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PROCESS FOR IMPREGNATING LEATHER AND PRODUCT

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This invention relates to the treatment of leather for the purpose of improving its resistance to abrasion and scuffing and for improving its surface.

The process of the invention is intended to be applied to those types of leathers on which it is desirable to preserve a grain or imitation grain surface. Such types include leathers for shoe uppers, shoe linings, hand bags, belts, garments, gloves, luggage, footballs, baseballs, book bindings, upholstery and related uses. The process is not intended for uses in which the grain is hidden or nonexistent, such as suede leather and chamois. Likewise, it is not intended for such heavy leathers as soles, insoles, and belting for mechanery. As distinguished from the heavy leathers, such as sole leather, and the suede and chamois leathers and also cordovan, to which the process is not applicable, we may define the types of leathers to which the process is applicable as light leathers with grain.

The resistance of leather to abrasion and scuffing is increased by as much as five times or more by treatment. The water vapor permeability of the leather is not materially reduced and this is desirable, but on the other hand, my process improves the natural characteristics of the leather, for instance, by providing greater water resistance, a tighter grain, an improved break, a better ability to hold a finish, and consequently much improved appearance as well as wearability. The process also aids in obtaining the property known as "show-through" or "pull-out" in which, in shoe making, portions of the leather pulled tightly over a curved surface, as at the toe, show a lighter and brighter shade. By the process it is practical and cheap to make ordinary side leather appear very similar to much more expensive cordovan leather. The leather feels much stronger and tighter after treating with my process and is not adversely affected.

These and other advantages will become more apparent from the following description of my process.

In general, the process comprises substantial impregnation with respect to the depth or thickness of the grain layer of the leather and partial impregnation with respect to the density of impregnation, with one or more synthetic resins. The grain layer, for practical purposes, can be defined as a visibly distinct layer at the outer surface of the skin in which the fibers are more densely arranged than in the subsurface layers of the skin and it varies in thickness in different types of skins from between approximately 15% to approximately 50% of the total thickness of the natural skin, as for instance between bull hides and sheep and kid skins respectively. The grain layer contains the hair follicles and sweat glands. It is used as the normal exposed finishing surface in leather goods, and it has a distinctive pattern or arrangement of surface characteristics which distinguishes one leather from another. However, it must be understood that the thickness of the grain layer in each given skin is not exact over the whole area and varies slightly from one area to another. Therefore, when I speak of grain impregnation I do not intend to be held to an exactness in depth of penetration which would preclude slightly more or less than precisely the depth of the grain layer of a skin at any particular point. Furthermore,

while the grain layer in a given skin remains generally consistent in thickness, the subsurface layer may vary drastically in thickness from one area to another so that the proportion of thickness of the grain layer to total thickness of skin will vary from one area to another quite out of proportion to its actual thickness. This latter variation occurs particularly in calf, sheep and kid skins.

There are certain other variations with respect to the depth of impregnation. The most important is that of split leather which has no grain. However, the treatment, particularly as applied to split leather, aids in obtaining an artificial grain surface. In such case the penetration of the material is controlled so that penetration occurs only part way through the thickness of the leather, but, nevertheless, substantially below the surface. In all cases the limits of penetration may be defined as not less than 15% and not more than 50% of the total thickness of the leather. A very small penetration, such as three to five per cent of the thickness of the leather is harmful rather than helpful to the purposes of the present invention. And while penetration may accidentally occur in places to a depth greater than 50% of the thickness of the leather as, for instance, in thin spots, this is accidental and in general penetration should be controlled to within the 50% maximum in order to preserve flexibility and vapor permeability. With certain grain leather, the grain layer may exceed 50% of the thickness, in which case the treatment may be confined to a penetration which is not entirely through the grain layer and still accomplish the same results. Such a condition may occur either naturally, as in sheepskin or in cowhide from which a split has been cut. In other types of leather where the grain leather is less than 20% of the thickness, the result will be achieved even though impregnation reaches somewhat beyond the grain layer, and in some cases this may be desirable.

The impregnating liquid may be generally described as a solution comprising a synthetic resin, a plasticizer for the resin, and a solvent for the resin and plasticizer. The function of the plasticizer is to maintain the resin in the impregnated leather in pliable condition. A substantally high proportion of plasticizer is used. The proportion can be defined as an amount which, when the solvent is dried out of the leather after treatment, leaves the resin sufficiently plasticized and soft so as not to reduce substantially the natural flexibility of the leather. On the other hand, the proportion of plasticizer must be low enough so that the treated leather surface shows a substantial increase in its resistance to wear. In general, the proportions of plasticizer to resin are fifty to seventy-five parts of plasticizer per hundred parts of resin greater than the proportions of plasticizer per hundred parts of resin normally used to form a free film, although this is not intended as a critical limitation.

The solvent selected for the plasticized resin should reduce the surface tension of the solution sufficiently to provide complete penetration to the desired depth. The function of the solvent is to provide a vehicle for the plasticized resin which wets the leather sufficiently to promote penetration.

With respect to the density of impregnation of the impregnated portion, the solvent serves the function of providing only partial impregnation of the interstices by leaving unfilled some of the microscopic spaces between the fibers of the leather substantially evenly distributed throughout the thickness of the impregnated portion when the solvent evaporates, thus maintaining absorptive properties and vapor permeability in the leather while at the same time accomplishing the desired purpose of increasing strength and resistance to scuffing.

The quantities of plasticizer and solvent used in pro-

portion to the resin will depend on the porosity of the leather to which it is applied and also upon the viscosity of the resin used. Only as much liquid should remain on the surface as inevitably coats the surface fibers in the process of penetration into the grain. After the grain impregnation, the leather is dried, leaving the plasticized resin in the leather.

A wide variety of resins may be used, including acrylic, methacrylic and vinyl resin. Normally, the plasticizer is added to the resin in the solution. The plasticized resin content of the impregnating liquid, i. e., the portion of the impregnating liquid which remains after drying and evaporation of the solvent, may vary from 15% to 30% by weight of the total, based on the proportion of weight to volume of the total, as measured in the metric system, depending upon the porosity of the leather with which it is to be used, the inherent viscosity of the resin and the viscosity and surface tension of the liquid portion of the solution. The porosity of the leather varies not only with the type of leather, for instance, calf, cowhide, sheepskin and so forth, but also with the tannage and amount of buffing, if any.

The amount of solution applied to the surface should not exceed one-third of the weight of the leather to which it is being applied except in unusual cases, such as when applied to sheepskin in which the grain layer constitutes over one-half of the thickness of the leather. On the other hand, in order to achieve the best results the amount should be sufficient to penetrate at least most of the grain layer. After the impregnation the leather is dried either at room temperature or in a heated tunnel. Then the leather is ready for finishing.

In addition to resins and plasticizers in solution, the solution may also contain dyestuff when desired.

The first step is to make the solution containing the one or more synthetic resins, plasticizers, solvent, and where desired, dyestuffs. When dyestuff is included, the preferable first step is to dissolve the dyestuff in the solvent. Therefore, a solvent should be selected which is a common solvent for all the ingredients. Then the synthetic resins are added and the mixture is agitated until the resins are thoroughly dissolved. The resins are dissolved more rapidly when the temperature is elevated. Some of the resins may be purchased already dissolved, in which case the resin solution is mixed with the additional solvents required to secure the proper proportion of resins. The plasticizers may be added, either at the same time as the resins or after the resins have been dissolved.

The exact proportion of a given resin and a given plasticizer which will be generally applicable for treating all types of leather may be determined as follows:

Selecting a resin and a plasticizer, the proportions of which are known for the purpose of forming a free film, I make up several solutions of the two in varying proportions in which the parts of plasticizer per hundred parts resin are forty to eighty parts greater than the proportions necessary to form a free film. I test with these proportions and select the combination which best produces the desired characteristics of resistance to abrasion (scuffing) and flexibility in test samples. I may select a resin which in its unplasticized state is too tacky to form a free film, but which is nevertheless useful for my purpose. In that case I lower the range of proportions of plasticizer in the experimental solution.

Having determined an optimum proportion of a particular combination of plasticizer and resin which, once determined, may be used in connection with all types of leather, it is now necessary to determine the proportion of plasticized resin, i. e., resin and plasticizer to the total solution, in other words, to determine how much solvent to use in a particular run with a particular type of leather. Since individual hides or skins of a particular type to be treated will vary somewhat, several samples from different skins should be selected for test purposes in order to determine an average optimum solution.

A solution is prepared on an experimental basis containing a proportion of plasticized resin to the total which may be near the upper limit indicated for the type of leather to which it is to be applied. This will not normally be found to be above 25% by weight to 100 parts total volume, metric. This solution, in the amount of approximately 25% of the weight of the leather, is brushed onto sample pieces, and if all of the solution penetrates into the leather, the proportion of resin is satisfactory. However, if some of the treating solution remains on the surface, the solution is diluted until in another trial all that is applied penetrates. Conversely, the proportion of plasticized resin may be increased until it is determined that beyond a given proportion some of the solution remains on the surface and the proportion has become too high. The proportion of plasticized resins determined in this manner will be satisfactory for subsequent runs with that particular leather.

The leather to which the solution is applied should be normally prepared for ordinary finishing operation. In other words, it should be tanned, dyed, fatliquored and dried. If it is to be buffed, such buffing should occur before the treatment. No finish of any kind should be applied prior to treatment. The treating solution is applied to the surface of the leather by brush, swab, roller, or sprayer. When a spray is used, it is important to account for the change in viscosity which may occur by evaporation of some of the solvent between the nozzle and the leather by adding sufficient additional solvent. A wide nozzle with low pressure is best. Too fine a spray builds up a surface coating and produces poor results.

The solution must be applied in one coat, or at least in one treatment, in which the total application occurs before any has had a chance to dry appreciably. With this in mind, it is sometimes desirable to go over the leather twice, but usually not more than three times, to secure uniformity.

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 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. Penetration may also be affected by evaporation of a very volatile solvent before the liquid has had a chance to penetrate into the leather and also by a resin having very long molecules, the size of which may inhibit proper penetration even at relatively low viscosities of the solution. Nevertheless, the proper viscosity can be determined for a given application with very little experimentation once the principle is understood.

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 required for best results, a 15% penetration of cowhide corresponds approximately to application of liquid solution in the amount of 15% of the weight of the leather, and correspondingly for other proportions. As previously stated, a small amount of penetration of less than three to five per cent 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 total skin thickness may vary from 20% to 40% and the optimum penetration for the run will then be determined at 30%.

It is to be understood that except for the limitations previously stated, the invention does not lie in the use of any particular resin, plasticizer or solvent, or in any stated proportions of each to the other, nor in any critical amount of solution applied, since these factors vary so greatly with each application. The invention lies in the principle that if leather is impregnated with a suitable resin, having plastic and flexible characteristics, to a depth substantially greater than what amounts to a mere surface treatment, but substantially less than the impregnation of the total thickness of the leather, the natural wearing characteristics and appearance of the leather is greatly improved.

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 my process of partial impregnation, whereas total thickness impregnation markedly reduces the moisture absorptive property and vapor permeability of the leather. Flexibility is also a desired characteristic and is not affected by my process, whereas it is also much reduced by total thickness impregnation. Furthermore, except for unusually porous leathers, a solution which penetrates total thickness of the leather from one side is insufficiently viscous for best grain protection according to my process. Total impregnation with plasticized resin with respect to density is also excluded from the invention because it eliminates desired porosity, and hence absorption and permeability. Since some of the spaces between the leather fibers must be left partially unfilled when the leather dries, the plasticized resin must be introduced in a vehicle which can be evaporated out of the leather so as to leave the unfilled interstices.

The non-impregnated thickness of the leather product of the present invention is substantially free from the plasticized resin so that its vapor permeability and flexibility is not substantially effected 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 resin 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 plasticized resin" it is meant that such remaining thickness does not contain a sufficient amount of resin to materially modify the natural properties thereof and it is not intended by such term to exclude small quantities of resin 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 plasticized resin solution is applied "to the grain surface only" does not exclude any kind of treatment which results in such small quantities of resin being present in the remaining thickness of the finished product.

A sufficient number of specific examples of the application of the invention will now be given so that anyone skilled in the art may thoroughly understand the practice of the process and without need for experimentation of inventive character in adapting the process to specific application.

In the following examples, the abrasion ratios given in each case show the increase in resistance to abrasion of leather treated according to my process but otherwise unfinished, as compared with unfinished and untreated leather of the same type. If my treated samples are given a finish and compared with ordinary untreated but finished samples, the increase in resistance to abrasion of my treated samples is much higher in each case. The abrasion ratio data is based upon abrasion tests made by scraping with a dull knife and comparing the number of strokes necessary to produce a similar abraded appearance. This method of testing has been found to give a truer test of actual scuffing conditions than that produced by the usual abrasion meters.

EXAMPLES.—PART A

Various plasticized synthetic resins used on a particular type of side leather

In the examples in Part A, the leather is cowhide side leather, combination tanned (chrome tanned with a moderate vegetable retan). It has been buffed lightly. The weight is 4 oz., e. g., it weighs roughly 4 oz. per sq. ft., and the thickness is about .062".

In each of these examples, the amount of treating solution applied was approximately one ounce per square foot of leather.

The proportions shown are based on the metric system, in which a milliliter of water weighs one gram. Since the resins are ordinarily measured by weight, they are shown in terms of grams. The plasticizers and solvents, being liquid, usually are measured in terms of volume, and thus are here shown in milliliters. Where the proportion of plasticized resin is shown, it is expressed as the ratio of the weight (in grams) of materials after drying to the volume (in milliliters) of the solution.

EXAMPLE 1

	Proportions
Resin: Vinylite VAGH (Bakelite Co.) (a vinyl chloride-acetate copolymer resin)	100
Plasticizers:	
Flexol DOP (Carbide & Carbon Chemicals Co.) (di(2-ethylhexyl) phthalate)	43
Flexol 4GO (Carbide & Carbon Chemicals Co.) (polyethylene glycol di(2-ethylhexoate))	22
Santicizer 141 (Monsanto Chemical Co.) (Alkyl-aryl phosphate)	22
Flexricin P–4 (Baker Castor Oil Co.) (methyl acetyl ricinoleate)	20
Flexol TOF (Carbide & Carbon Chemicals Co.) (tri(2-ethyl hexyl) phosphate)	9
Solvents:	
Methyl ethyl ketone	350
Denatured ethyl alcohol	110
Toluene	310

Since the resin has a specific gravity of 1.39, its proportion in terms of volume is 72. Thus the total volume amounts to 958. The film formed by evaporating this solution, comprising resin plus plasticizers (average specific gravity-.993), weighs 215 units. Thus the proportion of plasticized resins (weight/volume) is 22.5%. The viscosity of this solution is about 40 centipoises at room temperature.

An infinite variety of slightly different solutions may be obtained by varying the proportions of the various plasticizers. Likewise, the proportions of the solvents may be changed, provided the total amount of solvent is not substantially changed. A variety of other solvents including aromatic hydrocarbons, alcohols, and selected esters may be substituted for the solvents shown, provided that there is always sufficient methyl ethyl ketone or some other ketone to secure good solubility.

EXAMPLE 2

To the above ingredients was added 9 parts of Artisil Direct Brown ENZ (Sandoz Chemical Works, Inc.) a ketone soluble dyestuff. This is used where a fairly dark reddish brown shade is desired, so that if the top finish is scuffed off, the leather does not show through in a lighter shade. Obviously other colors are used when other shades are desired. When light shades are desired and the leather has been colored already in the drums, there is no need for any dyestuff in the treating solution.

The addition of the dyestuffs does not change the other characteristics of the solution, except for a slight increase in the proportion of solids and the viscosity.

In both of the above examples the resistance to abrasion (as indicated by scraping with a dull knife) of the treated pieces was 3.5 times that of untreated control samples.

EXAMPLE 3

Resin: Vinylite VYHH (Bakelite Co.) (a vinyl chloride-acetate copolymer with higher proportion of vinyl acetate)	100
Plasticisers:	
Flexol DOP (described above)	43
Flexricin P–4 (described above)	43
Solvents:	
Methyl ethyl ketone	310
Butyl acetate	100
Toluene	170
Xylene	52

The specific gravity of the resin is 1.36, and of the plasticizers .96. Thus the total volume is 792 and the proportion of plasticized resins is 23.0%.

There is a smaller proportion of plasticizers than in Example 1, since VYHH is a more flexible resin than VAGH.

The viscosity of the above solution is about 43 centipoises.

The abrasion resistance of the treated pieces was 2.9 times that of the control samples.

EXAMPLE 4

Resin: Vinyl Solution 732–49C (American Resinous Chemicals Corp.) (a 20% solution of vinyl chloride acetate copolymer in methyl ethyl ketone+toluol)	500
Plasticizers:	
Flexol DOP (described above)	48
Flexol 4GO (described above)	48
Solvents:	
Methyl ethyl ketone	90
Toluene	90
Xylene	72

This is an instance where the resin comes in solution form. The solution is merely mixed with the additional solvent and the plasticizers.

The proportion of plasticized resins is 23% in this case. The viscosity is about 41 centipoises.

The resistance to abrasion of the treated pieces averaged 2.8 times that of the untreated control samples.

EXAMPLE 5

Resins:	
Vinyl Solution 732–49C (described above)	250
Vinyl Solution 732–15 (American Resinous Chemical Corp.) (a 30% solution of vinyl chloride-acetate copolymer resin in methyl ethyl ketone and toluene. This resin has a lower molecular weight than 732–49C)	167
Plasticizers:	
Flexol DOP (described in Ex. 1)	44
Flexol 4GO (described in Ex. 1)	44
Solvents:	
Methyl ethyl ketone	150
Toluene	150

This is an example of a mixture of two vinyl chloride-acetate resin solutions, using equal amounts of each resin. The plasticized resin content is 187 parts by weight, and the proportion is 23.3%.

The viscosity is 40 centipoises.

The resistance to abrasion in this instance was 2.7 times that of the untreated control samples.

EXAMPLE 6

Resin:	
Vinylite VAGH (described in Ex. 1)	80
Vinyl Solution 605–22 (American Resinous Chemicals Corp.) (a 20% solution of vinyl chloride-acetate copolymer resin in methyl ethyl ketone and toluene. This resin has a higher molecular weight, chloride content, and inherent viscosity than the others)	100
Plasticizers:	
Flexol DOP	40
Flexol 4GO	40
Santicizer 141	40
Solvents:	
Methyl ethyl ketone	410
Toluol	415

This is an example of mixing two different vinyl chloride-acetate resins, one in solid-like form and the other in solution. The 605–22 is too viscous to be desirable alone, but it may be used as part of the resins.

The proportion of plasticized resin is 21½%.

The viscosity is about 36 centipoises.

In this case the ratio of resistance to abrasion was 3.0 to 1.

EXAMPLE 7

Resin:	
Vinylite VAGH (described in Ex. 1)	84
Butyl Methacrylate Solution 54–18B (American Resinous Chemicals Corp.) (a 40% solution of polymerized methyl methacrylate in toluene)	40
Plasticizers:	
Flexol DOP (described in Ex. 1)	40
Flexol 4GO (described in Ex. 1)	20
Flexol TOF (described in Ex. 1)	23
Santicizer 141 (described in Ex. 1)	20
Solvents:	
Methyl ethyl ketone	320
Butyl acetate	100
Toluene	200
Xylene	40

This is an example of adding a methacrylate resin to the vinyl resin. The butyl methacrylate is tackier but has lesser resistance to abrasion.

The plasticized resin proportion is 23%.

The viscosity is about 37 centipoises.

The improvement in resistance to abrasion over untreated leather was 3.0 to 1.

EXAMPLE 8

Resin: Vinylite AYAF (Bakelite Co.) (a polymerized vinyl acetate resin of moderately high molecular weight) ---------- 100
Plasticizers:
Flexol 4GO (described in Ex. 1) ---------- 25
Dibutyl phthalate (available from numerous sources) ---------- 10
Santicizer 8 (Monsanto Chemical Co.) (mixture of N-ethyl ortho and para toluene sulfonamides) ---------- 15
Solvents:
Methyl ethyl ketone ---------- 250
Ethanol ---------- 170
Toluene ---------- 150

The specific gravity of the resin is 1.18, and the average for the plasticizer is 1.06. Thus the total volume is 705 parts, and the weight of the plasticized resin is 153 with a proportion of 21.4%.

The viscosity is about 44 centipoises.

The resistance to abrasion was 2.7 times that of the untreated controls.

EXAMPLE 9

Resin:
HM 130 (E. I. du Pont de Nemours & Co.) (a polymerized-acrylic resin) ---------- 100
Plasticizers:
Santicizer 141 (described in Ex. 1) ---------- 45
Santicizer 8 (described in Ex. 1) ---------- 15
Solvents:
Methyl ethyl ketone ---------- 250
Toluene ---------- 150
Xylene ---------- 135

The proportion of plasticized resin is 23½%.

The viscosity is about 36 centipoises.

The resistance to abrasion was 2.9 times that of the untreated pieces.

This is an example of using a commercial acrylic resin.

EXAMPLE 10

Resin: Polymerized methyl acrylate (30%) (polymerized by P. F. Lawler, for 24 hours at 56° C. in a 30% solution, with 0.06% benzoyl peroxide as an accelerator) ---------- 333
Plasticizers:
Santicizer 141 (described in Ex. 1) ---------- 25
Flexol 4GO (described in Ex. 1) ---------- 10
Flexol DOP (described in Ex. 1) ---------- 10
Solvents:
Dioxane ---------- 80
Methyl isobutyl ketone ---------- 70
Butyl acetate ---------- 75
Ethyl acetate ---------- 75

This is an example of using a flexible resin which needs less plasticizer than the resins previously shown.

The proportion of plasticized resin is 21.2%.

The viscosity is about 44 centipoises.

The resistance to abrasion was 2.2 times that of the untreated controls.

EXAMPLE 11

Resin: Butyl methacrylate solution 54–18B (40%) (described in Example 7) ---------- 250
Plasticizers:
Santicizer 141 (described in Ex. 1) ---------- 15
Flexol 4GO (described in Ex. 1) ---------- 11
Flexol DOP (described in Ex. 1) ---------- 11
Solvents:
Methyl ethyl ketone ---------- 200
Butyl acetate ---------- 100
Toluene ---------- 140

The proportion of plasticized resin is 24%.

The viscosity is about 41 centipoises.

The resistance to abrasion was 2.6 times that of the untreated controls.

This is an example of the methacrylate group of resins. Butyl methacrylate becomes flexible and tacky with a minimum amount of plasticizer. In contrast, methyl methacrylate is much stiffer and requires large amounts of plasticizer. Because of the high molecular weight of methyl methacrylate, it is difficult to secure adequate penetration, even at low viscosities.

EXAMPLE 12

Resin: Geon 400x74 (B. F. Goodrich Chemical Co.) (a modified vinyl chloride polymer resin) ---------- 100
Plasticizer:
Flexol DOP ---------- 33
Flexol 4GO ---------- 16
Flexol TOF ---------- 8
Flexricin P4 ---------- 16
Santicizer 141 ---------- 17
Solvents:
Methyl ethyl ketone ---------- 350
Xylene ---------- 350

The proportion of plasticized resin is about 22%, and the viscosity about 40 centipoises.

The ratio of resistance to abrasion was 4.1 to 1.

EXAMPLES.—PART B

Same plasticized synthetic resin used on various types of leather

In the following examples the proportions of resin and plasticizer in the solution is the same as in Example 1: i. e., Vinylite VAGH 100 parts by weight with 116 parts by volume of mixed plasticizer. In order to adapt the treating liquid to the varying porosity of different types of leather, the viscosity is adjusted by adding varying amounts of solvents. The more porous the leather, the higher is the optimum viscosity of the treating liquid. For each type of leather, the examples show the proportion of solids and the approximate viscosity.

The amount of solution applied depends largely upon the thickness of the leather. This is shown, according to trade terminology, in terms of "ounces" in which an ounce equals one sixty-fourth of an inch. Very roughly, a square foot of 3 oz. leather weighs 3 ounces, avoirdupois.

The examples show the abrasion ratio: the ratio of resistance to abrasion of the treated leather to that of untreated leather from the same skin.

EXAMPLE 13

Leather: Chrome tanned side leather, 2½ oz., very lightly buffed
Solution: 22% plasticized resin; about 38 cps.
Amount: About ⅝ oz. per sq. ft.
Abrasion ratio: 3.5

EXAMPLE 14

Leather: Chrome tanned side leather, 3½ oz. moderately buffed
Solution: 23½ plasticized resin; about 45 cps.
Amount: About ⅞ oz. per sq. ft.
Abrasion ratio: 3.1

EXAMPLE 15

Leather: Combination tanned (chrome and very thorough vegetable retan) side leather, 4½ oz., substantial buffing
Solution: 21½ plasticized resin; about 36 cps.
Amount: About 1¼ oz. per sq. ft.
Abrasion ratio: 3.4

EXAMPLE 16

Leather: Combination tanned (chrome and moderate vegetable retain) side leather, 4 oz. moderate buffing
Solution: 24% plasticized resin; about 48 cps.
Amount: About one oz. per sq. ft.
Abrasion ratio: 3.7

EXAMPLE 17

Leather: Description same as Example 16 but tanned tighter
Solution: 21% plasticized resin; 34 cps.
Amount: About one oz. per sq. ft.
Abrasion ratio: 2.7

EXAMPLE 18

Leather: Side leather for garment—cowhide, chrome tanned, with higher chrome content and high proportion of grease, 2½ oz., lightly buffed
Solution: 19% plasticized resin; about 27 cps.
Amount: About ⅝ oz. per sq. ft.
Abrasion ratio: 3.0

N. B. The high grease cntent reduces the leather's porosity (makes it tight); this, combined with light buffing, necessitates a solution with low viscosity.

EXAMPLE 19

Leather: Garment sheepskin, chrome tanned, not buffed, fairly high grease content, 2 oz.
Solution: 22% plasticized resin; about 39 cps.
Amount: About ⅔ oz. per sq. ft.
Abrasion ratio: 3.1

N.B. Sheepskin is naturally quite porous, but high grease content and absence of buffing require about average viscosity in this case.

EXAMPLE 20

Leather: Chrome sheepskin for slippers, not buffed, 2 oz.
Solution: 23% plasticized resin; about 43 cps.
Amount: About ⅔ oz. per sq. ft.
Abrasion ratio: 3.2

EXAMPLE 21

Leather: Vegetable tanned sheepskin for hat linings (sweat bands); not buffed, 2–2½ oz.
Solution: 22% plasticized resin; about 39 cps.
Amount: About 0.7 oz. per sq. ft.
Abrasion ratio: 3.7

EXAMPLE 22

Leather: Chrome tanned sheepskin for shoe linings, plated, not buffed, 1¾–2 oz.
Solution: 21½% plasticized resin; about 36 cps.
Amount: About ½ oz. per sq. ft.
Abrasion ratio: 4.1

EXAMPLE 23

Leather: Chrome tanned calfskin, not buffed, 2 oz.
Solution: 22% plasticized resin; about 39 cps.
Amount: About ½ oz. per sq. ft.
Abrasion ratio: 2.5

EXAMPLE 24

Leather: Same description as Example 23, but from another tanner
Solution: 20% plasticized resin; about 30 cps.
Amount: About 1.2 oz. per sq. ft.
Abrasion ratio: 2.1

EXAMPLE 25

Leather: Chrome tanned kid for shoe uppers, no buffing, 1¾ oz.
Solution: 20% plasticized resin; about 30 cps.
Amount: About 0.4 oz. per sq. ft.
Abrasion ratio: 2.2

N. B. The proportion of plasticized resins must be fairly low because: (1) no buffing, (2) the leather is purposely tanned tight to minimize penetration of usual finishes.

EXAMPLE 26

Leather: Split from cowhide, well greased; chrome tanned 4½ oz.
Solution: 23½% plasticized resin; about 45 cps.
Amount: About 1¼ oz. per sq. ft.
Abrasion ratio: 3.8

EXAMPLE 27

Leather: Split from chrome tanned cowhide; not so much grease as Example 26, 3½ oz.
Solution: 24½% plasticized resin; about 51 cps.
Amount: About 1 oz. per sq. ft.
Abrasion ratio: 3.6

EXAMPLE 28

Leather: Vegetable tanned side leather for shoe linings; slight buffing, 2½ oz–3 oz.
Solution: 18½% plasticized resin; about 25 cps.
Amount: About ⅔ oz. per sq. ft.
Abrasion ratio: 2.8

This is an example where the particular tanning process results in a less porous leather than similar leather from other tanneries.

I claim:

1. Process of treating lightweight unfinished grain leather which comprises impregnating said leather from the grain surface inwardly with a liquid solution comprising synthetic, thermoplastic, water insoluble resin, a plasticizer for the resin and an organic solvent for the resin and plasticizer, by applying said solution to the grain surface only of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, the proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth not less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% of the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

2. Process of treating lightweight unfinished grain leather which comprises impregnating said leather from grain surface inwardly with a liquid solution comprising a vinyl copolymer resin in which vinyl chloride is the principal component, a plasticizer for the said resin, and an organic solvent for the resin and plasticizer, by applying said solution to the grain surface only of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, the proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth not less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% of the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

3. Process of treating lightweight unfinished grain leather which comprises impregnating said leather from the grain surface inwardly with a liquid solution comprising methyl acrylate resin, a plasticizer for the said resin and an organic solvent for the resin and plasticizer, by applying said solution to the grain surface only of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, the proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth no less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% of the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

4. Process of treating lightweight unfinished grain leather which comprises impregnating said leather from the grain surface inwardly with a liquid solution comprising vinyl acetate resin, a plasticizer for the said resin and an organic solvent for the resin and plasticizer, by applying said solution to the grain surface only

of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, the proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth not less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% based on the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

5. Process of treating lightweight unfinished grain leather which comprises impregnating the grain layer of the leather from the grain surface inwardly with a liquid solution comprising butyl methacrylate resin, a plasticizer for the said resin and an organic solvent for the resin and plasticizer, by applying said solution to the grain surface only of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, the proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth not less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% of the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

6. A leather product for use as shoe uppers and the like, said product having substantially increased wear resistance and improved break over the untreated leather and having a water vapor permeability suitable for shoe uppers and a satisfactory flexibility and comprising a lightweight grain leather, which is impregnated from the grain surface inwardly with the dried residue of an organic solution of a plasticized, thermoplastic, water insoluble resin, the penetration of said plasticized resin in said leather from the grain surface inwardly being not less than 15% and not more than 50% of the average thickness of said leather the remaining thickness of said leather being substantially free from said plasticized resin.

7. A leather product for use as shoe uppers and the like, said product having substantially increased wear resistance and improved break over the untreated leather and having a water vapor permeability suitable for shoe uppers and a satisfactory flexibility and comprising a lightweight grain leather, which is impregnated from the grain surface inwardly with the dried residue of an organic solution of a plasticized vinyl copolymer resin in which vinyl chloride is the major component, the penetration of said plasticized resin in said leather from the grain surface inwardly being not less than 15% and not more than 50% of the average thickness of said leather, the remaining thickness of said leather being substantially free from said plasticized resin.

8. A leather product for use as shoe uppers and the like, said product having substantially increased wear resistance and improved break over the untreated leather and having a water vapor permeability suitable for shoe uppers and a satisfactory flexibility and comprising a lightweight grain leather, which is impregnated from the grain surface inwardly with the dried residue of an organic solution of a plasticized methyl acrylate resin, the penetration of said plasticized resin in said leather from the grain surface inwardly being not less than 15% and not more than 50% of the average thickness of said leather, the remaining thickness of said leather being substantially free from said plasticized resin.

9. A leather product for use as shoe uppers and the like, said product having substantially increased wear resistance and improved break over the untreated leather and having a water vapor permeability suitable for shoe uppers and a satisfactory flexibility and comprising a lightweight grain leather, the grain surface of which is impregnated with the dried residue of an organic solution of a plasticized vinyl acetate resin, the penetration of said plasticized resin in said leather from the grain surface inwardly being not less than 15% and not more than 50% of the average thickness of said leather, the remaining thickness of said leather being substantially free from said plasticized resin.

10. A leather product for use as shoe uppers and the like, said product having substantially increased wear resistance and improved break over the untreated leather and having a water vapor permeability suitable for shoe uppers and a satisfactory flexibility and comprising a lightweight grain leather, which is impregnated from the grain surface inwardly with the dried residue of an organic solution of a butyl methacrylate plasticized resin, the penetration of said plasticized resin in said leather from the grain surface inwardly being not less than 15% and not more than 50% of the average thickness of said leather, the remaining thickness of said leather being substantially free from said plasticized resin.

11. The process of claim 1 wherein the proportion of plasticizer to resin is from about 50 to about 75 parts of plasticizer per 100 parts of resin greater than the proportion of plasticizer per 100 parts of resin normally required to form a free resin film.

12. The product of claim 6 wherein the proportion of plasticized resin in said solution is between about 15% and 30% based on weight of plasticized resin to total volume of solution and the amount of solution is between about 15% and 50% of the weight of the leather.

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