The invention described herein, if patented, may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

Our invention relates to a new and novel method of preparation of a useful fibrous product and the fibrous product itself. More specifically, a leather which has been previously tanned, or partially tanned, is treated with an emulsion containing certain resins, plasticizers, bonding agents and emulsifying agents, to produce a leather which is more water-resistant than leathers produced by conventional treatments and which has improved scuff resistance, wear resistance, and other desirable properties resulting from the resin impregnation. The permeability of the leather and its stiffness may or may not be affected, as may be desired. While particularly advantageous for leather, the emulsion may be used for the treatment of fabrics, felts, webbing, paper, furs, and other fibrous products.

According to the present invention, comparatively stable emulsions of the compounds to be added are prepared by dissolving the compounds in an organic solvent and dispersing the solution in water to form an emulsion. A colloid mill, or similar equipment, may be used for the dispersion. The emulsion is added to the leather while the leather is in a damp condition, and most conveniently while still in the leather-treating drum so that the desired materials penetrate into the leather under perfect control and are deposited in the location desired and in the desired quantities throughout the leather, so that when the leather is dry and the polymerization completed, a material is produced which has the desired permeability and which has the desired flexibility and which is more uniform and stronger than the original skins from which it was produced. While the method of impregnation may be used for the treatment of fabrics and other fibrous products, the description herein set forth will be described as it applies to leather. The method for use on other materials is similar, depending upon the starting material chosen and the degree of impregnation desired, as is obvious to those skilled in the art.

The emulsions used in our method are emulsions prepared by the dispersion of an organic solvent containing resins, oils, plasticizers, etc., in solution in water with the aqueous phase as the continuous phase; the term "emulsion" as used herein is intended to cover the dispersion of a true solution as well as the dispersion of colloids, and the dispersion prepared by the methods disclosed, even though the solids may be themselves dispersed in the aqueous phase rather than be dispersed in the solvent in the continuous phase. The emulsion used should be reasonably stable; under some instances materials which are present for other purposes may additionally function as emulsifying agents, but for convenience and certainty it is normally expedient to add a small quantity of an emulsifying agent such as ordinary tannery soap, sulfated cod oil, and/or sulfated neat's-foot oil, or one of the sulfated or sulfonated surface-active emulsifying agents such as laurel sulfate or one of the proprietary agents of the same general class, such as Tergitol, Nacomol, Duponol, Igepon, etc. The emulsifying agent should be present in such quantity that the emulsion will be stable for at least 24 hours, and preferably for about a week. The emulsion must be used while stable, so that the emulsion "breaks" during the penetration into the leather causing the emulsified material to penetrate comparatively uniformly throughout the structure of the leather, the water originally present in the leather being displaced to a certain extent and the water phase of the emulsion itself remaining in the drum as an inert carrier. When drained from the drum the water contains only a small fraction of the materials originally dispersed in the water. The breaking of the emulsion is critical. If the emulsion breaks too slowly the leather is pounded too much during the drumming, whereas if it breaks too fast, the resins are deposited on the surface of the leather. The emulsion must break so that the resins and other materials are deposited through the leather, and must break readily from the drumming. The pH of the solution affects the stability of the emulsion. During the treatment the emulsion must be on the acid side, normally below a pH of 6.5, and preferably below 5.0. Any ammonia released, as for example from hydrolytic products of allicon amine compounds, must be neutralized by the addition of acid or buffers.

In the conventional treatment of leather, after tanning the hide, fats are added by a process known as "fat-liquoring," during which sufficient fats and oils are introduced into the leather to cause the fibers to slide on each other, which causes the leather to be more flexible. In our process, certain agents such as sulfonated castor oil, and/or sulfated cod oil serve the dual purpose of an emulsifying agent and a fatting residue. Some of the fat for fatting the leather is normally introduced before our resin treatment,
but the amount of fat used is reduced below normal to the extent that fats are added by the fat-liquor ingredients used in the resin emulsion as an emulsifying agent. Additional fats may be introduced at this time by dissolving them in the oil phase of the emulsion. These fats may be double- or multiple-purpose materials. For example, paraffin oil serves both as a fat for the leather and as a plasticizer for the resins.

The amount of resin used in the leather treatment may be varied, depending upon the type of leather desired and the type of leather which is used. The leather may be treated with resin compositions of the following types:

I(a) Silicon-containing oils which are unpolymerizable, plus plasticizers and bonding agents, dispersed as an emulsion as mentioned above.

I(b) Silicon-containing resins which are unpolymerizable, but are polymerizable, plus bonding agents, dispersed as an emulsion as mentioned above.

II(a) Silicon-containing oils, unpolymerizable, plus plasticizers and bonding agents, plus additional resins and/or drying oils.

II(b) Silicon-containing resins, unpolymerizable but polymerizable, plus plasticizers and bonding agents, plus resins and/or drying oils.

III(a) Silicon-containing oils, unpolymerizable, plus plasticizers and bonding agents, plus partially polymerized resins or preformed resins.

III(b) Silicon-containing resins, unpolymerizable but polymerizable, plus plasticizers, bonding agents, plus partially polymerized resins and/or pre-formed resins.

The silicon-containing compounds may be silicone-type resins which may be prepared by the hydrolysis of certain organo-halosilanes; or they may be silicone amine resins which are prepared by the acylation of anhydrous ammonia of certain organo-halosilanes; or they may be the mixture of one or more silicone or silicone amine resins, or both; or compounds in which both the silicone and silicon amine type linkages occur in individual molecules.

The raw hide is put through the conventional steps of soaking, liming, bating, picking, chrome tanning, sorting, splitting, to weight, shaving to even, and coloring processes according to conventional tannery practices. After the coloring without the necessity of removing the leather from the drum, it is washed with water heated to the fat-liquoring temperature, and that portion of the fat liquor which is not a portion of the subsequent resin emulsion is added in the conventional manner, and the drum is run until the fat is properly absorbed. It is then heated to the temperature at which the particular emulsion works best, which must be determined by experience inasmuch as slight variations, such as the degree of the polymerization of the resins and the lability of the emulsion caused by variations in batches of wetting agents and variations in the colloidal mill setting affect the temperature range desired. The emulsion is added, the drum run until the emulsion properly enters the leather, the water drained and the hide dried, which also cures the resins. The fat-liquoring of the leather may be partially or totally accomplished during the emulsion treatment, as may part or all of the dye treatment. The leather should be dyed concurrently with or prior to the resin emulsion treatment, the faying of the leather may be accomplished prior to, concurrently with, or subsequent to the resin treatment, or partially at each of these times.

The leather as treated by our process does not "snap" as much as conventional leathers, so that it will lie flat for cutting, enabling higher production rates on cutting tables. Additionally, the leather does not require damping as a preliminary operation to cutting, which saves time in the production of goods from the leather. The leather is very resistant to wear, and very sturdy. The leather produced by using a polymerizable silicone oil is softer, sleeker and less wear resistant than the leather produced by the polymerizable silicone-containing compounds. A polymerizable or oxidizable compounds should be present to bind unpolymerizable compounds if it is desired to prevent "bleeding.”

The temperature at which the leather is treated with the emulsion may be varied, however, it must be high enough that the fats in the emulsion do not solidify, and preferably high enough that penetration of emulsion into the leather is not unduly delayed. Further, it must not be so high that the resins will polymerize prematurely or separate out on the surface of the skin or on the inside of the drum. Dependent upon the choice of ingredients and the stability of the emulsion, the temperature range during the treatment may be varied markedly; however, a temperature range of 100° F. to 130° F. is a normal operating range, and a range of 120° F. to 130° F. is preferred because it is more economical and rapid. Care must be taken that the operation is conducted so that the resins in the emulsion penetrate the leather. If the emulsion is not sufficiently stable, or if the temperature is too high, it is found that the emulsion has a tendency to break before penetration so that the resins remain on the surface of the leather and on the inside of the drum. The condition is readily noted during the operation, and the resin may be observed on both the skins. The drum should be run until the emulsion has broken and penetrated completely, which may vary from 10 minutes to 5 hours, though 30 minutes is a normal operating period, depending upon the temperature and the emulsion. The emulsion should break in from 2 to 15 minutes, with the additional time required for thorough penetration. The leather when removed from the drum is dried sharply. A temperature of 135° F. to 140° F. for about 8 hours is preferred to remove the solvent and polymerize the resins. If slow-curing resins or thick leather is used, longer heating may be required. If a temperature below 135° F. is used, too long a period may be required for polymerization. If a temperature of over 160° F. is used, the leather may be damaged by the heat. It is observed of that each fiber contains its proportionate share of the additives, and accordingly each fiber becomes resistant to the action of moisture. However, the interstices between the fibers are not filled, and accordingly the leather retains the porosity, the flexibility, and the resilience which makes leather so useful for certain purposes. When gloves or similar items are made from leather so treated, the permeability to moisture vapor is not deleteriously
reduced so that the natural moisture of the user’s hands or feet is allowed to escape, but at the same time liquid water is prevented from entering. Our leather possesses the highly desirable quality of permitting passage of water vapor and other gases, yet preventing the penetration of liquid water to a degree that has not previously been known in the leather trades. Additionally, because of the uniform penetration of the emulsion into the skin, the flanks and belly of the skin, which are usually the most difficult to treat and which usually are softer and do not possess the wear-resistant qualities of the remainder of the skin, are toughened and made firm so that these portions compare more favorably with other portions of the hide as to quality, than is the case with previous and conventional methods of leather treatment. If permeability is not important, as in leather belting, the resin content of the leather may be increased sufficiently to fill completely the leather by using more of the resins, with a corresponding increase in water resistance, and wear resistance, and toughness.

If resins are used without the addition of silicon resins, but otherwise in accordance with our invention, a leather is produced which has a certain degree of water resistance and other desirable properties over that treated by normal fat-liquoring and finishing operations. It is useful and very valuable because of these characteristics, but, however, it does not possess the remarkably high degree of water resistance that is imparted to the leather by the silicon-containing materials. The silicon-containing resins appear to have hydrophobic properties which are unique and highly desirable, and appear to impart this property to the leather or other fiber when it is treated in accordance with our invention.

Natural skin and the leather made therefrom are normally nearly free from silicon compounds. Analysis shows from 0.0% to 0.05% of silicon present. As made in accordance with our invention, the leather will show a silicon content of from 0.5% to 3.0% silicon. Leather prepared in accordance with this invention has the silicon present in a silicon compound, including carbon to silicon bonds. Entirely different results and methods are obtained than are found in certain of the prior methods of finishing leather in which silicon as silicon dioxide, sand for instance, or diatomaceous earths, is introduced into the leather. The organic character of silicon present is an essential element of the leather treatment.

In the preparation of our emulsions, because some of the silicon-containing resins polymerize so readily it is frequently not practicable to isolate the resin and weigh it out. Therefore, the silicon-containing resin, or other resin, is kept in solution in an organic solvent, such as xylene, and sufficient quantities of the solution added to give the desired amount of resin, and this quantity of solvent is deducted from subsequent amounts of solvent which may be added to dissolve all organic components preparatory to emulsification.

In order that those skilled in the art may more fully understand the nature of our invention, the following examples are given by way of explanation, but not limitation:

**Example I.** — A side of leather running from 2 to 2½ inches on the Woburn gauge (single) was treated as follows: The piece of leather in the drum, the crust weight of which before drying was 645 grams and which was heated to 130° F., was added 720 grams of an emulsion and 1000 ml. of water. The emulsion contained about 25% of total solids, including 10% silicon-containing compounds resulting from the hydrolysis of equal proportions of methyl tri-chlorosilane and dimethyl chlorosilane, which were hydrolyzed in the presence of ether and xylene; the ether being removed by evaporation under vacuum and the solution concentrated to a 50% solution. Sufficient of this solution was used so that 10% of silicon-containing compound and 10% of xylene were each present in the finished emulsion. To the xylene solution was added 1.5% castor oil, 0.7% dibuty phthalate, 0.7% tricresyl phosphate, 0.7% styrene, 1.5% octadecylamine, 6% sulfated nea’s-foot oil, 1.5% sulfated cod oil, 0.7% Moellon oil (a blown cod oil), 0.7% tannery soap and 1.5% "Tergitol," a commercial wetting agent made by Carbon & Carbide Chemicals Corporation; the remainder of the emulsion was water. The emulsion was prepared by dissolving the organic ingredients in the xylene, after which the material was fed with the proper quantity of water through a laboratory colloid mill. The speed of the mill was about 12,000 revolutions per minute. The setting of the colloid mill was such that the emulsion prepared would be stable for approximately a week at room temperature.

After addition of the emulsion and water to the leather, the drum was run for approximately 30 minutes, during which time the emulsion was absorbed by the leather, broke in the leather, and penetrated uniformly and thoroughly throughout the leather. The leather was removed from the drum and dried sharply at 135° to 140° F., for 8 hours. The leather was then conditioned, after which it was ready for use. The weight of the finished leather was 820 grams. The leather as thus produced possessed a body and feel which was comparable with leather from ordinary finishing procedures, but possessed a far greater resistance to water and to wetting, because of the resin treatment. The water resistance of the leather was increased at least three-fold, and the leather, even if thoroughly wet due to long and protracted immersion, would dry back to its original state in one-third the time of conventional leathers, and remained flexible and practically unaffected by the water after drying rather than becoming stiff as do most leathers. The leather dries with less shriveling and does not dry crisp.

**Example II.** — An emulsion was prepared containing by weight 5.9% of silicone fluid, Dow-Corning Series 200, 350 centistokes viscosity, and 2.3% silicone fluid, Dow-Corning Series 300, 1250 centistokes viscosity. These silicone fluids are an unpolymerizable silicone fluid, apparently comprising mainly methyl silicone compounds; 1.2% of air-blow castor oil; 5.9% of sulfated nea’s-foot oil; 1.2% of sulfated cod oil; 0.6% tricresyl phosphate; 0.6% dibuty phthalate; 1.3% tristearin; 0.6% octadecylamine; 2.9% of a special emulsifying mixture consisting of ½ ordinary tannery soap, ½ oxidized sulfated cod oil, and ½ laurel sulfonate; 8% xylol; and water.

A quantity of emulsion which contained 179 grams of solids was added, with water, as in Example I, to a skin of 660 grams crust weight, and gave the leather a final weight of 885 grams which was very resistant to water. The use of the unpolymerizable silicon compounds gave a somewhat softer leather than the leather of Example I.

**Example III.** — A silicon resin was prepared by the hydrolysis of a mixture of 65% methyl tri-
cholorosilane and 35% dimethyl dichlorosilane. An emulsion was prepared containing 6.8% of the above silicone resin, 1.1% air-blown castor oil, 3.0% natural castor oil, 1.2% sulfated castor oil, 0.6% tricresyl phosphate, 0.6% dibutyl phthalate, 4.5% tristearine, 0.6% octadecylamine, 2.8% of the special emulsifying mixture, 0.11% of a 6% solution of cobalt naphthenate in kerosene, the solution being a standard commercial product, and the remainder water. A 10 quantity of the emulsion which contained 220 grams of solids was added to a skin of 775 grams crust weight, resulting in a final skin of 1050 grams weight.

Example IV.—A silicone resin was prepared by the hydrolysis of a mixture of 90% ethyl trichlorosilane, and 10% diethyl dichlorosilane, following the procedure of Example I. A partially polymerized styrene resin was prepared by heating styrene, adding 0.1% of benzoyl peroxide in small portions as the styrene was near boiling, until the styrene had polymerized to a viscosity of 30 to 40 poises when measured at 20°C, the styrene was then cooled and diluted with xylene to prevent further polymerization. An emulsion was prepared using such quantities of the xylene solution of the final emulsion contained 7.2% of silicone resin, 2.9% of the partially polymerized styrene resin, 2.4% of xylene soluble coumarone-indene resin, 0.7% of partially polymerized vinyl acetate, 1.1% of castor oil, 0.9% of paraffin oil, 1.9% of sulfated neat's-foot oil, 0.5% of sulfated castor oil, 2.4% of oiticica, 1.5% of raw amber linseed oil, 1.3% of tricresyl phosphate, 0.5% tristearine, 0.9% of octadecylamine, 3.2% of paraffin wax (M. P. 125°F.), 1.4% of the special emulsifying mixture, 0.1% of cobalt naphthenate solution, 12.5% xylol, and the remainder water. A skin of 1125 grams crust weight was treated with a quantity of the emulsion containing 340 grams of solid, and water as in Example I, giving a skin of the final weight of 1465 grams. The skin had a firm, solid feel, it was neither greasy, sticky nor tacky, and was very resistant to water, and wears remarkably well.

Example V.—A silicon-containing resin was prepared by hydrolysis of a mixture of 90% ethyl trichlorosilane and 10% diethyl dichlorosilane, following the procedure of Example I. The emulsion was prepared by the use of such quantities of the solution of resins that the final emulsion contained 8.8% of the silicone, 3.6% of partially polymerized styrene resins prepared as in Example IV, 15% of a styrene resin polymerized to a melting point of 100°C, 0.4% of air-blown castor oil, 0.4% of paraffin oil, 0.4% of sulfated neat's-foot oil, 0.9% of sulfated castor oil, 1.3% oil of oiticica, 0.4% of linseed oil, 0.9% of paraffin wax (M. P. 125°F.), 0.9% of tricresyl phosphate, 0.4% of tristearine, 0.4% of octadecylamine, 2.2% of the special emulsifying mixture, 11.7% of xylol, 0.001% each of benzoyl peroxide and dicyclohexylamine, and the remainder water. A skin of 850 grams crust weight was drummed with water and a quantity of the emulsion containing 254 grams solids for 1 hour at 100°F., and gave a skin with a final weight of 1160 grams which made a superior glove leather. The leather was very resistant to both water and wear when tested by handling wet brick.

Example VI.—An emulsion was prepared containing 2.7% silicone fluid (Dow-Corning Series 200, 300 centistokes viscosity), 2.3% partially polymerized styrene prepared as in Example IV, 15% of a silicone resin (melting point 100°C.), 0.5% air-blown castor oil, 0.5% paraffin oil, 4% sulfated neat's-foot oil, 0.8% sulfated cod oil, 2.1% of tetrahydrofuran, 0.8% tetrahydrofuran, 0.8% tricresyl phosphate, 0.5% tristearine, 0.5% octadecylamine, 1.9% of the special emulsifying mixture, 15.5% xylol, 0.001% each of benzoyl peroxide and dicyclohexylamine, the remainder of the emulsion being water. A skin weighing 915 grams was drummed with a quantity of the emulsion containing 380 grams solids, and gave a finished leather weighing 1125 grams, which was particularly soft but resistant to water.

Example VII.—An emulsion was prepared containing 8.7% of silicone fluid (Dow-Corning Series 200, 300 centistokes viscosity), 1.4% of a 50-50 styrene-chlorostyrene resin (melting point 125°C.), 2.8% styrene resin (melting point 75°C.), 1.9% of styrene resin (melting point 95°C.), 0.6% castor oil, 0.6% paraffin oil, 3.8% sulfated neat's-foot oil, 0.8% sulfated cod oil, 1.4% oil of oiticica, 1.0% linseed oil, 1.4% paraffin wax (melting point 125°F.), 1.2% tricresyl phosphate, 0.5% tristearine, 0.6% octadecylamine, 2.5% of the special emulsifying mixture, 12.5% xylol, and the remainder water. A leather was prepared by treating a skin of 900 grams crust weight with a quantity of the emulsion containing 270 grams solids. The leather obtained weighed 1250 grams. Good wear resistance was obtained with this leather.

Example VIII.—A silicon amine resin was prepared by the ammonolysis in liquid ammonia of a mixture of 82% ethyl trichlorosilane and 18% diethyl dichlorosilane. The silanes were dissolved in dry xylene and added slowly with stirring to liquid ammonia, after which the surplus ammonia and some of the xylene was removed by a vacuum and the xylene solution used to prepare the emulsion. An emulsion was prepared containing such quantities of the above solution that the final emulsion contained 9.0% of the silicon amine resin, 0.9% of air-blown castor oil, 2.8% of sulfated neat's-foot oil, 1.2% of sulfated cod oil, 0.9% of tricresyl phosphate, 0.6% of dibutyl phthalate, 4.3% tristearine, 0.6% octadecylamine, 2.6% of the special emulsifying mixture, 11.5% xylol, and the remainder water. A skin of glove leather of 1010 grams crust weight was treated with a quantity of the emulsion containing 284 grams solids, and gave 1340 grams of finished leather which was flexible, durable, of even texture, non-tacky, non-sticky, desirably "dead," and which was very highly resistant to the action of water, and which dried remarkably rapidly if wetted by the prolonged action of water.

The specific plasticizers, bonding agents, etc., as given in the specific examples are not particularly critical. It is usually found that mixtures of plasticizers are more efficient that the same quantity of any one plasticizer, and accordingly, in commercial operations mixtures are used. The plasticizer may consist of any one or more of the following plasticizers, including such compounds as paraffin oil, paraffin wax, castor oil, neat's-foot oil, tricresyl phosphate, dibutyl phthalate, tristearine, microcrystalline petroleum wax, dimethyl phthalate, diethyl phthalate, diphenyl phthalate, or other aryl or alkyl or mix of phthalate, tributyl phosphate, dibutyl tetrarate, dimethyl tetrarate, trimethyl phosphate, methylphthalyl ethylglycolate, triacetin, tripropionin, or other commercial plasticizers.
The octadecylamine is added as a bonding agent. If octadecylamine or other long-chain aliphatic amine is added, the resinous materials are more firmly bonded to the leather, giving improved characteristics. Whereas a satisfactory leather may be produced without the use of such bonding agents, by their use a leather is produced which is longer-wearing, and in which the resins will remain more firmly bonded throughout the useful life of the leather.

Resins which may be used in conjunction with the silicon-containing oils or resins, or less desirably alone, include the styrene and chlorostyrene resins, the resins from vinyl alcohols, vinyl acrylate, diethyl dihdy, and other vinyl resins, methyl methacrylate, butyl methacrylate, or other methacrylate resins and/or co-polymers of such resins. These resins are termed "pre-formed" resins because the polymerization is substantially complete prior to use, as distinguished from para-tertiary trichlorosilane, as disclosed below, in which some polymerization has occurred before use in the emulsion, but which further polymerizes after deposition in the leather.

Drying oils include such common commercial oils as China-wood oil, oil of cottenseed, perilla oil, linseed oil, etc.

Partially polymerized resins include the partial polymers formed by the polymerization to an intermediate point of such compounds as styrene, cumarone-indene, modified Bakelite, etc.

The silicon-containing compounds suitable for leather impregnation in accordance with our invention are preferably hydrolyzed or ammonolyzed compounds of organic halosilanes whose monomer prior to hydrolysis or ammonolysis has the formula

\[ \text{RSiX}_n \] Wherein \( n \) is between about 1 and 2, but not necessarily a whole number, \( X \) is a halogen, and \( R \) is a hydrocarbon radical linked to the silicon by a carbon-to-silicon bond, which hydrocarbon radical is not necessarily the same throughout the compound. These fully substituted silicon compounds may include the products of polymer products of ammonolysis or hydrolysis, or mixtures thereof, of such silicon compounds as methyl trichlorosilane, dimethyl dichlorosilane, para-tertiary trichlorosilane, di-para-tolyldichlorosilane, hexyl trichlorosilane, di-para-tolyl dichlorosilane, tri-para-tolyl dichlorosilane, polydimethyl dichlorosilane, polyethyl dichlorosilane, polypropyl dichlorosilane, polyisobutyl dichlorosilane, polyhexyl dichlorosilane, polyvinyl dichlorosilane, polyvinyl chloride, or other monosilane, di-alkyl, or alkyl-aryl substituted alkyl-aryl, or alkyl-aryl substituted aryl-halo-silanes. Pure compounds, commercial mixtures of such compounds or commercial mixtures of such compounds may be used. Reasonable quantities of tetrahalosilanes may be present in the compounds and frequently are present in commercial preparations, due to the methods used in the preparation of the organosilicon compounds. Suitable mixtures may be prepared by mixing the silanes before reaction, or by the resins or their intermediates at any stage. Similar compounds produced by other methods are also suitable. The hydrolysis products of the aforementioned organosilicon compounds are characterized by an \( \text{Si-O-Si} \) bond between adjacent repeating units, as is more fully explained in U. S. Patents Nos. 2,258,218 to 2,258,222, Rochow. The polymeric ammonolysis products of the aforementioned organosilicon compounds are characterized by an \( \text{Si-N-Si} \) bond between two adjacent repeating organosilicon units, as is more fully explained in the pending application of Nicholas D. Cheronis, Serial No. 72,548, filed January 24, 1949, now Patent No. 2,579,418 (a continuation-in-part of applications Serial No. 516,475 filed September 14, 1944, Serial No. 788,797 filed November 13, 1947, and Serial No. 66,602 and October 26, 1948, all of which are now abandoned); the ammonolysis products of organotrichlorosilanes are particularly valuable in that they are capable of substantially complete autocondensation at room temperature or at comparatively slightly elevated temperatures non-injurious to leather.

Suitable compounds may be prepared by the action of the organo-halo-silanes on primary amines instead of an ammonia; with primary amines as the ammonolyzing agent, the nitrogen bond between two adjacent units is substituted by a hydrocarbon radical

\[ \text{Si}(\text{N})\text{R} \]

while with ammonia as the ammonolyzing agent, the nitrogen bond is substituted by hydrogen

\[ \text{Si}(\text{OH}) \]

as is more fully explained in the pending application, Nicholas D. Cheronis, Serial No. 72,548. Di-amines and di-silicones, i.e., compounds which have an amine group or a silane group at two different locations of the molecule, are also useful in the preparation of resins for use in our invention. The nitrogen-containing compounds appear to bond more firmly to the leather because the amine characteristics of the resins cause them to stick more firmly to the leather. The silicon amine compounds may be prepared and disclosed in the pending application in the name of Nicholas D. Cheronis, Serial No. 72,548, by introducing ammonia or a primary amine and of an organohalo-silane dissolved in an inert solvent (e.g. ether or preferably toluene) into a cooled reaction vessel in the absence of water, to produce a solution of a polymeric substance, and with the aid of a suitable solvent to produce a resin characterized by repeating units of silicon linked to nitrogen as an integral part of the polymer chain. Application Serial No. 72,548 has now matured into Patent No. 2,579,418, Nicholas D. Cheronis, granted December 18, 1951. If the ammonolysis products are allowed to stand in contact with water, as in the emulsion, while in an incompletely polymerized state, some hydrolysis occurs, but the partially hydrolyzed product imparts excellent properties to the fibrous materials treated therewith.

The term "polymeric ammonolysis" as used hereinafore includes the partial polyamides and polymers wherein repeating organosilicon units are joined together by an inorganic non-silicon linkage as an integral part of the polymer chain; those silicon resins, wherein the repeating units are predominantly made up from organosilicon compounds substituted by one monovalent hydrocarbon radical per 1 silicon atom are principally useful for the purposes of the present invention. For example, the product of hydrolysis of methyl trichlorosilane would have a molecular weight of 94, a partial...
polymer a weight of from 170 to around 5,000, and a polymer from 5,000 up. There is no clear line, the characteristics of the material rather than its actual molecular weight is the controlling factor. Each molecule will not have the same size, once polymerization begins, but the average size is taken as the unit for measurement. From the standpoint of this invention, the critical factor is the solubility. If the polymeric compounds are sufficiently soluble in the organic solvent to disperse in the proportions given, the compounds are satisfactory. If polymerization is carried to the insolubilizing state, before impregnation, proper penetration is impeded.

In accordance with commercial practice, the term “polymer” is used to denote the product formed by chain condensation or polymerization, whether or not simple molecules are eliminated, and whether or not there is a resultant change in percentage composition of the compounds. The silicon-containing compounds eliminate water or ammonia as they increase in chain size, which would correspond to the classic definition of “condensation,” but the term “polymerization” is regarded as generic to this type of reaction.

Xylene is a very efficient solvent to use, because all of the compounds used are soluble in it, and its vapor pressure, etc., is favorable. Toluene, benzene, or other aromatic naphthas, and other inert (that is non-reactive with the silicon compound) water-insoluble organic solvents may be used as solvent if availability renders it expedient.

We claim:

1. The process of making a water-resistant leather which comprises the steps of partially fat-lathering a tanned and dyed skin, introducing into the interfiber space of said skin an aqueous emulsion of (1) an inert water-insoluble organic solvent comprising dissolved therein a liquid organic-solvent-soluble silicon resin capable of further polymerization, said resin being characterized by repeating units of silicon joined together by a nitrogen linkage as an integral part of the polymer chain in which the repeating units predominantly are made up from silicon atoms substituted by one monovalent hydrocarbon radical per one silicon atom; (2) a fat-lathering compound and (3) a plasticizer for said silicon resin; breaking said emulsion inside said skin, whereby said silicon resin is deposited on the fibers of said skin in exchange for water naturally contained in said skin; and drying the skin at a temperature above room temperature, whereby said silicon resin is deposited on the fibers of said leather in exchange for water naturally contained in said leather.

2. The process of making a water-resistant leather which comprises the steps of partially fat-lathering a tanned and dyed skin, introducing into the interfiber space of said skin an aqueous emulsion of (1) an inert water-insoluble organic solvent comprising dissolved therein a liquid organic-solvent-soluble silicon resin capable of further polymerization, said resin being characterized by repeating units of silicon joined together by an oxygen linkage as an integral part of the polymer chain in which the repeating units predominantly are made up from silicon atoms substituted by one monovalent hydrocarbon radical per one silicon atom; (2) a fat-lathering compound and (3) a plasticizer for said silicon resin; breaking said emulsion inside said skin, whereby said silicon resin is deposited on the fibers of said skin in exchange for water naturally contained in said skin; and drying the skin at a temperature above room temperature, whereby said silicon resin is deposited on the fibers of said leather in exchange for water naturally contained in said leather.

3. The process of making a water-resistant leather which comprises the steps of partially fat-lathering a tanned and dyed skin, introducing into the interfiber space of said skin an aqueous emulsion of (1) an inert water-insoluble organic solvent comprising dissolved therein a liquid organic-solvent-soluble silicon resin capable of further polymerization, said resin being characterized by repeating units of silicon joined together by a nitrogen linkage as an integral part of the polymer chain in which the repeating units predominantly are made up from silicon atoms substituted by one monovalent hydrocarbon radical per one silicon atom; (2) a fat-lathering compound and (3) a plasticizer for said silicon resin; breaking said emulsion inside said skin, whereby said silicon resin is deposited on the fibers of said skin in exchange for water naturally contained in said skin; and drying the skin at a temperature above room temperature, whereby said silicon resin is deposited on the fibers of said leather in exchange for water naturally contained in said leather.

4. A water-resistant air-permeable leather containing on its individual fibers a solid coating of a silicon resin deposited thereon by the method of claim 1.

NICHOLAS D. CHERONIS.
EDWIN W. NEWBURY.

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