

1

3,103,447

LEATHER AND METHOD FOR PRODUCING IT

John A. Lowell and Harold L. Hatton, Philadelphia,
Frank J. Glavis, Elkins Park, and Peter R. Euechler,
Langhorne, Pa., assignors to Rohm & Haas Company,
Philadelphia, Pa., a corporation of Delaware
No Drawing. Filed Jan. 5, 1961, Ser. No. 80,742
13 Claims. (Cl. 117—76)

This invention is concerned with the improvement of leather and involves an impregnation thereof with certain materials for the purpose of preparing it for finishing. It is particularly concerned with a treatment which provides leathers having improved break, fuller substance, and improved resistance to abrasion and scuffing.

It is already known to impregnate leathers with organic solvent solutions of certain polymeric substances and plasticizers therefor. The products obtained by such treatments tend to change with time as plasticizer is gradually lost. It is also known to coat leathers with aqueous solutions of ammonium salts of acidic copolymers, but the application of such a coating is accompanied by only a limited amount of impregnation if any so that the coated product obtained is not particularly improved in respect to break, and depends substantially entirely upon the character of the coating itself to protect the underlying leather from abrasion and scuffing. In such instances, any abrasive effect which pierces the coating on the leather, damages the leather itself and is difficult to repair.

In accordance with the present invention, the leather is impregnated with a certain polymeric material in an aqueous solution in such manner that the entire corium minor is penetrated and a substantial amount of polymer is deposited within the corium minor and at the junction of the corium minor and the corium major. The nature of the polymer is also important in that it contains acid units which cause the polymeric substances to adhere the corium minor layer to the corium major therebeneath. In other words, the treatment of the present invention involves substantially complete penetration of the corium minor and involves considerable permeation of penetration of the polymer through all of the areas of the corium minor and not merely the filling of the hair follicles and openings to the sebaceous glands.

It has been found, in accordance with the present invention, that aqueous solutions of ammonium or amine salts of acid-containing copolymers which in acid form are insoluble in aqueous media provide the necessary capacity for penetration of the leather, a deposition in insoluble form, and binding action for adhering the corium minor to the corium major. The copolymers used in accordance with the present invention are those of a polymerizable monoethylenically unsaturated acid, and especially of acrylic acid or methacrylic acid, with esters, such as the saturated monohydric aliphatic alcohol esters of acrylic or methacrylic acid obtained from cyclohexanol or alkanols having 1 to 18 carbon atoms, or with vinyl esters of a fatty acid having from 1 to 18 carbon atoms such as vinyl acetate, vinyl laurate, or vinyl stearate.

The comonomers that may be included with the acid may be any neutral comonomer such as vinyl chloride, vinylidene chloride, styrene, vinyltoluene, acrylonitrile and methacrylonitrile. In addition, small amounts of neutral hydrophilic comonomers may be included such as acrylamide, methacrylamide, or N-methylol acrylamide. The amount of such hydrophilic comonomers may be as high as 5% or more of the total weight of copolymer, the upper limit being dictated by the requirement that the copolymer in acid form be insoluble in water.

The invention is, of course, applicable to full-grain leathers, but more particularly it is suited to snuffed or

2

buffed grain leathers and improves the break characteristic of leathers of these types, as well as improving the resistance to scuffing and abrasion. It also renders the subsequently finished leathers more readily repaired if any scuffing penetrates through the finish coats.

The ability of the solution to penetrate the leather depends upon the viscosity and surface tension of the ingredients and their proportions. Viscosity can be lowered by proper selection of the aqueous solvent and by increasing the amount of solvent. However, the desirable viscosity in a particular application depends also upon the porosity of the leather in a particular application. This, in turn, is affected by many factors, such as the type of skin, i.e., calf, cowhide, goat, etc., the method of tanning, the extent of the tannage, the condition of tanning, such as pH, the oil and grease content, previous processes such as liming and bating, the mechanical handling of the skin and the tanning and drying processes, such as setting out and staking, and the amount of buffing.

The depth of penetration is controlled primarily by the amount of solution applied, once the penetrability of the solution has been regulated so as to allow it to penetrate in the first place. The depth of penetration is increased with increasing amounts of solution. Cowhide upper leather will absorb roughly its own weight of liquid. Since a penetration of at least 15% of the thickness of the leather is generally required for best results, a 15% penetration of cowhide corresponds approximately to application of liquid solution in weight of 15% of the weight of the leather, and correspondingly for other proportions. Furthermore, a small amount of penetration of less than three to five percent of the thickness of the leather is worse than no treatment and results in a very coarse break which is undesirable.

As between individual skins of a particular type to be treated, particularly sheepskin, the total thickness of the skin will vary and therefore the proportion of the thickness of the grain layer to total thickness of the skin may vary considerably. Therefore, an average quantity of solution per unit of area must be determined and used for a particular run. For instance, in a particular run the variation of grain layer thickness to total skin thickness may be from 20% to 40% and the optimum penetration for the run will then be determined at 30%.

As previously stated, a small degree of penetration with respect to thickness is more harmful than beneficial. It is recognized that attempts have been made to improve the characteristics of leathers by impregnation of the entire thickness of the leather. However, such total thickness impregnation must also be avoided in the present process because in addition to the substantially greater cost of materials involved, in total thickness impregnation the natural characteristics of the leather are impaired. For instance, it is desirable that shoe upper leather be capable of absorbing perspiration vapor and dispersing it to the outside. For this purpose high quality shoe upper leather has absorptive qualities and vapor permeability and these characteristics are inhibited little if any by our process of partial impregnation, whereas total thickness impregnation markedly reduces the moisture absorptive property and vapor permeability of the leather.

The non-impregnated thickness of the leather product of the present invention is substantially free from the copolymer so that its vapor permeability and flexibility is not substantially affected by the treatment. It is believed that this is one of the reasons why the overall vapor permeability and flexibility of the treated product throughout its entire thickness is not reduced to such an extent as to make the product unsuitable for use as shoe uppers as is the case when the entire leather thickness is impregnated with the resin solution of the

present invention. However, it will be appreciated that comparatively small quantities of copolymer may be present in the remaining thickness, or on the flesh surface, of the leather without reducing the natural flexibility and vapor permeability thereof sufficiently to make the overall flexibility and vapor permeability unsatisfactory. For example, the leather may have small holes or cuts passing from the grain surface into the flesh layer through which the solution flows when it is applied to the grain surface. Consequently, when it is stated herein that the remaining thickness of the leather is "substantially free from said copolymer" it is meant that such remaining thickness does not contain a sufficient amount of copolymer to materially modify the natural properties thereof and it is not intended by such term to exclude small quantities of copolymer in such remaining thickness which are insufficient to reduce the vapor permeability and flexibility properties thereof to a degree which will render the overall flexibility and permeability of the leather product unsuitable for the purposes set forth. Furthermore, the statement used herein that the copolymer salt solution is applied "to the grain surface only" does not exclude any kind of treatment which results in such small quantities of copolymer being present in the remaining thickness of the finished product.

The proportion of said in the acid/ester copolymers may range from about 5% to 35% by weight of the total copolymer and the molecular weight of the copolymer should be relatively low as compared to the usual acid copolymers of this type. In order to provide effective penetration as required by the present invention, the molecular weight should be such that a solution of 22% thereof in water has a viscosity of about 5 to 56 cps. at a pH of 6.5 to 7.5 and a temperature of 25° C.

The copolymers may be made in conventional fashion by copolymerizing the acids and esters by a conventional dispersion technique after which the acid copolymers may be converted to the salt form by the addition of ammonium hydroxide or a water-soluble amine such as triethylamine. While any volatile water-soluble amine may be employed, it is generally preferable and most economical to use ammonium hydroxide. Alternatively, the acid may be copolymerized with the ester in an aqueous solution thereof which includes a water-miscible solvent to dissolve the ester and acid. The prepared polymer solution is then converted to the ammonium or amine salt by diluting with an aqueous solution of the appropriate base. Regardless of which procedure of polymerization is employed, the molecular weight may be controlled by the use of conventional techniques, e.g., the employment of a chain regulator such as a long-chain mercaptan or a chloro-hydrocarbon such as bromotri-chloromethane, the amount of the chain regulator being employed to provide the molecular weight within the range specified hereinabove.

While any copolymerizable unsaturated acid such as acrylic acid, itaconic acid, aconitic acid, maleic acid, or fumaric acid may be employed, the use of methacrylic acid is preferred because of its copolymerization properties which lead to the formation of copolymers of ready solubility in dilute aqueous solution of ammonium hydroxide or amines with subsequent penetrability by the aqueous polymer salt solution obtained therefrom. The choice of the comonomer to be used with the acid depends in part upon the flexibility or stiffness desired in the product. When ethyl acrylate or an acrylic acid ester of an alcohol having three or more carbon atoms is the ester employed, highly flexible products are obtained without the use of plasticizers, and as the alkanol increases in size, the flexibility generally increases. Thus, n-butyl acrylate produces a copolymer somewhat more flexible than the ethyl acrylate for a given molar ratio of ester in the copolymer. When methyl acrylate or a methacrylic acid ester of a lower alkanol having 1 to 3

carbon atoms is employed, stiffer products are produced and in general, the use of methyl methacrylate exclusively is permissible only when the use of the leather is such that a stiff product is permissible, as in some types of mechanical leathers. Vinyl acetate also tends to produce a relatively stiff product, but higher vinyl esters such as vinyl butyrate are capable of producing relatively flexible products. Methacrylic acid esters with alkanols having 4 or more carbon atoms may be employed and they give products which are more flexible than the products obtained with the lower alkyl methacrylates. Of course, the esters may be mixed in various proportions to provide variations in flexibility and stiffness as well as other properties. For example, there may be employed a copolymer containing both ethyl acrylate or butyl acrylate with methyl methacrylate to provide somewhat greater stiffness than would be obtained without the methyl methacrylate. Valuable copolymer salts are also obtained from mixtures of the acid monomer with ethyl acrylate or butyl acrylate in admixture with acrylonitrile, vinylidene chloride, vinyl chloride and so on.

The concentration of the copolymer salt solution may vary widely depending upon the tendency of the particular salt to form solutions having a practical viscosity for penetration. For example, concentrations of 10% to 25% may be employed for most of the copolymer salts. The use of higher concentrations up to 35% may be permissible with the salts of extremely low molecular weight or those containing a relatively low proportion of acid in the copolymer, whereas it may be necessary to use concentrations even lower than the first range mentioned when the copolymer contains a large proportion of acid groups or is of molecular weight near the upper limit of the range given above.

The solution of the copolymer salt may be in a medium which is entirely aqueous or it may be an aqueous medium containing water-miscible solvents such as methyl or ethyl acetate, lower alcohols such as methyl or ethyl alcohol, n-propyl alcohol, isopropyl alcohol, t-butyl alcohol, ketones such as acetone, methyl ethyl ketone, or ethers such as dioxane, tetrahydrofuran, diethylene glycol, the monomethyl or monoethyl ether of diethylene glycol or of ethylene glycol, or any other water-miscible solvent, to the extent of their miscibility with water and their compatibility with the polymer. The use of a water-miscible solvent may be particularly desirable in certain instances to reduce the viscosity or lower the surface tension and favor rapid impregnation thereby. The proportion of organic solvent may vary widely from about 1% to about 80% by weight of the water in the solvent medium.

The copolymer salt solution may also contain additional materials such as dyes, pigments and other polymeric materials in small proportions. The amount of such additional polymeric substances should be kept relatively low as compared to the copolymer salt, and is preferably not over 10% of the weight of the copolymer salt. The use of a dye or pigment is sometimes desirable to reduce the number of subsequent finish coatings when a colored leather is to be produced. The proportion of pigment, however, should not be enough to hinder the entry and penetration of the copolymer salt solution into the leather and thus prevent the complete penetration of the copolymer salt through the thickness of the corium minor. In general, the amount of pigment should not exceed 8 parts per 100 parts by weight of the aqueous solution used for impregnation.

The copolymer salt solution may be applied in any fashion provided it is applied under such conditions that time is available for adequate penetration before extensive drying of the solution occurs. The solution may be swabbed on or it may be applied by brushing on the grain surface of the leather. The swabbing, brushing, or wiping action employed may be extended in duration as the means to assure adequate penetration and deposi-

tion, and for this purpose, the normal equipment that is used simply for coating leather is ordinarily inadequate, since such equipment involves a mere brushing to spread the coating evenly over the surface followed substantially immediately by drying. For the purpose of accomplishing the impregnation by a brushing operation, it is necessary that the brushing be continued for a comparatively extended period of time while the impregnating material is applied to the surface of the leather and maintained thereon in wet condition. Thus, an extended period of concurrent application and brushing should be carried out to prevent the drying of the material on the surface before extensive penetration can be accomplished. Hence, ordinary spraying or seasoning equipment for leather coating cannot be employed without modification.

More or less of the copolymer salt may be left as a coating upon the leather at the end of the impregnation process depending upon the particular manner of effecting the impregnation. However, whether or not a substantial amount of polymer material is left at the surface, it is essential that the copolymer salt be forced to penetrate through the corium minor or grain layer and to deposit the copolymer salt within the entire thickness thereof, and at the junction of the corium major. Mere filling of hair pockets with the copolymer salt will not suffice. Although it is not essential to follow the impregnation treatment of the present invention with a finishing treatment involving the application of one or more coats of a finishing composition, it is generally preferred to provide such a finishing treatment. While the copolymer salt may remain in the leather after drying as the ammonium or amine salt or partial salt, it is believed that the copolymer is left in the water-insoluble free acid form as a result of volatilization of the ammonia or amine during drying.

The impregnation may be effected at room temperature or at somewhat elevated temperatures up to 80° C., the higher temperatures being particularly useful when it is desirable to obtain an even lower viscosity with a given concentration of certain of the copolymer salts.

After deposition of the copolymer salt within the body of the leather, the leather is subjected to a drying step. This may be carried out at room temperature or it may be accelerated by heating to somewhat elevated temperatures such as at about 60 to 70° C. On drying, the ammonia or amine, as well as the water and any organic solvent present is volatilized, leaving the dry water-insoluble acid copolymer within the body of the leather.

The impregnation of the present invention is adapted to be applied to any type of leather such as that obtained from the skins of calves, cattle, goats, sheep, horses, and regardless of the particular manner of tanning. Thus, the leather may be that obtained by chrome tanning, zirconium tanning, vegetable tanning, or tanning by the use of synthetic tanning agents. It is particularly valuable with chromium-tanned leather. At the time of the application of the impregnation, the leather should generally be that obtained after the drying of the tanned, dyed, and/or fat-liquored leather.

The impregnation treatment of the present invention improves the break, the filling, and the resistance to abrasion and scuffing of the leather. The improvement is such that even with tanned leathers of poor quality, impregnated leathers of high quality can be obtained that are suitable for use as shoe uppers, shoe linings, handbags, belts, garments, gloves, luggage, footballs, baseballs, bookbindings, upholstery and other related uses. The improvement in the break referred to is so outstanding that inferior grades of leathers which command a low price because they ordinarily cannot be finished into high quality leather having good break characteristics can be treated by the present invention and converted into high quality leathers having good characteristics as far as break is concerned. In other words, the present invention serves to upgrade leathers, whether the inferiority of the leather treated is that inherent in the particular hide

from which the leather was produced or that resulting from the tanning and/or other operations by which it was produced. Because of this capacity of the present invention, it may be applied to the leathers obtained from loose flanks and bellies which are ordinarily of such inferior grade that they have been discarded or used only as so-called "offal" leathers. When applied to such poor grade materials, the finished leathers that can be obtained are so improved in quality that they can be used for the making of shoes, upholstery, bags, belts, briefcases, etc., where high-grade leathers are needed. In addition, sufficient filling action is provided by the polymer salt to firm the loose areas such as bellies and flanks of the leather so that more of these articles of commerce can be obtained from the leather than would otherwise be possible.

After application of the impregnation, whether or not it involves the leaving of any of the copolymer salt on the surface, the leather may be, and preferably is, finished by the application of one or more coatings. This subsequent coating may be any polymeric or other material normally employed for leather finish coatings. It may, of course, be pigmented, dyed, or not, as desired. Conventionally used finishing materials such as nitrocellulose lacquers or aqueous dispersions or organic solvent solutions of vinyl or acrylic polymers have been found suitable for finishing such impregnated leathers.

In finishing, the surprising discovery was made that the adherence of these leather finishes to such impregnated leather was better than to the surface of the same leather prior to impregnation. In addition, the wet-molding qualities of the finished impregnated leathers are greatly enhanced.

The process of the present invention is characterized particularly with the application of hydrophilic polymers in aqueous solutions. This assures inexpensive and safer operation. There is no fire or health hazard of the type often accompanying the use of organic solvent systems which are frequently flammable and toxic and require special precautions in handling and may require vapor or fume removal and recovery systems. Though the polymers deposited do not redissolve in water, they do swell in water. This enables them to undergo the mulling and lasting operations in the shoe factory. The mulling operation involves the dampening of the leather by hot water or by exposure to high temperature and humidity and then pulling the dampened leather with great force over a last for shoes. The leather swells under this mulling treatment. Hydrophobic polymers which refuse to swell under this treatment respond poorly to the lasting operation because of the great difference between their non-swelling behavior and the swelling of the leather fibers. This differential in swelling causes a rupture of the bonding between the leather and the polymer. Our polymers which also swell do not have as great a differential in swelling and have greater stability to the lasting operation.

In the following examples which are illustrative of the invention, the parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

(a) Preparation of Polymer

A monomer mix is prepared from the following:

	Grams
Ethyl acrylate	187.0
Methacrylic acid	33.0

A 3-liter, 3-neck, round-bottom flask is equipped with a Teflon paddle, a reflux condenser, a thermometer, and a dropping funnel, and to this flask is charged 780.0 grams of water. The contents of the flask are brought to a temperature of 95° C. by application of external heat (electric mantle), and a charge of 7.0 grams of ammonium persulfate is added to the aqueous charge in the

flask. Immediately thereafter, the monomer mix is added at a uniform rate such that its addition requires twenty to twenty-five minutes. During this time refluxing will take place at an intermediate rate. Immediately upon completion of the addition of the monomer mix, the refluxing will stop, but heating at 95–100° C. is continued for one-half hour. At the end of this heating period, the batch is cooled to 50–60° C., and to the flask are added 23.5 grams of 28% ammonia. Stirring is continued for one-half hour. Test data are as follows:

Total solids	21.7%.
Viscosity	14 cps. (25° C.).
pH	7.3.

(b) Application of Polymer

To one hundred parts by weight of the product from the above preparation, the following ingredients were stirred in: Ethanol (Grade 2B) 8 parts, water 93 parts, and a wetting agent such as 2.5 parts of *t*-octylphenoxyethanol or 15 parts of a 5% solution of fluorocarbon surfactant FC 128 (Minnesota Mining and Manufacturing Corporation).

This mixture was then applied to uncolored snuffed grain fully chrome-tanned side leather with very poor break characteristics by swabbing it on with a felt pad thoroughly wet with the mixture. The mixture was absorbed very rapidly by the leather and the felt and the felt pad had to be re-wet several times during the application. This application was then rapidly repeated twice more while the leather was still wet. No drying was permitted between applications so that the polymer was moved into the leather by the repeated applications.

A portion of the leather was left untreated during the impregnation so that comparisons could be made between treated and untreated areas.

The leather was hung to dry for three hours at 55° C. in a slowly moving current of air. Then it was plated with a sand blast plate in a press at 175° F. and 1000 p.s.i. pressure. Examination of the leather by those skilled in the art indicated an outstanding improvement in break both before and after the plating step. Vigorous scrubbing across both the impregnated and unimpregnated areas of the leather with a newly-minted United States coin of 50 cents denomination produced extensive rupture of fibers in the untreated area but the appearance of the scuffed area in the treated section was unchanged except for a very slight increase in gloss where it had been scrubbed. The flanks of the impregnated leather felt full and round but still very flexible and were of good value for cutting into shoe or other materials.

EXAMPLE 2

To 100 parts of the product of the polymerization process described in Example 1(a) 8.2 parts of *t*-octylphenoxyethanol were added. This mixture was agitated vigorously and then 56.1 parts of water were stirred in. This formulation was then applied to unfinished snuffed grain chrome-retanned leather by the swabbing procedure outlined in Example 1(b). A portion of the leather was left unimpregnated as in the preceding example. The leather was dried, plated with a sand blast plate at 175° F. and then the entire sample, including both impregnated and unimpregnated areas, was finished as follows:

	Parts
Water	32
Aqueous pigment dispersion (35%)	23
Con. ammonium hydroxide (28%)	1/8
Aqueous latex of 65% vinylidene chloride/35% ethyl acrylate copolymer (42% solids)	15
Sodium dioctyl sulfosuccinate (60%)	5
Total	75 1/8

The leather was dried at 55° C. This process was then repeated. After these two season coats the leather was plated in a press with a sand blast plate at 180° F. and a pressure of 2000 p.s.i. A topcoat was then sprayed on. This topcoat was composed of:

	Parts
Emulsion in water of an amyl acetate solution of plasticized nitrocellulose (content of nitrocellulose—6%)	120
Water	97.5
Aqueous pigment dispersion (35%)	15.1
Montan wax dispersion (16%)	5.2
Total	237.8

The finished leather was then allowed to dry at 55° C. The improvement in break caused by the impregnation was outstanding.

The resistance to scuffing was similar to that of Example 1.

EXAMPLE 3

A copolymer of 80% of ethyl acrylate with 20% of methacrylic acid having a viscosity of 61 cps. at a pH of 6.8 and a concentration of 21.6% in water was prepared as in Example 1(a) and applied to chrome-tanned full-grain leather by the procedure of Example 1(b). The impregnated leather showed good resistance to scuffing and good break characteristics. These improvements were brought out even more strongly on comparison of the finished product obtained by Example 2.

EXAMPLE 4

A copolymer of 95% of ethyl acrylate and 5% of itaconic acid having a viscosity of 6 centipoises at a pH of 6.5 and at 25° C. in an aqueous solution of 22% concentration was prepared as in Example 1(a) and applied to the same leather as was used in Example 1(b) by the same method. The impregnated leather had good break characteristics and good resistance to scuffing was obtained. These characteristics were retained in the product obtained by finishing as in Example 2.

EXAMPLE 5

A copolymer of 66% of *n*-butyl acrylate and 34% of acrylic acid having a viscosity of 65 centipoises at a pH of 6.5 and a temperature of 25° C. in an aqueous 22% solution thereof was prepared by the procedure of Example 1(a). This copolymer was applied as in Example 1(b) and the leather obtained was then treated by the process of Example 2, giving a finished leather having an excellent break and good resistance to scuffing.

EXAMPLE 6

A copolymer was prepared by the general procedure of Example 1(a) of 60% of methyl acrylate, 25% of 2-ethylhexyl acrylate and 15% of methacrylic acid having a viscosity of 20 centipoises at 22% concentration in water, pH of 7.0 and 25° C. A leather was impregnated by the copolymer and finished by the procedures of Examples 1(b) and 2, giving outstanding break and scuff-resistance properties.

EXAMPLE 7

A copolymer was prepared by the general procedure of Example 1(a) of 62% of ethyl acrylate, 28% of vinylidene chloride, and 10% of methacrylic acid having a viscosity of 30 centipoises at 22% concentration in water, pH of 7.0 and 25° C. A leather was impregnated by the copolymer and finished by the procedures of Examples 1(b) and 2, giving outstanding break and scuff-resistance properties.

EXAMPLE 8

A copolymer was prepared by the general procedure of Example 1(a) of 62% of ethyl acrylate, 28% of *n*-butyl methacrylate, and 10% of methacrylic acid having a vis-

cosity of 40 centipoises at 22% concentration in water, pH of 7.0 and 25° C. A leather was impregnated by the copolymer and finished by the procedures of Examples 1(b) and 2, giving outstanding break and scuff-resistance properties.

We claim:

1. A process for treating leather which comprises impregnating the leather on the grain side only with an aqueous solution containing at least about 7% by weight of a water-soluble ammonium salt of a water-insoluble copolymer of 5 to 35% by weight of an acid selected from the group consisting of acrylic, methacrylic, and itaconic acids and at least one ester selected from the group consisting of a vinyl ester of a saturated fatty acid having from 1 to 18 carbon atoms and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated monohydric aliphatic alcohol having 1 to 18 carbon atoms, the polymer having a molecular weight such that a solution of 22% thereof in water has a viscosity from about 5 to about 65 cps. at a pH of about 7 and a temperature of 25° C., the amount of solution applied in this fashion being at least 15% by weight of the leather whereby the impregnation penetrates through the corium minor and copolymer is deposited down to the junction of the corium minor with the corium major.

2. A process according to claim 1 in which the aqueous solution contains a volatile water-miscible organic solvent in an amount from about 1% to about 80% by weight of the water.

3. A process according to claim 1 in which the aqueous solution is at a temperature between room temperature and 80° C. during impregnation.

4. A process according to claim 1 in which the copolymer is a copolymer of ethyl acrylate and 5 to 35% by weight of methacrylic acid.

5. A process according to claim 1 in which the copolymer is a copolymer of ethyl acrylate, vinylidene chloride, and 5 to 35% by weight of methacrylic acid.

6. A process according to claim 1 in which the copolymer is a copolymer of methyl acrylate, 2-ethylhexyl acrylate and 5 to 35% by weight of methacrylic acid.

7. A process according to claim 1 in which the copolymer is a copolymer of ethyl acrylate, n-butyl methacrylate, and 5 to 35% by weight of methacrylic acid.

8. A process according to claim 1 in which the copolymer is a copolymer of ethyl acrylate and 5 to 35% by weight of acrylic acid.

9. A process according to claim 1 in which the copolymer is a copolymer of ethyl acrylate and 5 to 35% by weight of itaconic acid.

10. A process according to claim 1 in which the copolymer is a copolymer of n-butyl acrylate and 5 to 35% by weight of acrylic acid.

11. A process according to claim 1 in which the impregnation is followed by a step of applying a leather coating composition containing a pigment.

12. A leather having good break and scuff-resistance qualities and containing distributed through the corium minor, a water-insoluble copolymer of 5 to 35% by weight of methacrylic acid and at least one ester selected from the group consisting of a vinyl ester of a saturated fatty acid having from 1 to 18 carbon atoms and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated monohydric aliphatic alcohol having 1 to 8 carbon atoms, the amount of copolymer so distributed within the corium minor corresponding per 100 parts by weight of the leather to the content of copolymer in at least 15 parts by weight of an aqueous solution containing at least 7% of the copolymer.

13. A leather having good break and scuff-resistance qualities and containing distributed through the corium minor, a water-insoluble copolymer of 5 to 35% by weight of an acid selected from the group consisting of methacrylic, acrylic, and itaconic acids and at least one ester selected from the group consisting of a vinyl ester of a saturated fatty acid having from 1 to 18 carbon atoms and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated monohydric aliphatic alcohol having 1 to 8 carbon atoms, the amount of copolymer so distributed within the corium minor corresponding per 100 parts by weight of the leather to the content of copolymer in at least about 15 parts by weight of an aqueous solution containing at least about 7% of the copolymer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,744,836	Schubert et al.	May 8, 1956
2,763,577	Lawler	Sept. 18, 1956
2,865,877	Hatton et al.	Dec. 23, 1958

FOREIGN PATENTS

717,883	Great Britain	Nov. 3, 1954
---------	---------------------	--------------