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PROCESS FOR TREATING LEATHER

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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 while retaining good leather temper.

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. When aqueous alkaline systems are employed with vegetable-tanned leathers, especially case and upholstery leathers where large amounts of uncombined tannins are present, the penetration is hindered by the aqueous alkaline systems.

In accordance with the present invention it has been found that leathers can be improved in break and resistance to scuffing without the use of plasticizers by impregnation of the leather from one side only with an aqueous dispersion (i.e. latex), having a pH of 2 to 5, of a solid, water-insoluble linear addition polymer having an apparent second order transition temperature value (T_i value as defined hereinafter) which is not over 30° C., and preferably not over 20° C., and polymer particle sizes having a surface average radius from about 250 to 1300 angstrom units provided the dispersion is of a concentration not over 20% solids by weight and contains 0.5 to 8%, preferably 1 to 5%, by weight of at least one surface-active agent, based on the total weight of dispersion. More than 8% of the surface-active agent may be used, but this has the disadvantage of tending to render the finished leather excessively water-sensitive. Optimum improvement is generally obtained from copolymers having a T_i in the range of 0° C. and −17° C., though the polymers used may have T_i values as low as about −46° C. or as high as 30° C.

The T_i value referred to is the apparent second order transition temperature or inflection temperature which is found by plotting the modulus of rigidity against temperature. A convenient method for determining modulus of rigidity and transition temperature is described by I. Williamson, British Plastics 23, 87–90, 102 (September 1950). The T_i value here used is that determined at 300 kg./cm.^{2}.

The invention is concerned with the impregnation of fully tanned leathers which have been fat-liquored but are unstuffed and unfinished except that they may be stained or dyed. The leather to be treated should be in a dry condition. While it may be "bone-dry" or anhydrous, it is preferably in an air-dried condition, that is a condition in which it has a moisture content in equilibrium with the ambient atmosphere or conventional conditioning atmospheres having a temperature of 65 to 75° F. and a relative humidity of 60 to 70%. The moisture content of an "air-dry" leather may be about 10% or more or less depending upon the particular leather, its tanning history, and so on.

The size of the dispersed particles of the polymer to be applied is important. If the size of the particles appreciably exceed the upper limit defined, the application of the dispersion would serve primarily to coat the surface of the leather since most of the polymer particles would be too large to penetrate through the pores of the leather

which on the grain side of full grain leather are quite small in comparison to the flesh side. It is essential that most of the polymer particles are sufficiently small to penetrate the pores of the corium minor; otherwise the effect sought by the present invention cannot be attained even if the polymer dispersion is held in contact with the leather for prolonged periods of time and a large amount of the dispersion is applied. The latter would merely increase the coating without enhancing the penetration simply because of the rapid clogging of the pore openings with the numerous large size particles present. It is well known how to obtain small particle size emulsion copolymers, such as by the use of relatively large amounts of emulsifier. When the monomers used tend to produce molecular weights so high that the particle size limits defined are exceeded, the use of chain transfer agents to reduce the molecular size may be resorted to. No claim is made herein to any particular method for obtaining the small particle size polymer dispersions since many such methods are well known to the workers in the polymerization art.

Polymers that are suitable include linear addition polymers of either thermoplastic or thermosettable type. They may be homopolymers or copolymers. In general, they are polymers of monoethylenically unsaturated molecules, though they may also contain substantial proportions of polyethylenically unsaturated molecules when such molecules are adapted to produce polymers of essentially linear, rather than cross-linked type. Thus, linear polymers of isoprene, chloroprene, and butadiene including synthetic rubber latices having appropriate particle size may be used. However, such rubber polymers are subject to deterioration on exposure to ultra-violet light and oxygen so that it is generally preferable to employ polymers or acrylic type, especially the esters, nitriles and amides of acrylic or methacrylic acid. The most important group of acrylic ester polymers are those obtained by the addition polymerization of at least one ester of acrylic acid or methacrylic acid with an alcohol lacking ethylenic unsaturation and having 1 to 18 carbon atoms, such as benzyl alcohol or saturated aliphatic monohydric alcohols having 1 to 18 carbon atoms, such as cyclohexanol, alkyl-substituted cyclohexanols, and (C_1–C_{18})-alkanols. Examples of polymers having suitable T_i values include polymethyl acrylate, polyethyl acrylate, polybutyl acrylate, and other homopolymers and copolymers of esters of acrylic acid with an alkanol having 1 to 18 carbon atoms and of methacrylic acid with an alkanol having 5 to 18 carbon atoms; also such esters substituted by chlorine and/or fluorine atoms. The copolymers may also include acrylonitrile, methacrylonitrile, styrene, vinyltoluene, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl (C_1–C_4)-alkyl ethers, and esters of methacrylic acid with an alkanol having 1 to 4 carbon atoms to the extent that such monomers can be included without causing the T_i value of the copolymer to exceed 30° C.

Preferred copolymers are those containing 0.5 to 35% of units derived from hydrophilic monomers containing a group having a reactive hydrogen as determined by the Zerewitinoff method, Ber., 40, 2023 (1907); 41, 2236 (1908); Kohler, J.A.C.S., 49, 3181 (1927)—provided the copolymers are water-insoluble. Examples include acrylamide, methacrylamide, N - methylolacrylamide, acrylic acid, methacrylic acid, itaconic acid, β-hydroxyethyl acrylate, tert-butylaminoethyl methacrylate, hydroxyethyl vinyl ether or sulfide, glycidyl methacrylate.

A more specific preferred group of copolymers are those of a mixture of monoethylenically unsaturated molecules comprising about 0.5 to 4% of an acid of the group consisting of acrylic acid, methacrylic acid, and itaconic

acid, and 96 to 99.5% by weight of at least one ester of acrylic acid or methacrylic acid with a saturated monohydric alcohol having 1 to 18 carbon atoms, the copolymer having a T_i value not over about 20° C. The entire ester component may be composed of an ester of acrylic acid with any alkanol having from 1 to 18 carbon atoms or of an ester of methacrylic acid with an alkanol having 5 to 18 carbon atoms.

The surface-active agents in the dispersion may be of anionic, nonionic, or cationic types, or mixtures thereof. When the polymer contains acid groups, the anionic or nonionic agents or mixtures thereof are preferred. Examples of anionic surface-active agents include the higher fatty alcohol sulfates, such as sodium lauryl sulfate, alkylaryl sulfonates, e.g., sodium or potassium isopropylbenzene sulfonates or isopropyl naphthalene sulfonates, alkali metal higher alkyl sulfosuccinates, e.g., sodium octyl sulfosuccinate, sodium N-methyl-N-palmitoyltaurate, sodium oleyl isothionate, alkali metal salts of alkylarylpolyethoxyethanol sulfates or sulfonates, e.g., sodium t-octylphenoxypolyethoxyethyl sulfate having 1 to 5 oxyethylene units.

Suitable cationic agents include laurylpyridinium chlorides, cetyldimethylamine acetate, and alkyldimethylbenzylammonium chlorides in which the alkyl group has from 8 to 18 carbon atoms, such as octyl, decyl, dodecyl, or octadecyl, and t-octylphenoxyethoxyethoxydimethylbenzylammonium chloride.

Suitable non-ionic agents include the following: alkylphenoxypolyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyloctylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols, dodecylphenoxypolyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene linked alkyl phenols; sulfur-containing agents such as those made by condensing 6 to 60 or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans, or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, ricinoleic and the like or mixtures of acids such as found in tall oil containing 6 to 60 oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as castor oil or octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide derivatives or etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan monostearate containing 6 to 60 oxyethylene units, etc.; also ethylene oxide condensates of long-chain or branched chain amines, such as dodecylamine, hexadecylamine, and octadecylamine, containing 6 to 60 oxyethylene groups; block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections.

Penetration may also be accelerated by adding a water-miscible organic solvent to the aqueous polymer dispersion. The solvents that may be used include alcohols, ketones, and esters. Examples include ethyl alcohol, methyl alcohol, isopropyl alcohol, or tert-butyl alcohol. Examples of ketones include acetone and methyl ethyl ketone. Examples of ethers include dioxane and diethyl ether. Examples of esters include ethyl acetate and methyl acetate. Examples of ether-alcohols include diethylene glycol, the monomethyl, and the monoethyl ether of diethylene glycol.

The particular solvent may be composed of a single solvent material or it may be composed of a mixture of any of the materials mentioned hereinabove. Naturally, the particular solvent employed depends upon the components of the polymers which may vary the solubility thereof. The amount of solvent may be from ½ to 35% by weight, but is preferably from 5 to 10%, by weight of the dispersion, if a solvent is used.

The polymers may be prepared in any suitable fashion and may have any molecular weight, such as from about 30,000 to 10,000,000 viscosity average. Such polymers are readily produced by emulsion polymerization in an aqueous medium which may or may not contain a chain transfer agent, depending on the molecular weight desired. The conditions of polymerization should be those which produce an aqueous dispersion of the polymer with a particle size in the range specified hereinabove.

In the case of the preferred acid-containing copolymers, the comonomer used with the acid determines the flexibility or stiffness obtained 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 increased 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 as part of the copolymer, the products obtained increase in stiffness as the amounts of these components increase. 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 copolymers 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. Optimum temper and flexibility are obtained when the copolymer used has a T_i value from −17° C. to 0° C.

The concentration of the copolymer in the dispersion may vary from 5 to 20% by weight and is preferably 10 to 15% by weight.

The polymer dispersion may also contain additional materials such as dyes, pigments and other polymeric materials in small proportions to the extent that they can be included without raising the pH above about 5. The additional polymeric substances may be soluble in the aqueous dispersion but the amount thereof should be kept relatively low as compared to the dispersed water-insoluble polymer to avoid excessive viscosity, and it is preferably not cover 10% of the weight of the water-insoluble polymer. 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 polymer dispersion into the grain side of a full grain or buffed leather and thus prevent the complete penetration of the polymer through the thickness of the corium minor. In general, the amount of pigment should not exceed 3 parts per 100 parts by weight of the dispersion used for impregnation.

The impregnation is effected by application to one side only of the leather. In the case of full-grain leathers, the application is generally made to the grain side only though in the case of shearlings, application solely to the flesh side should be made. In the case of split leathers similar effects are obtained whether the impregnation is made on one side or the other.

The polymer dispersion may be applied in any fashion provided it is applied to one side only under such condi-

tions that the proper amount of dispersion and/or time is available for the appropriate extent of penetration before extensive drying of the dispersion occurs.

In the case of full grain or buffed leathers, the dispersion 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 is extended in duration as the means to assure adequate penetration and deposition, that is to the juncture of the corium minor with the corium major, 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 for the impregnation of full grain, snuffed or buffed leathers in accordance with the present invention.

Thus, in accordance with the present invention, full grain and/or buffed leather is impregnated with the polymer latex 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 results obtained with the preferred copolymers which contain acid units are outstanding in durability apparently because these polymeric substances adhere the corium minor layer to the corium major therebeneath more strongly than polymers lacking the acid groups. The treatment of these leathers from the grain side by the present invention thus involves substantially complete penetration of the corium minor and involves considerable permeation or 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.

In the case of impregnating split leathers or the flesh side of the shearlings, the dispersion is generally applied under conditions such that penetration of 15 to 40% of the thickness, and preferably 15 to 25% of the thickness occurs. However, in the case of shearlings, the penetration may extend completely through the corium major to, but not appreciably beyond, the juncture thereof with the corium minor. Since the surface of the leather to be impregnated, and later finished, is in this case much more open to impregnation than the surface of full-grain, snuffed or buffed leathers, the dispersion may be simply sprayed on the face of the leather or lightly swabbed, wiped or brushed on, the amount applied being limited so that penetration will extend through at least 15% of the thickness but not exceed 40% and preferably not exceed 25% of the thickness. At least about 90% of the polymer incorporated into the body of the leather should be distributed in the zone extending from the surface through which the polymer dispersion is applied to a depth of at least 15%, but not over 40%, of the thickness of the leather. The penetrability of the dispersion can be regulated by adjusting the content of polymer and surface active agent.

Whereas the depth of penetration, in the case of full grain, snuffed, or buffed leathers depends largely on the factor of time as mentioned above, in the case of split leathers or impregnation of the flesh side of the shearlings, the depth of penetration is controlled primarily by the amount of dispersion applied. The depth of penetration is increased with increasing amounts of dispersion. A penetration of at least 15% of the thickness of the leather is required. 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.

When impregnating either the flesh side of any leather or a split leather, care should be taken, by limiting the amount of dispersion applied or other conditions of application, to avoid penetration and deposit of the dispersed polymer in any substantial amount in more than 40% of the thickness of the leather. Impregnation of the entire thickness of the leather or "saturation" must 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 seriously impaired. For instance, it is desirable that shoe upper leather be capable of absorbing perspiration vapor and allowing its dissipation to the outside of the shoe. For this purpose high quality shoe upper leather has absorptive qualities and vapor permeability and these characteristics are inhibited little if any by the process of partial impregnation in accordance with the present invention, whereas total thickness impregnation markedly reduces the moisture absorptive property and vapor permeability of the leather. Also, the leather temper is lost and the impregnated leather becomes like a sheet of plastic when impregnated throughout its thickness.

The non-impregnated thickness of the leather product of the present invention is substantially free from the polymer 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 polymer dispersion of the present invention. However, it will be appreciated that comparatively small quantities of polymer may be present in the remaining thickness 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 dispersion 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 polymer" it is meant that such remaining thickness does not contain a sufficient amount of polymer to materially modify the natural properties including the temper of the leather and it is not intended by such term to exclude small quantities of polymer 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.

More or less of the polymer 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 on the surface, it is essential, in the case of full grain and buffed leathers, that the polymer be forced to penetrate through the corium minor or grain layer and to deposit the polymer within the entire thickness thereof, and at the junction of the corium major. In the case of split leathers and impregnation of the flesh side of any leather, the impregnation should extend through about 15% but not over 40%, and preferably not over 25% of the thickness of the leather. In the case of shearlings, however, the deposition of the polymer may occur throughout the corium major. Mere filling of hair pockets with the polymer 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.

The impregnation may be effected at room temperature or at somewhat elevated temperatures up to 30 or 35° C. After deposition of the polymer 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 or 70° C. On drying, the water and any organic solvent present is volatilize, leaving the dry water-insoluble polymer 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. At the time of the application of the impregnant, the leather should generally be that obtained after the drying of the tanned, dyed, and/or fat-liquored leather.

The invention is, as stated, applicable to full-grain leathers, but more particularly it is suited to snuffed or 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 impregnation treatment of the present invention improves the break, the filling, and the resistance to abrasion and scuffing of the leather without detrimental loss of leather temper. 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 co-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 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 impregnant, whether or not it involves the leaving of any of the polymer on the surface, the leather may be, and preferably is, finished by the application of one or more coatings. This subsequent coating may be formed of 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.

The process of the present invention is adapted to produce leathers having improved break and scuff resistance without the necessity of employing an alkaline aqueous medium which tends to reduce penetration of some types of leather excessively, thereby tending to provide non-uniform impregnations, to limit impregnation unduly, and to slow down the rapidity of impregnation.

The impregnated leathers obtained by the process of the present invention are generally characterized by a mellower and more natural feel and temper than those obtained by impregnation with polymer solutions. As is apparent from the description of the invention hereinabove, the leather is impregnated through a definite part of its thickness only. This cannot be accomplished by effecting the impregnation in a drum. Drumming causes penetration from all surfaces and of course favors penetration from the flesh side which in the case of full grain and buffed leathers is not the side to be finished. Drumming is not only incapable of imparting as much improvement in break for a given amount of polymer, but with most of the polymers having a T_i below 30° C. and especially with those of a T_i below 20° C., leather temper is seriously affected (the product feeling more like a piece of plastic than leather) and all surfaces of the leather acquire a tacky feel. To overcome this characteristic, it is necessary to provide an appropriate finish on all surfaces of the leather goods.

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

Example 1

An impregnating composition was prepared of an aqueous dispersion of an emulsion copolymer of 98% by weight of ethyl acrylate and 2% by weight of methacrylic acid, the dispersed particles of which had a surface average radius of about 800 angstrom units. The composition had a pH of 3.7 and contained about 18% by weight of the dispersed copolymer, about 2¼% of sodium octylphenoxyethyl sulfate, about 0.2% of sodium lauryl sulfate and about ¼% of octylphenoxypolyethoxyethanol containing an average of about 38 oxyethylene units per molecule.

This composition was then applied by swabbing to the grain side of an air-dry buffed side leather which had been fat liquored, chrome tanned and vegetable retanned but had not been finished. The swabbing operation was done by dipping the swab into the impregnant, swabbing one square foot of the leather with the soaked swab, dipping the swab back into the impregnant and swabbing again over the same area as rapidly as possible, while it was still wet, dipping the swab into the impregnant a third time, and again wiping it over the same area while it was still wet with the second swabbing. This was repeated on the other areas until the whole side of leather had been impregnated. A portion of the leather was left untreated so that comparisons could be made.

The leather was hung to dry for three hours at 55° C. in a slowly moving current of dry air. Then it was plated with a sandblast plate in a press at 150° F. and 2500 pounds per square inch pressure. Examination of the leather showed a significant improvement in break both before and after the plating step. Vigorous rubbing across both the impregnated and non-impregnated areas of the leather with a newly minted United States 25-cent coin produced rupture of surface much more readily in the untreated area. The leather was then finished as is generally done in the tannery.

Example 2

Example 1 was repeated except that 2% of tert-octylphenoxypolyethoxyethanol having about 10 oxyethylene groups was used in place of the 2¼% of the first mentioned surface-active agent. Similar results are obtained.

Example 3

Example 1 was repeated except that the concentration was reduced by dilution with water so that the polymer solids is reduced to 5%, 10%, and 15% respectively. Good break improvement results in each case.

Example 4

Example 1 was repeated except that the impregnating composition also contains 1% of a polyoxyethylated castor oil containing an average of about 60 oxyethylene units.

Example 5

Example 1 was repeated except that 10 parts of the water was replaced with 10 parts of ethyl alcohol.

Example 6

Example 1 was repeated except that ¼% of Nigrosine Jet Black WSJ (C.I. No. 865) was added to the impregnating composition.

Example 7

Similar results were obtained when Example 1 was repeated with each of the following polymer compositions:

(a) An aqueous dispersion having 16% concentration and a pH of 3.5 of an emulsion copolymer of 86% of ethyl acrylate, 10% of acrylonitrile, and 4% of butyl acrylate. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 0.2% sodium lauryl sulfate, 1% sulfated sperm oil, 2.8% octylphenoxyethoxyethanol having an average of 10 oxyethylene units, the percentages being based on the entire weight of the impregnating composition.

(b) An aqueous dispersion having 10% concentration and a pH of 4.0 of an emulsion copolymer of 49% of ethyl acrylate, 49% butyl acrylate, and 2% acrylic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 1% sodium lauryl sulfate and 2.0% of an octylphenoxypolyethoxy ethanol having an average of 38 oxyethylene units per molecule, the percentages being based on the weight of impregnating composition.

(c) An aqueous dispersion having 10% concentration and a pH of 5.0 of an emulsion copolymer of 65% of ethyl acrylate, 33% of methyl methacrylate, and 2% of itaconic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 2.0% sodium oleyl sulfate and 3.0% of octylphenoxypolyethoxyethanol having an average of 30 oxyethylene units per molecule, the percentages being based on the weight of the impregnating composition.

(d) An aqueous dispersion having 16% concentration and a pH of 4.5 of an emulsion copolymer of 88% ethyl acrylate, 10% of methyl methacrylate, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 0.25% of sulfonated castor oil, 1.75% of alkyl aryl sulfonate and 2% of a condensation product of tert-dodecyl amine with a mixture of ethylene oxide and propylene oxide containing an average of about 50 oxyethylene units and about 30 oxypropylene units, the percentages being based on the weight of the impregnating composition.

(e) An aqueous dispersion having 16% concentration and a pH of 3.5 of an emulsion copolymer of 88% ethyl acrylate, 10% of butyl acrylate, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 0.25% sulfated castor oil, 1.75% of a sodium t-octylphenoxypolyethoxyethanol sulfate having an average of about 5 oxyethylene groups and 2% of a monoester of glycerol with stearic acid, the percentages being based on the weight of the impregnating composition.

(f) An aqueous dispersion having 16% concentration and a pH of 4.2 of an emulsion copolymer of 86% ethyl acrylate, 4% of butyl acrylate, and 10% of vinylidene chloride. The polymer particles had a surface-average radius of 700 angstrom units and the dispersion contained 1% sulfated castor oil, 1% sulfonated methyl ester of neats foot oil, 2% heptylphenoxypolyethoxyethanol having an average of about 10 oxyethylene units, the percentages being based on the weight of impregnating composition.

(g) An aqueous dispersion having 16% concentration and a pH of 2.7 of an emulsion copolymer of 89.2% of ethyl acrylate, 10.8% of methyl methacrylate. The polymer particles had a surface-average radius of 900 angstrom units and the dispersion contained 0.25% pyridinium hydrochloride, 1% octylphenoxypolyethoxyethanol containing an average of 39 oxyethylene units and 2.75% of another containing an average of 10 oxyethylene units, the percentages being based on the weight of impregnating composition.

(h) An aqueous dispersion having 16% concentration and a pH of 3.8 of an emulsion copolymer of 75% ethyl acrylate, 23% butyl acrylate, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 1% sulfated castor oil, 1% of a sodium octylsulfosuccinate, and 2% of an octylphenoxypolyethoxyethanol having an average of 8 oxyethylene units, the percentage being based on the weight of impregnating composition.

(i) An aqueous dispersion having 16% concentration and a pH of 4.3 of an emulsion copolymer of 88% ethyl acrylate, 10% of 2-ethylhexyl acrylate, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 900 angstrom units and the dispersion contained 0.25% sodium oleyl sulfate and 0.75% of octylphenoxypolyethoxyethanol having an average of 39 oxyethylene units and 3% of a hexadecylthiolphenol, the percentages being based on the weight of impregnating composition.

(j) An aqueous dispersion having 16% concentration and a pH of 3.5 of an emulsion copolymer of 75% of ethyl acrylate, 13% of glycidyl methacrylate, 10% of methyl acrylate, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 900 angstrom units and the dispersion contained 0.5% sulfated castor oil, 1.5% of a sodium salt of t-octylphenoxypolyethoxy ethyl sulfate having an average of 15 oxyethylene units and 2% of an ethylene oxide derivative of oleic acid having an average of 25 oxyethylene units, the percentages being based on the weight of impregnating composition.

(k) An aqueous dispersion having 16% concentration and a pH of 3.0 of an emulsion copolymer of 90% ethyl acrylate and 10% of N-vinyl pyrrolidone. The polymer particles had a surface-average radius of 900 angstrom units and the dispersion contained 0.25% benzyldimethylstearylammonium chloride, 1% octylphenoxypolyethoxyethanol having an average of 39 oxyethylene units, 1.75% of another having an average of 10 oxyethylene units, and 1% of a polyoxyethylated vegetable oil having an average of 30 oxyethylene units, the percentages being based on the weight of impregnating composition.

(l) An aqueous dispersion having 10% concentration and a pH of 5.0 of an emulsion copolymer of 88% ethyl acrylate, 10% styrene, and 2% of methacrylic acid. The polymer particles had a surface-average radius of 800 angstrom units and the dispersion contained 0.5% sodium sulfate, 1.5% of an ethylene oxide condensate of dodecylamine having an average of 20 oxyethylene units and 2% sulfonated lauryl phenyl ether, the percentages being based on the weight of impregnating composition.

(m) An aqueous dispersion having 16% concentration and a pH of 4.5 of an emulsion polymer in which a mixture of butyl acrylate and methacrylic acid is grafted on a copolymer of vinylidene chloride with butyl acrylate

and ethyl acrylate, the proportions of the various monomers being 43% butyl acrylate (in first-mentioned mixture), 1% methacrylic acid, 50% vinylidene chloride, 3% butyl acrylate (in substrate copolymer) and 3% of ethyl acrylate. The particles of the polymer had a surface-average radius of 900 angstrom units and the dispersion contained 0.25% sodium oleyl sulfate, 1.75% oleic amidoethanesulfonic acid and 2% octylphenoxypolyethoxyethanol having an average of 10 oxyethylene units, the percentages being based on the weight of impregnating composition.

(n) An aqueous dispersion having 12% polymer concentration and a pH of approximately 3.5 prepared with ammonium persulfate as a catalyst and containing a copolymer of 85 mole percent of ethyl acrylate and 15 mole percent of methacrylic acid. In contrast to the high molecular weight (in the millions) of the preceding copolymers, this copolymer had a molecular weight which was quite low being about 20,000 to 40,000 viscosity average. The particles had a surface-average radius of 1200 angstrom units and the dispersion contained 1% of polyoxyethylated vegetable oil having an average of 40 oxyethylene units and 2% of sulfated octylphenoxyethyl sulfate, the percentages being based on the weight of impregnating composition.

(o) An aqueous dispersion having 12% polymer concentration and a pH of 3.3 of a copolymer of 90 mole percent of ethyl acrylate and 10 mole percent of methacrylic acid having a low molecular weight (about 20,000 to 30,000 viscosity average) and in which the particles had a surface-average radius of 610 angstrom units and the dispersion contained 1% of a polyoxyethylated vegetable oil having an average of 20 oxyethylene units and 2% of an octylphenoxypolyethoxyethanol having an average of 10 oxyethylene units, the percentages being based on the weight of impregnating composition.

(p) An aqueous dispersion having a pH of about 4 and containing 20% of a copolymer, having a particle size such that the surface-average radius was 800 angstrom units, of about 85% ethyl acrylate, 10% of tert-octyl acrylate, and 5% of methacrylamide. The dispersion contained 0.25% sodium oleyl sulfate, 1.75% sulfated neats foot oil and 2% of dioctylphenoxypolyethoxy ethanol having an average of about 30 oxyethylene units, the percentages being based on the entire impregnating composition.

(q) An aqueous dispersion having a pH of about 4, containing 10% of a copolymer of about 70% ethyl acrylate, 20% of methyl methacrylate, 5% acrylamide, and 5% of N-methylol acrylamide, having a particle size such that the surface-average radius was 800 angstrom units. The dispersion contained 0.25% sodium lauryl sulfate, 1% propylene glycol monolaurate and 1% of a sodium salt of alkylarylpolyether sulfate, the percentages being based on the entire weight of impregnating composition.

Example 8

One heavy spray coat of the following composition was applied to one face of a split leather and to the flesh side of a shearling. The composition was an aqueous dispersion having 20% solids, the solids content being made up of a copolymer of 75% of ethyl acrylate, 23% of butyl acrylate, and 2% of methacrylic acid and containing on weight of impregnating composition 0.20% sodium oleyl sulfate, 1.0% of octylphenoxypolyethoxyethanol having an average of about 39 oxyethylene units and 2% of a similar surfactant but containing only an average of about 10 oxyethylene units. After spraying, the leather was hung to dry for three hours at 55° C. in a slowly moving current of dry air. The impregnated surfaces were then finished and the finished leather showed improved pull-up characteristics, good fill and fiber bonding and good layout, improved resistance to scuffing and improved break characteristics. The temper of the leather was not adversely affected.

I claim:

1. A process for treating leather which comprises applying to the leather, fully tanned and fat-liquored and in air-dry condition, on one side only an aqueous dispersion having a pH of 2 to 5 and containing at least about 5% by weight but not over 20% by weight of a water-insoluble linear addition polymer of monoethylenically unsaturated molecules and 0.5 to 8% by weight of a surface-active agent, the polymer having a T_1 value not over 30° C. and the dispersed particles of the polymer having a surface average radius between 250 and 1300 angstroms, the amount of pigment, if any, not being in excess of 3 parts per 100 parts by weight of the dispersion the impregnation being effected to distribute at least 90% of the polymer through at least 15% but not over 40% of the thickness of the leather.

2. A process as defined in claim **1** in which the impregnating composition is applied only to the grain side and the impregnation is effected to penetrate through the corium minor and to deposit polymer down to the junction of the corium minor with the corium major.

3. A process as defined in claim **1** in which the impregnating composition is applied only to the flesh side of a shearling and the impregnation is effected to penetrate through the corium major and to deposit polymer down to the junction of the corium major with the corium minor.

4. A process as defined in claim **1** in which the impregnating composition is applied only to one side of a split leather and the impregnation is effected to deposit polymer substantially only in that portion of the thickness of the leather extending from the aforesaid side to a depth from about 15% to not over 40% of the total thickness of the leather.

5. A process according to claim **1** in which the polymer is an acrylic polymer containing polymerized units of at least one ester of acrylic acid or methacrylic acid with a saturated aliphatic monohydric alcohol having 1 to 18 carbon atoms.

6. A process according to claim **1** in which the polymer is a copolymer of 0.5 to 35% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and itaconic acid and at least 65% by weight of at least one ester of acrylic acid or methacrylic acid with an alkanol having 1 to 18 carbon atoms.

7. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate and 0.5 to 4% by weight of methacrylic acid.

8. A process according to claim **1** in which the polymer is a copolymer of methyl acrylate, 2-ethylhexyl acrylate and 0.5 to 4% by weight of methacrylic acid.

9. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate, n-butyl methacrylate, and 0.5 to 4% by weight of methacrylic acid.

10. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate and 0.5 to 4% by weight of acrylic acid.

11. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate and 0.5 to 4% by weight of itaconic acid.

12. A process according to claim **1** in which the polymer is a copolymer of n-butyl acrylate and 0.5 to 4% by weight of acrylic acid.

13. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate, vinylidene chloride, and 0.5 to 4% by weight of methacrylic acid.

14. A process according to claim **1** in which the polymer is a copolymer of ethyl acrylate, methyl methacrylate, and 0.5 to 4% by weight of methacrylic acid.

15. A process according to claim **1** in which the leather treated is a vegetable tanned leather.

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