It had retained its original color and appearance and was free from stickiness and unpleasant odor. On subjection to the modified Maeser test above, it was found to withstand 5000 flexes to the First Leak and the Total Water amounted to one gram.

(b) In similar fashion, chrome-tanned horse fronts of the same character were drummed in 400% of a mineral thinner solution of the copolymer containing one part by weight of the copolymer in seven parts by weight of the mineral thinner so as to provide 50% of the copolymer based on the dry leather weight. After three hours drumming, the skins were removed, allowed to drain several hours and then hung in a warm room for 48 hours as above. Their feel and appearance were similar to that previously obtained but the modified Maeser tests gave values of about 1400 flexes to the First Leak after which time a total of one gram of water was obtained. Comparable test runs on the same type of glove leather without impregnation with the copolymer gave values of 500 flexes to the First Leak and a large value of about 120 grams Total Water. It thus appears that the special method of application imparts improved water-repellency when tested under dynamic conditions even when the initial concentration of the water-repellent impregnant within the initial hydrophobic solvent is only about 4 to 5% as compared to a concentration of 12.5% when impregnation is effected without the subsequent introduction of hydrophilic solvents.

(c) Polymers of lauryl methacrylate, octyl acrylate, lauryl acrylate, myristyl acrylate, homopolymers of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_{12}\text{NHCONH}_2$, and also copolymers of 95% octyl acrylate with 5% β -ureidoethyl methacrylate, 85% cetyl acrylate with 15% β -ureidoethyl acrylate, 90% lauryl acrylate with 10% of



and 25% decyl acrylate with 75%



were applied to chrome-tanned horse fronts by the procedure of paragraph (a) above. The resulting leathers showed excellent resistance to transmission of liquid water while remaining highly permeable to water vapor.

Example 2

(a) Chrome-tanned horse fronts in air-dry condition were treated with 20% of the same polymer in mineral thinner as described in Example 1(a). In this case, however, 10% (by volume of the initial solvent) of isopropyl alcohol, containing 30 parts water (by volume) per 100 parts, was then added and drumming continued for one-half hour. Two further similar additions were then made and drumming continued one hour, after which the skins were processed as described in Example 1. In testing as before, these leathers showed nearly 4000 flexes to First Leak and almost 5 grams Total Water.

(b) The same procedure was followed except that only 10% of the polymer was used. The leather showed 3000 flexes to First Leak and 8 grams Total Water.

Example 3

Chrome-tanned horse fronts in air-dry condition were treated with 20% of the same polymer in mineral thinner as described in Example 1(a). In this case, however, 10% (by volume of the initial solvent) of methoxyethanol was added and drumming continued one-half hour. One further similar addition was made and drumming continued one hour; then skins were removed and processed as usual. In testing for water-repellency these leathers showed over 5000 flexes to First Leak and 1½ grams Total Water.

Example 4

Chrome-tanned horse fronts in dry condition were treated with 20% of the copolymer of Example 1(a) in a solution containing 45% mineral oil and 50% toluene, all percentages on dry skin weight. After drumming for 4 hours, 3% (by volume of the initial solvent) of isopropyl alcohol, containing 4 parts water (by volume) was added, and drumming continued one-half hour. Two further similar additions were made at half-hour intervals

drumming being continued throughout and one hour after the last feed; then the skins were removed and processed as usual. In testing for water-repellency these leathers showed an average of 5000 cycles to First Leak and 1½ grams Total Water.

Example 5

Dry chrome-tanned heavy duty cowhide glove leather was drummed with 400% (on the leather weight) of a mineral thinner solution of 10% (on the leather weight) of octadecyl isocyanate. After drumming three hours, 25% (by volume of initial solvent) of isopropyl alcohol containing 10% water by volume was added in five feeds at half-hour intervals, drumming being continued throughout and one hour after the final addition. On removal, draining and drying in a warm room 48 hours, the Maeser test showed 17,500 flexes before First Leak and Total Water of 2 grams. Without addition of the hydrophilic solvent, the test showed only 2500 flexes before First Leak and Total Water of 4½ grams.

Example 6

Dry chrome-tanned horse front glove leather was drummed with 400% (on leather weight) of a mineral thinner solution of 5% (on leather weight) of a methyl polysiloxane (Dow-Corning 1109). After drumming 3 hours, 50% (by volume of initial solvent) of isopropyl alcohol containing 10% water by volume was added in five feeds at half-hour intervals drumming being continued throughout and for one hour after the final addition. On removal, draining and drying in a warm room 48 hours, the Maeser test showed 13,000 flexes before First Leak and Total Water of 2 grams. Without addition of the hydrophilic solvent, the test showed only 1000 flexes before First Leak and Total Water of 17 grams.

Example 7

Dry chrome-tanned horse front glove leather was drummed with 500% (on leather weight) of a solution in a blend of 5 parts mineral thinner and 3 parts carbon tetrachloride of 10% (on leather weight) of octadecylketene. After drumming 3 hours, 50% (by volume of initial solvent) of isopropyl alcohol containing 10% water by volume was added in five feeds, drumming being continued throughout and one hour after the final addition. On removal, draining and drying in a warm room 48 hours, the Maeser test showed 4700 flexes before First Leak and Total Water of 1 gram. Without addition of the hydrophilic solvent, the test showed only 440 flexes before First Leak and 46 grams of Total Water.

Example 8

Dry chrome-tanned horse front glove leather was drummed with 400% (on leather weight) of a solution in mineral thinner of 20% (on leather weight) of the copolymer of Example 1(a) and 2% (on leather weight) of the silicone of Example 6. After drumming 3 hours, 50% (by volume of initial solvent) of isopropyl alcohol containing 10% water by volume was added in five feeds, drumming being continued throughout and one hour after the final feed. On removal, draining and drying in a warm room 48 hours, the Maeser test showed 9700 flexes before First Leak and Total Water of 1½ grams. Without the addition of the hydrophilic solvent, the test showed only 1000 flexes and 4½ grams Total Water.

Example 9

A dry chrome-tanned deerskin for glove or garment leather was drummed with 400% of a solution in mineral thinner of 20% of the copolymer of Example 1(a) and 2% of the silicone of Example 6. In this case, 10% (by volume of initial solvent) of isopropyl alcohol, containing 30 parts water (by volume) per 100 parts, was added and drumming continued one-half hour. Two

further similar additions were made at half-hour intervals and drumming continued throughout and one hour after the last feed; then the skins were removed and processed as usual. In testing for water-repellency, the leather was flexed over 40,000 times and the testing was stopped before any leaking occurred; at the time testing was stopped, it showed only 1¼ grams of Total Water.

Example 10

A dry, stuffed army retan side leather (which is a chrome-tanned leather heavily retanned with vegetable extract) was substituted for the chrome-tanned horse fronts and carried through the process of Example 1(a). The resulting leather, while not nearly as water-repellent as straight chrome-tanned leather, on testing, showed three times as many flexes to First Leak and half the amount of Total Water that the same leather showed without treatment with the copolymer.

Example 11

Dry chrome-tanned horse fronts were treated with 20% of beef tallow in a solution containing 400% mineral thinner. After drumming 3 hours, 150% (by volume of initial solvent) of isopropyl alcohol containing 10% water by volume was added in eight feeds at 20-minute intervals, drumming being continued throughout and ½ hour after the final addition. On removal, draining, and drying in a warm room 48 hours, the Maeser test showed 2,500 flexes before First Leak and Total Water of 1.5 grams. Without addition of the hydrophilic solvent, the test showed only 630 flexes before First Leak and Total Water of 50 grams. The untreated leather showed 590 flexes before First Leak and Total Water of 66 grams. (All values are averages of three tests.)

Example 12

Dry chrome-tanned horse fronts were treated with 20% of carnauba wax in a solution containing 1000% of carbon tetrachloride. After drumming 3 hours, 54% (by volume of initial solvent) of isopropyl alcohol containing 10% (by volume) of water was added in six feeds at 20-minute intervals, drumming being continued throughout and ½ hour after the final addition. On removal, draining, and drying, the Maeser test showed 1200 flexes before First Leak and Total Water of 2.5 grams. Without addition of the hydrophilic solvent, the test showed only 1000 flexes before First Leak and Total Water of 48 grams whereas the untreated leather showed 590 flexes before First Leak and Total Water of 66 grams. (All values are averages of three tests.)

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. The method of treating leather comprising agitating the air-dry leather with a solution in a volatile hydrophobic organic solvent medium of a hydrophobic impregnant until substantial impregnation is effected, adding a water-soluble hydrophilic solvent selected from the group consisting of volatile organic solvent and aqueous solutions of volatile organic solvents comprising at least a predominant proportion of organic solvent in which the impregnant has substantially less solubility as compared to the hydrophobic solvent while continuing the agitation until additional impregnation is effected, removing the leather from the liquid system, draining it, and drying it.

2. The method of impregnating leather comprising agitating the air-dry leather with 200% to 1000%, on the weight of the leather of a solution in a volatile hydrophobic organic solvent medium of 1% to 50% on the weight of the leather of a hydrophobic impregnant until substantial impregnation is effected, adding 3% to 150% by volume, based on the volume of initial solvent, of a water-

soluble hydrophilic solvent selected from the group consisting of volatile organic solvents and aqueous solutions of volatile organic solvents comprising at least a predominant proportion of organic solvent in which the impregnant has substantially less solubility as compared to the hydrophobic solvent and continuing the agitation until additional impregnation is effected, removing the leather from the liquid system, draining it, and drying it.

3. A method as defined in claim 2 in which the impregnant comprises a polymer of at least one monoethylenically unsaturated compound.

4. A method as defined in claim 2 in which the impregnant comprises a polymer of at least one ester of an acid of the group consisting of acrylic, methacrylic and itaconic acids with a higher aliphatic alcohol having from 8 to 30 carbon atoms.

5. A method as defined in claim 2 in which the impregnant comprises a polymer of an ester of methacrylic acid with an alcohol having from 8 to 30 carbon atoms.

6. A method as defined in claim 2 in which the impregnant comprises a copolymer of cetyl methacrylate with stearyl methacrylate.

7. A method as defined in claim 2 in which the impregnant comprises tallow.

8. A method as defined in claim 2 in which the impregnant comprises a long-chain isocyanate having 8 to 30 carbon atoms.

9. A method as defined in claim 2 in which the impregnant comprises octadecyl isocyanate.

10. A method as defined in claim 2 in which the impregnant comprises a long-chain ketene having 8 to 30 carbon atoms.

11. A method as defined in claim 2 in which the impregnant comprises octadecyl ketene.

12. The method of impregnating leather comprising agitating the air-dry leather with 200% to 1000% of, on the weight of the leather, a solution in a volatile hydrophobic organic solvent medium of 1% to 50% on the weight of the leather of a hydrophobic impregnant until an equilibrium condition of distribution of the impregnant between the medium and the leather is substantially attained, then adding a sufficient amount of a water-soluble hydrophilic solvent selected from the group consisting of volatile organic solvents and aqueous solutions of volatile organic solvents comprising at least a predominant proportion of organic solvent in which the impregnant is insoluble, to form a system having two liquid phases and continuing the agitation until a new equilibrium condition of distribution between the liquid system and the leather is attained whereby to effect further exhaustion of the impregnant from the solution and further deposition of the impregnant on the leather, removing the leather from the liquid system, draining it and drying it.

13. A method as defined in claim 12 in which the water-soluble solvent is added in successive portions at spaced intervals, the agitation being continued after each addition until a new equilibrium condition of distribution between the liquid system and the leather is substantially attained before the next addition.

14. A method as defined in claim 12 in which the hydrophilic solvent comprises a water-soluble organic solvent and at least 3% by weight of water.

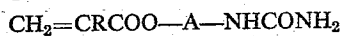
15. A method as defined in claim 12 in which the hydrophilic solvent comprises methoxyethanol.

16. A method as defined in claim 12 in which the hydrophilic solvent comprises isopropyl alcohol and 3% to 30% by weight of water.

17. A method as defined in claim 16 in which the impregnant comprises a polymer of at least one ester of an acid of the group consisting of acrylic, methacrylic and itaconic acids with a higher aliphatic alcohol having from 8 to 30 carbon atoms.

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18. A method as defined in claim 16 in which the impregnant comprises a water-insoluble polymer of a compound having the formula



where R is methyl or hydrogen and A is an alkylene group having from 2 to 14 carbon atoms.

19. A method as defined in claim 16 in which the impregnant comprises a copolymer of cetyl methacrylate with stearyl methacrylate.

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