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WATER RESISTANT LEATHER AND PROCESS OF MAKING THE SAME

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This invention relates to leather and more particularly to the treatment of leather to render it resistant to water penetration without detrimental modification of its other properties.

Leather is a valuable material, particularly for the manufacture of shoes and other articles of clothing, because of its pliability and porosity. The porosity is important on two scores. In the first place, the pores are so fine as to be of some value in giving the leather heat insulating properties. Secondly, and more important, when used in shoes or other close-fitting garments, the pores of the leather permit breathing, i. e. the escape of water vapor given off by the body, and thus maintain the comfort and health of the wearer. Leather however, has the disadvantage that the collagen fibers of which it is composed are hydrophilic in nature. Accordingly, water is taken up quite rapidly by leather and freely passes therethrough.

Heretofore, because of its importance, extensive research has been directed toward solution of the problem of producing waterproof leather. These efforts have for the most part, however, been directed toward filling the pores of the leather by "stuffing" it with oils, greases, and/or waxes during its manufacture, by applying "dubbing" or the like to finished leather articles, or by impregnating it with plastic materials such as resins or rubber. In the first two methods mentioned practically no improvement in waterproofness is obtained unless the amount of grease, oil, wax, or similar material placed in the pores of the leather is so great, about 50% or more, as to completely block the pores. Even with very large amounts of such pore-filling materials, the improvement in waterproofness is of limited scope and value since it is lost when the leather is flexed. This results from the fact that, as pointed out above, the leather fibers are hydrophilic and during flexing, therefore, the water either passes through the fibers or through the channels where the pore-filling material has pulled away from the pore walls.

Leather can be given a rather high degree of waterproofness by impregnation with resins or rubber. However, the resultant produce is completely non-porous and its flexibility is also reduced. Both the latter method and the "stuffing" referred to above, insofar as they block the pores of the leather, are undesirable for many purposes, leather which has been rendered completely impervious, for example, being no more suitable for use in making boots and shoes than sheet rubber. Experience in the armed services and elsewhere has shown conclusively the necessity of porosity in footwear and the extreme undesirability of using non-porous footwear, even when it is partially or wholly waterproof, except for limited periods of time.

An object of the present invention is, therefore, to provide leather which is substantially waterproof under conditions of use which involve bending and flexing, yet which has a high degree of porosity so as to permit passage of water vapor.

Another object of the invention is to provide leather which, although resistant to water penetration, is soft, flexible and porous.

A further object of the invention is to provide a process which will permit simplification of the methods now in use for tanning and finishing leather.

Still another object of the invention is to provide leather which is waterproof but is still flexible at low temperatures.

Other objects are to provide a treatment for leather to render it waterproof which is inexpensive, does not involve extensive apparatus, and is permanent in effect. Additional objects will be evident from the following specification and claims.

Applicant has made the discovery that certain derivatives of succinic acid are effective in accomplishing the foregoing objects. Among such derivatives that have been found suitable are alkylated succinic acids, such as alkyl or alkenyl substituted succinic acids. The surprising effectiveness of such compounds in waterproofing leather treated therewith in accordance with the present invention will be observed from the following examples:

EXAMPLE 1

A piece of finished upper leather 3¾ x 4⅜ inches in size was extracted with petroleum naphtha to remove any wax, grease, or oil. It was then treated with 10% of iso-octadecenyl succinic acid in solution in ethyl alcohol. After the treating agent had been absorbed in the leather, the specimen was heated for about 15 minutes at a temperature of 65° C.

The resistance to water penetration of the leather specimen so treated was determined by a flexing test developed in the leather laboratory of the National Bureau of Standards which subjects the leather to conditions which more nearly simulate natural use than former methods. In this test, the details of and apparatus for which are set forth in an article by Mieth Maeser in the Journal of the American Leather Chemists' Association, vol. XLII, page 401, et seq., August 1947, leather specimens are continuously flexed while covered with water. The time or the number of flexing cycles required for water to penetrate a specimen is taken as the measure of its waterproofness.

In an article on page 42 of the ASTM Bulletin for December 1947, it is stated with reference to this flexing test:

"A large number of commercial shoe-upper leathers have been tested by the new method. These leathers show, in general, a low water resistance. The average resistance of a large number of samples is approximately 200 cycles or flexes, which would correspond to walking distance of about ¼ mile. Stuffing the leather with large quantities of grease does not greatly improve the water resistance of leather until the amount of grease exceeds 50 per cent by weight. Leathers having grease contents in excess of 50 per cent are much more water resistant and may show resistances exceeding 10,000 flexes. Such leather, however, is not suitable for use in shoes or garments because of its impermeability to water vapor.

"Leather having an appreciable water resistance at room temperature shows much less resistance at lower temperatures, probably due to increased stiffness and cracking of the greases at the reduced temperature. This finding indicates that waterproofing of shoes at moderate temperatures may be easier than at reduced temperatures.

"In general, the studies show that leather offers higher resistance to penetration by water from the flesh side than from the grain side. The grain layer represents the principal water barrier and is more easily penetrated when in the normal position due to the higher stresses formed at the creases.

"Waterproofing agents tested by the Bureau have been found to have little effect in waterproofing leather. Among those tested have been several of the new water-repellant materials whose application to shoe-upper leather generally results in slightly reducing rather than improving the water resistance. No material has been tested which has shown any promise in waterproofing shoe leather; however, some of these materials are effective for preserving the leather in storage and in service."

The specimen of leather treated according to Example 1 showed no water penetration on the Maeser machine, described in the article referred to above, after more than 1,300 flexing cycles.

EXAMPLE 2

A sample of the same type of leather as used in Example 1 was extracted with naphtha, dried, and without

further treatment, subjected to test in the same manner as in Example 1. This specimen showed penetration by water in less than 50 flexing cycles. It is evident, therefore, that the treatment with the succinic acid derivative was very effective in preventing penetration by water in the flexing test.

Other examples of leather specimens treated with alkylated succinic acids are set forth below. The specimens used were all approximately 3¾ x 4⅜ inches in size.

EXAMPLE 3

A piece of upper leather was extracted with carbon tetrachloride to remove the grease, etc., and was then treated with 5% of iso-octadecenyl succinic acid in a carbon tetrachloride solution. It was then heated to a temperature of about 65° C. for 15 minutes and subjected to the Maeser dynamic water penetration test described above. This specimen showed no penetration by water after more than 3,000 flexing cycles.

Other specimens of upper leather treated in substantially the same way as in Example 3 have shown resistance to water penetration in the Maeser test for periods in excess of 6 hours, which corresponds to more than 31,000 flexing cycles.

EXAMPLE 4

A sample of "army upper retan," i. e. leather which had been chrome and vegetable tanned but not "stuffed" or impregnated with grease, oil, or wax, was treated in its usual moist condition with approximately 6% of its dry weight of iso-octadecenyl succinic acid in a carbon tetrachloride solution. After being heated at a temperature of 65° C. for approximately 2 hours in an atmosphere saturated with water vapor, the specimen was dried and was found to be quite flexible. In the Maeser flexing test, this specimen showed no penetration by water in more than 5,000 flexing cycles.

EXAMPLE 5

Another specimen of upper leather which had been chrome tanned but not vegetable tanned was treated with about 15% of iso-octadecenyl succinic acid in solution in ethyl alcohol. After drying at 65° C., the specimen was tested in the Maeser flexing apparatus and showed no water penetration after more than 5,000 flexing cycles.

Flexing of leather in the absence of lubrication for the fibers of which it is composed produces a large amount of internal friction. The "stuffing" of leather has the function, aside from blocking the leather pores in an ineffectual effort to obtain waterproofness, of providing lubrication for the leather fibers. In the tests of applicant's leather waterproofed with derivatives of succinic acid it was found that in many cases, because of the small amount of treating agent used or because of an inherent lack of lubricating properties in certain of the derivatives, the leather was insufficiently lubricated.

As a result, the internal friction of the unlubricated leather fibers during the flexing tests produced a weakening or breakdown of the leather structure which permitted water prematurely to penetrate the specimen in spite of the resistance to normal water penetration given the leather by the treating material. Accordingly, as will be noted from the examples, in cases where the leather treated according to applicant's invention with succinic acid derivatives did not appear to be sufficiently lubricated for practical use, it was further treated with a small amount of lubricant.

As the numerous tests at the Bureau of Standards, referred to above, have conclusively shown, small amounts of ordinary lubricants for leather have no significant effect in preventing water penetration of leather. These prior tests were confirmed by tests made by applicant on the lubricants employed by him which included several types of hydrocarbon oils, neat's-foot oil, glyceryl mono-oleate and oleic acid. From these tests it was determined that in no case did oil or grease lubricants alone, even when used in amounts as high as 20% based on the weight of the leather, give leather resistance to water penetration in the Maeser test of more than 175 flexing cycles.

When adequately lubricated, as for example with 10% of mineral oil, specimens treated like the specimen used in Example 3 have shown no water penetration after more than 62,000 flexing cycles. The results with substituted succinic acids of shorter chain length and thus of lesser inherent lubricating quality are also improved by the addition of lubrication as shown by the following example.

EXAMPLE 6

A specimen of finished leather extracted with carbon tetrachloride to remove the grease, wax, etc. therein was treated with 10% of n-tetradecenyl succinic acid in carbon tetrachloride solution. After heating for approximately 30 minutes at 65° C., 10% of light mineral oil was added to the specimen. This specimen showed no water penetration after more than 7,500 flexing cycles.

Even though in some cases applicant's waterproofing derivatives of succinic acid are not themselves effective, (at least in the amounts necessary to give waterproofness), to provide adequate lubrication for the leather, it will be recognized that there is a great advantage in being able to provide waterproofness of leather with a small amount of a treating material and subsequently or simultaneously to obtain adequate lubrication with far smaller amounts of oils or other lubricating materials than have been customarily used in the past. Such a dual treatment is important in connection with the waterproofing of leather to be used at low temperatures such as are encountered in Arctic regions or in the stratosphere.

Leather for such use should be flexible at low temperatures and yet at higher temperatures should be resistant to penetration by water. The ordinary oils and greases which have previously been used to give flexibility to leather have not only given substantially no waterproofness to leather at ordinary temperatures, but have become brittle and hard at low temperatures and thus made the leather non-flexible. By the practice of the present invention leather may be rendered waterproof by a small amount of a succinic acid derivative. Such leather lubricated with an oil having a very low pour point will retain its flexibility at temperatures as low as —70° C. Moreover, because of the small amounts of waterproofing and lubricating agents which are required, the porosity of leather so treated will be much higher than that of the ordinary "stuffed" leather. Since it is well recognized that under Arctic conditions boots and shoes must be porous so that the water vapor from the feet may be carried away and not freeze in the footwear, leather treated by the dual process described above is of great value.

It has also been found that alkylated succinic acids can be water solubilized by reaction with volatile bases and thus leather can be treated therewith without the use of an organic solvent.

EXAMPLE 7

Ten percent of n-octadecenyl succinic acid was rendered water soluble by treatment with ammonia and applied in water solution to a specimen of upper leather, degreased in the same manner as in Examples 1 and 3. During a period of heating at 65° C. the ammonia was driven off and the specimen was then further treated by impregnating it with 10% of mineral oil. The treated specimen showed no water penetration in the Maeser flexing test after more than 2,100 flexing cycles.

EXAMPLE 8

A specimen of leather which had been chrome tanned and subsequently re-tanned with vegetable tanning material, but not "stuffed," was treated in water with 8% of iso-octadecenyl succinic acid which had been rendered water soluble or dispersible by reaction with morpholine. The treated leather was kept for about 2 hours in an atmosphere saturated with water vapor at 65° C. during which time the morpholine was driven off. After drying, the specimen was subjected to the Maeser flexing test. No water penetration occurred with this specimen in more than 5,000 flexing cycles.

It will be understood that alkylated succinic acids may also be applied to leather as anhydrides, hydration of the anhydrides after application producing the acid for imparting waterproofness. In the following example one method of using an anhydride is illustrated.

EXAMPLE 9

A piece of "army upper retan" leather was treated with 7% of the anhydride of iso-docosenyl succinic acid admixed with 15% of lubricating oil. The treated specimen was heated for 2 hours at 65° C. in an atmosphere

saturated with water vapor. In the course of this heat treatment the anhydride combined with water to form the acid. After drying, the leather was tested for resistance to water penetration and it was found that after more than 10,000 flexing cycles, no water had penetrated the specimen.

Also suitable for use in carrying out the objects of the present invention are the acid- or half-esters of alkylated succinic acids with both mono- and polyhydric alcohols, where such half-esters have a low affinity for water. Examples of the use of such half-esters follow.

EXAMPLE 10

A specimen of finished upper leather was extracted with carbon tetrachloride and was then treated with 10% of the half-ester of isopropyl alcohol with n-octadecenyl succinic acid in solution in carbon tetrachloride. After heating for 30 minutes at 65° C. the specimen was lubricated with 10% of light mineral oil and tested in the Maeser dynamic testing machine. The specimen showed no appreciable water penetration after 4,000 flexing cycles.

EXAMPLE 11

A sample of leather similar to the sample used in Example 10 was similarly extracted and was then impregnated with 10% of the n-decanol half-ester of n-octadecenyl succinic acid in a carbon tetrachloride solution. The specimen was kept at a temperature of 65° C. for about 2 hours in an atmosphere saturated with water vapor and, after drying, was tested for water penetration. The specimen showed no penetration of water after more than 5,000 flexing cycles.

EXAMPLE 12

A specimen of leather degreased as in the preceding examples, was treated with 10% of the half-esters formed by reacting n-hexadecanol with a mixture of the anhydrides of n-hexyl succinic acid, n-heptyl succinic acid and n-octyl succinic acid. After being heated for about 2 hours in an atmosphere saturated with water vapor at a temperature of 65° C., this specimen was dried, treated with 5% of lubricating oil, and tested for water penetration. No penetration occurred in more than 2,500 flexing cycles.

EXAMPLE 13

A piece of upper leather degreased by extraction with carbon tetrachloride was treated with 10% of the half-ester of n-hexadecanol with n-decyl succinic acid in a carbon tetrachloride solution. After heat treatment in the same manner as in the previous example, the leather was dried, further treated with 10% of lubricant and tested for resistance to water penetration. No penetration occurred in more than 5,000 flexing cycles.

EXAMPLE 14

A sample of upper leather which had been chrome and vegetable tanned but not "stuffed" was treated by applying to it 20% of the glyceryl mono-ester of n-octadecenyl succinic acid in chloroform solution. After being held for 2 hours in an atmosphere saturated with water vapor at 65° C., the specimen was dried and tested in the Maeser machine. Water penetration was observed in less than 100 flexing cycles. The low resistance to peneration by water of the specimen is believed to be due to the fact that the mono-glycerol ester of octadecenyl succinic acid, because of the extra hydroxyl groups in the compound, has a rather strong affinity for water.

In the following example there is employed another glyceryl ester which, having only one hydroxyl group, is less hydrophilic than the ester in the preceding example and is, therefore, effective in waterproofing leather.

EXAMPLE 15

Twenty percent of the half-esters produced by reacting glycerol mono-oleate with the anhydride of n-octadecenyl succinic acid was applied in a chloroform solution to a leather specimen of the same type as used in Example 14. After such application the leather was held in an atmosphere saturated with water vapor at a temperature of 65° C. for 2 hours, and then, after drying, was tested for water penetration. No penetration occurred in more than 13,000 flexing cycles.

The water resistant character of leather treated in accordance with Example 15, is shown by the following.

EXAMPLE 16

The specimen from Example 15, after removal from the Maeser testing machine, was boiled in water for about 15 minutes. It was then dried and was re-tested in the Maeser machine. The test was stopped after more than 5,200 flexing cycles, no water having penetrated the specimen.

Applicant has also found the acid- or half-soaps or salts which are obtained by neutralization of one of the carboxyl groups of an alkylated succinic acid with a base to be quite effective in rendering leather waterproof. The following series of examples sets out a number of the tests made with such half-soaps or salts.

EXAMPLE 17

A specimen of finished chrome and vegetable tanned upper leather was degreased by extraction with carbon tetrachloride and was then treated with 10% of the potassium half-soap of iso-octadecenyl succinic acid dissolved in carbon tetrachloride. After heating at approximately 65° C. for 30 minutes, the specimen was lubricated with 10% of oil and tested for water penetration. After more than 20,000 flexing cycles, no such penetration had occurred.

EXAMPLE 18

The half-soap of lithium iso-octadecenyl succinic acid was prepared and applied in solution in carbon tetrachloride to a degreased upper leather specimen in an amount equal to 10% of the weight of the leather. After treatment in the same manner as in Example 17, the specimen was tested for water penetration in the Maeser machine and it was found that, after more than 3,500 flexing cycles, no water had penetrated the leather.

EXAMPLE 19

A piece of upper leather which had been subjected to both chrome and vegetable tanning but which had not been "stuffed" was treated with 15% of the lithium half-soap of n-tetradecenyl succinic acid in solution in chloroform. The specimen was then held in an atmosphere saturated with water vapor at 65° C. for about 2 hours, dried, and tested for water resistance. After more than 1,300 flexing cycles in the Maeser testing machine, no water penetration had occurred.

EXAMPLE 20

Ten percent of the barium half-soap of iso-octadecenyl succinic acid was applied in carbon tetrachloride solution to a specimen of degreased upper leather. The specimen, after heating for 30 minutes at 65° C., was lubricated with 10% of oil. In the Maeser water penetration test, the specimen was subjected to more than 23,000 flexing cycles without water penetration.

EXAMPLE 21

A sample of degreased upper leather was treated with 10% of the cadmium half-soap of iso-octadecenyl succinic acid in a carbon tetrachloride solution. The specimen was dried at 65° C. for 30 minutes and was then lubricated with 10% of oil. No water penetration was found after more than 41,000 flexing cycles.

EXAMPLE 22

A degreased upper leather specimen was treated with 10% of the half-soap produced by reacting lead acetate with iso-octadecenyl succinic acid, the half-soap being dissolved in carbon tetrachloride. The solvent was then driven off during heating for about 30 minutes at 65° C. This specimen showed a good resistance to water in the Maeser test, no penetration occurring after more than 2,500 flexing cycles.

EXAMPLE 23

A piece of upper leather degreased with carbon tetrachloride was treated with 5% of its weight of the zinc half-soap of iso-octadecenyl succinic acid dissolved in carbon tetrachloride. After driving off the solvent during heating for about 30 minutes at 65° C., the specimen was tested for water penetration. No penetration occurred in more than 2,000 flexing cycles.

EXAMPLE 24

Another specimen of degreased leather was treated with 2% of the zinc half-soap of iso-octadecenyl succinic acid dissolved in carbon tetrachloride, heated in the same manner as in the preceding example, and lubricated with 10% of oil. This specimen showed no penetration by water after more than 2,600 flexing cycles in the Maeser testing machine.

EXAMPLE 25

Five percent of the zinc half-soap of iso-octadecenyl succinic acid was applied in a carbon tetrachloride solution to a piece of degreased leather. The solvent was driven off during heating for 30 minutes at 65° C. The treated leather was then further treated by the application of 10% of oil as a lubricant and tested in the Maeser machine for waterproofness. After more than 60,000 flexing cycles, no water had penetrated the leather.

EXAMPLE 26

A piece of degreased upper leather was saturated with a carbon tetrachloride solution containing 10% of the weight of the leather of the aluminum half-soap of iso-octadecenyl succinic acid. The treated specimen was heated at 65° C. for 30 minutes and was then lubricated with 10% of oil. In the Maeser flexing test, no penetration of the leather by water occurred in more than 2,500 flexing cycles.

EXAMPLE 27

The mixture of half-soaps produced by reacting a long chain aliphatic secondary amine with a mixture of n-decenyl and n-dodecenyl succinic acids was dissolved in chloroform and a piece of degreased upper leather was saturated with sufficient of the solution to leave approximately 10% of the reaction product in the leather. After being heated at 65° C. in an atmosphere saturated with water vapor for 2 hours, the specimen was dried and lubricated with 10% of oil. In the Maeser testing machine no water penetration of the leather occurred after more than 1,300 flexing cycles.

As previously mentioned, the permeability of leather to water vapor is of great importance where the leather is used in making articles of clothing such as shoes. Where leather is treated in accordance with the usual procedure by "stuffing" so that large amounts of oil, grease, and/or wax fill the pores of the leather, the water vapor permeability is very low. In the following table, the permeability of upper leather treated in various ways is shown, the figures given being the grams of water as vapor passing through the leather specimens in a period of 100 minutes under the same controlled conditions. The results of Maeser flexing tests on these samples are also given.

Table

	Water Vapor, grams/100 min.	Water Penetration, Flexing cycles
"Stuffed" leather	.084	Less than 100.
Heat treated "stuffed" leather	.026	Do.
Degreased leather, heat treated	.481	Do.
Degreased leather treated with 25% of iso-octadecenyl succinic acid and then heat treated.	.365	More than 1,300.[1]

[1] Test stopped after 15 minutes with no penetration.

The heat treatment, referred to in the table consisted in heating the leather to approximately 65° C. for 30 minutes. The degreased leather was obtained by repeatedly extracting stuffed leather with petroleum naphtha. The iso-octadecenyl succinic acid was applied to the leather in substantially the same manner as set out in Example 5.

It will be seen from the data in the table that the degreased and heat treated leather has a very good permeability to water vapor but no resistance to penetration by liquid water. The "stuffed" leather has a permeability of approximately ⅙ that of the degreased leather, while heat treatment of the "stuffed" leather reduces the permeability still further by melting the impregnating grease etc., and compacting it in the pores. However, neither the original "stuffed" leather nor the same leather heat treated had significant resistance to water penetration. On the other hand, the degreased leather which had been treated in accordance with the present invention had, even after heat treatment, a permeability which was more than 75% as great as that of the degreased leather and a high resistance to water penetration.

It will be evident, therefore, that the treatment of leather in accordance with the present invention to render it resistant to water penetration is extremely valuable since the water vapor permeability of leather so treated is many times greater than that of "stuffed" leather which is ordinarily used.

The resistance to water penetration imparted to leather by impregnating it with derivatives of succinic acid in accordance with the present invention is maintained over long periods of time as shown by the following examples:

EXAMPLE 28

The specimen of Example 1, after storage for over six months at room temperatures with varying humidity conditions, was, without any further treatment, re-tested in the Maeser machine. No water penetration was observed after more than 5,000 flexing cycles.

EXAMPLE 29

The specimen of Example 5, after storage for over six months at room temperatures with varying humidity conditions, was, without any further treatment, re-tested for resistance to water penetration. No penetration was observed after more than 5,000 flexing cycles.

As pointed out above, alkylated succinic acids, as well as the half-esters and half-soaps or salts thereof may be used in carrying out the waterproofing of leather in accordance with the present invention. However, as was previously mentioned, the derivatives of succinic acid used must have a very low affinity for water in the form in which they remain in the leather. The longer chain length alkylated acids are quite satisfactory in this respect and it is possible, as shown in the foregoing examples, to form with alkylated acids having shorter carbon chains half-esters or half-soaps which are very effective.

While not intending to be bound by any theory concerning the manner in which the succinic acid derivatives produce waterproofness of leather, it is believed, from observation of the many tests which have been carried out, that a reaction occurs between the free carboxyl group or groups of the succinic acid derivatives and either the fibers of the leather or, in certain cases, with the chrome or other metal complex which has been produced in the leather by reaction of chrome or other metal tanning solutions with the collagen of the leather fibers.

Regardless of what the actual action is, the succinic acid derivatives are firmly held in the leather. Referring back to Examples 15 and 16, it will be seen that the treated specimen, after being boiled in water, was still very resistant to water penetration. Other specimens have, after impregnation with succinic acid derivatives, been extracted with organic solvents and found to still be so water resistant as to show no penetration by water in the Maeser test after thousands of flexing cycles as, for instance:

EXAMPLE 30

The specimen used in Example 9 was dried and extracted with chloroform. After redrying, it was reinserted in the Maeser machine for further test for water resistance. The test was stopped after more than 30,000 flexing cycles with no evidence of water penetration.

The tests set forth in the preceding examples clearly indicate that by the treatment of leather with succinic acid derivatives, in accordance with the present invention, the leather fibers have been changed by rendering their surfaces hydrophobic instead of hydrophilic. Support is given to this conclusion by the fact that when oil as a lubricant is applied to leather which has been waterproofed by previous treatment with succinic acid derivatives, the oil is absorbed and spreads in the leather much more readily than it does with untreated leather. Such behavior is strong evidence that the leather fibers have been rendered oil receptive.

As a result of this change in the surface character of

the leather fibers, an oil lubricant applied to leather water-proofed with succinic acid derivatives will be held in the leather more permanently and, by thus providing better lubrication of the leather fibers, will result in the leather having improved wearing quality. It has also been found that the succinic acid derivatives employed for waterproofing leather are effective to inhibit the browth of fungi on the leather when it is exposed to moist atmospheres for prolonged periods of time. This characteristic is important as the mildewing or molding of leather is a serious problem in damp climates where the use of waterproof leather will often be required.

In the article referred to above describing the Maeser testing machine, it will be noted that the Maeser test also involves a determination of the weight of water penetrating the leather during a predetermined number of flexing cycles. No figures are available on the amount of water penetrating the samples mentioned in the examples given above, since in only a few cases had any water penetrated the specimen of leather before the test was stopped. Since, by applicant's invention it is possible to produce porous leather which is wholly impenetrable by water under the conditions of the Maeser test for periods of time so much longer than any leather heretofore known, the amount of water which may eventually pass through the leather is a negligible factor in the usefulness of the treated leather.

In treating leather in accordance with the present invention to render it waterproof, the succinic acid derivatives employed may be applied to the leather in a number of different ways, the choice of which depends upon the condition of the leather, the apparatus available, and the type of succinic acid derivative used. Thus, in some instances, application of alkylated succinic acids or their anhydrides solubilized with ammonia, morpholine, or other similarly volatile base, may be employed where it is desired to avoid the use of organic solvents. The succinic acid derivatives used are all soluble in an organic solvent such, for example, as carbon tetrachloride, chloroform, trichlorethylene and alcohol and may, therefore, be applied very conveniently in solution. In other cases, water emulsions of the treating agents may be used, or, where the succinic acid derivatives or their respective anhydrides are liquids, they may be applied directly.

Any lubricant which may be desired or necessary for the leather may be applied before, after, or in conjunction with the succinic acid derivatives employed. The lubricant must, of course, be water insoluble, since otherwise it would not be permanent, but it may be applied as such or may be applied in solution in an organic solvent or as an emulsion in water. It is to be noted that "stuffed" leather, without extraction of the oil, grease, etc., incorporated therein, can be rendered very resistant to water penetration by treatment with applicant's waterproofing materials. Since, however, the permeability to water vapor of the "stuffed" leather is already very low, the usefulness of such treatment is small.

It has been determined by research workers in the leather field that autoxidation of lubricants present in the leather to form peroxides and low molecular weight water soluble acids is one of the principal causes for the deterioration of leather. Oxidation may also cause breakdown or decomposition of certain of the succinic acid derivatives which may be used in the waterproofing of leather. The stability of such lubricants and derivatives may be increased and their breakdown or oxidation retarded or completely prevented by the incorporation of a small amount of an anti-oxidant. An anti-oxidant which is particularly suitable for this use because of its lack of odor and color is 2,6-di-tert-butyl-para-cresol. The stability of the succinic acid derivatives may also be increased in many cases by hydrogenation thereof.

It will be seen from the foregoing that the method of treating leather with the waterproofing compounds of the present invention may be varied as required by circumstances or as convenient. It should be noted, however, that leather treatment with succinic acid derivatives to obtain porous, waterproof leather is possible without substantial modification of the present method of manufacturing leather by substituting such treatment for the "stuffing" step of the present method.

It is important, of course, to secure uniform treatment of the leather by obtaining even distribution of the succinic acid derivative therein. Heating the leather, after application of the succinic acid derivative being used for waterproofing, has been found advantageous for this purpose. It is believed that the heating assists the spreading of the treating agent throughout the leather and this insures its uniform distribution therein. It is also considered likely that any reaction of the treating agent with the leather or tanning materials which does occur is promoted or hastened by the heating.

In many cases, it is desirable to prevent drying of the leather during heating and, as will be noted above, the heating may in such cases be carried out in an atmosphere saturated with water vapor. While the temperature of such heating, when used, is not critical so far as the invention is concerned, the use of very high temperatures must, of course, be avoided since the leather would be damaged thereby. When heating leather to which a succinic acid derivative has been applied for waterproofing, it is particularly important that the leather should not be heated above the temperature at which it will shrink. The shrinkage temperature of leather varies in accordance with the tanning process which has been used and, accordingly, the heating temperatures permissible in any particular case will depend upon the type of leather and the previous tanning treatment.

The amounts of succinic acid derivatives which have been found most effective in rendering leather resistant to water penetration vary to some extent with the type of leather and the particular succinic acid derivative employed. Good results, however, have been obtained with amounts as low as 2%, based on the original weight of the leather, although with such low amounts of treating agent additional lubricant is always necessary to make the leather pliable.

The use of succinic acid derivatives in amounts greater than 15% to 20% of the weight of the leather has not been found to add materially to their effectiveness in preventing water penetration of leather. Therefore, although the use of larger amounts is not deleterious from the standpoint of water penetration, it is in most cases undesirable since the high permeability to water vapor of leather treated in accordance with the present invention will obviously be somewhat reduced if amounts of treating material larger than necessary for imparting resistance to water penetration are put into the leather.

The leather used in the examples of this application has been leather of the type used for shoe uppers since the Maeser testing machine is particularly adapted for determining the resistance of such leather to water penetration. Other types of leather are, however, susceptible to treatment in accordance with the present invention to make them waterproof. Thus, a shoe can be made in which not only the uppers, but also the sole are impenetrable by water and other leather products can be made waterproof.

In the foregoing specification, there has been described applicant's novel and useful method of producing highly porous leather which is extremely resistant to water penetration even under the severe conditions imposed by the Maeser testing machine. It will be understood that the invention is to be construed broadly and that failure to specifically point out all of the applications thereof which will be apparent to those skilled in the art is not intended as an abandonment thereof. On the contrary, it is intended that the invention should only be limited by the appended claims.

What is claimed is:

1. The method of making leather resistant to water penetration which comprises introducing into the leather a monomeric, acidic succinic acid derivative having low water solubility selected from the group consisting of succinic acids and the anhydrides, half-esters and half-soaps of said succinic acids, said derivative containing an organic hydrophobic waterproofing group substituted on a non-acidic carbon atom of succinic acid.

2. The method according to claim 1 wherein the succinic acid derivative is alkylated.

3. The method of making leather resistant to water penetration which comprises introducing into the leather an alkylated succinic acid having low water solubility.

4. The method of making leather resistant to water penetration which comprises introducing into the leather

a half-ester of an alkylated succinic acid having low water solubility.

5. The method of making leather resistant to water penetration which comprises introducing into the leather a half-soap of an alkylated succinic acid having low water solubility.

6. The method of making leather resistant to water penetration which comprises introducing into the leather the anhydride of an alkylated succinic acid which has low water solubility.

7. Leather impregnated with a monomeric, acidic succinic acid derivative having low water solubility and selected from the group consisting of succinic acids and the anhydrides, half-esters, and half-soaps of said succinic acids, said derivative containing an organic hydrophobic waterproofing group substituted on a non-acidic carbon atom of succinic acid.

8. Leather according to claim 7, wherein the succinic acid derivative is alkylated.

9. Leather impregnated with an alkylated succinic acid having low water solubility.

10. Leather impregnated with a half-ester of an alkylated succinic acid having low water solubility.

11. Leather impregnated with a half-soap of an alkylated succinic acid having low water solubility.

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