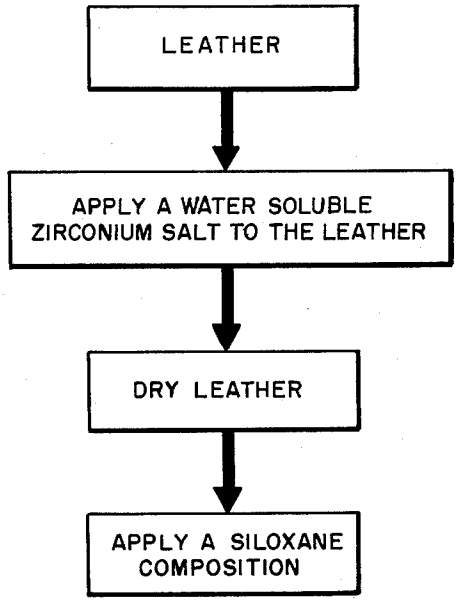
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METHOD OF PRODUCING LEATHER WITH IMPROVED WATER RESISTANCE AND ARTICLE RESULTING THEREFROM

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INVENTOR.
DONALD E. FINDLAY
BY Robert F. Fleming Jr.

ATTORNEY

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METHOD OF PRODUCING LEATHER WITH IMPROVED WATER RESISTANCE AND ARTICLE RESULTING THEREFROM

Donald E. Findlay, Midland, Mich., assignor to The Dow Corning Corporation, Midland, Mich., a corporation of Michigan

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This application relates to a leather of improved resistance to water penetration.

Excellent leather water repellents are disclosed in the patent to Chester Carlyle Currie, Re. 23,879 and in the patent of Melvin J. Hunter and Charles F. Dudley, Patent No. 2,728,736. An improved variation of the latter composition is disclosed in the copending application of John W. Gilkey, Serial No. 635,617, filed January 23, 1957, now Patent No. 2,884,393. All of the compositions in the above patents and application produce leather which is quite resistant to the penetration of water. As a result these types of compositions are enjoying increasing commercial success for use on shoes and other leather articles.

In spite of the excellent nature of these compositions, however, there is often encountered a wide variation in the water resistance which is obtained when these compositions are applied to various types of leather and often to leather from different sections of the same hide. The cause of these variations is not clearly understood. It is known that in part they are due to imperfections in the leather such as scars from insect bites or other wounds. However, this cause alone accounts for only a small portion of the variation. Other more insidious effects such as prior treatment of the leather, the nature of the fibers in the leather and other unknown causes far outweigh these obvious mechanical imperfections. As a result in commercial operation there is often a large amount of rejected leather which will not pass the commercial specifications for silicone treated leather.

A measure of the water resistance of the leather is obtained by flexing the treated material on a Dow Corning Corporation Sylflex leather tester machine while immersed in water as described in "Industrial Laboratories," July 1955, page 94. It has been found that a leather showing a flex of less than 4,000 is not acceptable for commercial use as, for example, in shoes. Leather having flexes greater than 4,000 is acceptable but obviously the higher the flex the better the leather. It has been found from experience that leathers can be classified as follows: Those where the flex is from 0 to less than 4,000 are poor and considered unacceptable. Those having flexes from 4,000 to 10,000 are graded fair, while those having flexes from 10,000 to 30,000 are considered good and leathers with flexes above 30,000 are considered excellent. It is obviously desirable to have 100% of all commercially produced leather in the excellent class or, failing this, it is certainly desirable to have all of the commercially produced leather above 4,000.

Even in the best of leather there is considerable variation from sample to sample. Consequently, in testing the samples for commercial control, an average of several samples is taken.

It is the object of this invention to provide an improved leather which shows a greater resistance to water penetration more consistently than has heretofore been possible. Another object is to upgrade leather which would not ordinarily be commercially acceptable into a commercially acceptable range of water resistance. Other objects and advantages will be apparent from the following description.

This invention relates to a leather article of improved

water resistance which has been treated by the method comprising (1) applying to the leather a dispersion of a water soluble zirconium salt in amount such that the zirconium pickup in the leather is at least .5% by weight based on the dry weight of the leather, (2) drying the leather and (3) thereafter applying to the leather at least 2% by weight based on the weight of the leather of a siloxane composition consisting essentially of (*A*) from 5 to 70% by weight of a methylpolysiloxane resin composed of trimethylsiloxane units and SiO_2 units in such proportion that the ratio of methyl radicals to silicon atoms is from .6:1 to 1.8:1, (*B*) from 15 to 80% by weight of polysiloxanes having the general formula

$$X_zSiO_{\frac{4-z}{2}}$$

where X is an alkyl or alkenyl radical of less than 6 carbon atoms or a monocyclic aryl radical and z has an average value from 2 to 2.9 inclusive and (*C*) from 15 to 50% by weight of a compound selected from the group consisting of

$$M(OZ)_4, \left[\begin{array}{l} RC{-}O{-} \\ \| \quad\quad \\ R'C \quad\quad \\ | \quad\quad \\ R''C{=}O \end{array}\right] MY_{4-n}$$

and aliphatic hydrocarbon soluble partial hydrolyzates thereof, in said compounds M being of the group consisting of zirconium and titanium, Z being of the group consisting of aliphatic hydrocarbon radicals of less than 13 carbon atoms and hydroxylated aliphatic hydrocarbon radicals of less than 13 carbon atoms and containing less than 4 hydroxy groups, R is an aliphatic hydrocarbon radical, R′ is of the group consisting of aliphatic hydrocarbon radicals and hydrogen atoms, R″ is selected from the group consisting of aliphatic hydrocarbon radicals and aliphatic hydrocarbonoxy radicals, n has a value from .75 to 4 and Y is an aliphatic hydrocarbonoxy radical.

The improvement obtained in the process of this invention occurs with any type of leather. This would include horsehide, goatskin, pigskin, cowhide, and sheepskin. It also applies to leather of any type which has been tanned, tawed or otherwise cured and to finished or unfinished leather.

The water soluble zirconium compound is best applied to the leather in the form of an aqueous solution or dispersion. This can be done in any suitable manner, but the best method is to immerse the leather in the aqueous dispersion of the water soluble zirconium compound until the leather is thoroughly wet with the dispersion. The water soluble zirconium compounds are substantive with respect to the leather so that they are preferentially deposited thereon. In carrying out the treatment with the zirconium compound the concentration of the compound is not critical except that there should be sufficient zirconium compound present to deposit at least .5% by weight zirconium based upon the dry weight of the leather. The upper limit of the amount of zirconium is not critical although practically speaking there is no advantage in going above 5% zirconium.

Any water soluble zirconium salt is operative in this invention, specific examples of which include zirconium acetate, zirconium formate, zirconium propionate, zirconium benzoate, zirconium oxychloride, zirconium sulfate, zirconium nitrate, zirconium oxybromide, and zirconium oxyfluoride.

After treatment with the zirconium salt it is preferable to adjust the pH to a point between 5 and 8 with a mild alkali such as sodium bicarbonate, ammonia and the like.

The temperature and time of treatment are not critical. However, excellent results are obtained when the leather is saturated with the zirconium solution for 15 to 45 minutes at temperatures ranging from 100 to 150° F.

The leather can be impregnated with the zirconium solution at any stage after tanning. Thus the leather can be treated either before or after fat liquoring. Preferably the treatment is made after fat liquoring.

After the treatment with the water soluble zirconium salt the leather is dried. This drying can take place at any suitable temperature. Air drying is satisfactory.

The leather is then treated with the siloxane composition (3) as hereinafter more fully defined. The siloxane compositions can be applied to the leather in any suitable manner such as by spraying, dipping, roller coating or knife coating. They can be applied either from solvent or as 100% solids.

Regardless of how the siloxane composition is applied to the leather there should be a sufficient amount so that there is at least 2% by weight siloxane composition based upon the weight of the leather. The upper limit of the amount of the siloxane composition is not critical although in general there is no advantage in going above 25% by weight based on the weight of the leather.

As can be seen, the siloxane compositions employed in this invention are three component materials which are composed essentially of a resinous siloxane (A), a fluid siloxane (B) and an organotitanium or zirconium compound (C). The compositions can be either mixtures of these three components or reaction products thereof.

The mixtures are prepared by merely mixing the three ingredients in the specified proportions. The reaction products are obtained by mixing the three ingredients in the specified proportion and thereafter allowing the titanium or zirconium compound (C) to react with the siloxane components. This reaction can occur either at room temperature or at elevated temperature and can be followed by the evolution of alcohol or methylalkoxysilanes from the mixture. It is to be clearly understood that both the mixtures and the reaction products are contemplated herein and are fully equivalent for the purpose of this invention.

The methylpolysiloxane resins (A) which are employed herein are composed essentially of trimethylsiloxane units and SiO_2 units but may contain traces of dimethylsiloxane units and/or monomethylsiloxane units. These copolymers may be prepared by cohydrolyzing Me_3SiD and SiD_4 where D is a hydrolyzable radical. A preferred method of preparing these materials is that of reacting methylchlorosilanes, methylalkoxysilanes or hexamethyldisiloxane with an acidic silica sol. Regardless of the method employed the ratio of methyl radicals to silicon radicals in the copolymer can range from .6:1 to 1.8:1 with the preferred range being from .9:1 to 1.5:1 as shown by infrared analysis.

Organopolysiloxane fluids (B) which are operative herein are those in which X can be any alkyl or alkenyl radical of less than 6 carbon atoms or any monocyclic aryl radical. Specific examples of operative siloxanes are dimethylsiloxane, vinylmethylsiloxane, vinylethylsiloxane, dipropylsiloxane, methylxenylsiloxane, or any mixture thereof and copolymers of these diorganosiloxanes with triorganosiloxanes such as trimethylsiloxane, phenyldimethylsiloxane, hexenyldiethylsiloxane and amyldimethylsiloxane. Monoorganosiloxane units can also be present in these siloxanes so long as the value of z remains substantially in the range specified.

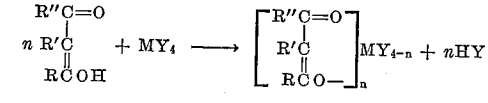
The organosiloxanes (B) are benzene soluble materials which can vary in viscosity from thin fluids to deformable solids. Fluid polymers having a viscosity ranging from 5 to 100,000 cs. at 25° C. are preferred.

The organotitanium and zirconium compounds (C) which are operative herein are of two general types. The first type is of the formula $M(OZ)_4$ in which M is titanium or zirconium. These materials are orthoesters of aliphatic alcohols. For the purpose of this invention Z can be any aliphatic hydrocarbon radical of less than 13 carbon atoms or any hydroxylated aliphatic hydrocarbon radical of less than 13 carbon atoms and containing less than 4 hydroxyl radicals and any partially hydrolyzed derivatives thereof which are hydrocarbon or halogenated hydrocarbon soluble. These partial hydrolyzates are materials where some of the OZ groups have been replaced by oxygen thereby forming MOM or MOH linkages.

Specific examples of operative zirconium and titanium orthoesters are tetramethylzirconate, tetraethyltitanate, tetradecylzirconate, octylene glycolyltitanate, tetra-2-ethylhexylzirconate, tetradodecylzirconate, tetraisopropyltitanate, and tertiary butyltrimethylzirconate. All of the above materials are commercially available or are prepared by standard procedures for preparing zirconium or titanium orthoesters.

The second type of zirconium and titanium ortho compounds which are operative herein are zirconium and titanium compounds having at least .75 beta-dicarbonyl residues per M atoms. These compounds are prepared by adding beta-dicarbonyl compounds such as beta-diketones and beta-ketoesters to reactive zirconium or titanium compounds such as titanium tetrachloride, zirconium tetrachloride or zirconium and titanium orthoesters of lower aliphatic alcohols.

Reaction occurs spontaneously upon mixing the beta-dicarbonyl compound and the reactive zirconium or titanium compound and is evidenced by warming up of the mixture. The reaction is believed to proceed by way of the enol forms of the beta-dicarbonyl compounds to wit:



where the Y's are the reactive groups such as alkoxy, chlorine, etc. It is further believed that the betadicarbonyl esters form chelates, that is, it is believed that one of the oxygen atoms is directly attached to a M atom through a primary valence bond and the other is bonded to a M atom through a coordinate linkage. It should be understood that applicant's invention is not limited by the above explanations.

For the purpose of this invention R'' can be any aliphatic hydrocarbon radical such as methyl, ethyl, butyl, octadecyl, allyl, isopropyl, or sec. amyl or any aliphatic hydrocarbonoxy radical such as methoxy, ethoxy, isopropoxy, allyloxy, t-butoxy or octadecyloxy; R' is hydrogen or any aliphatic hydrocarbon radical such as methyl, ethyl, propyl, isobutyl, allyl or octadecyl; R can be any aliphatic hydrocarbon radical such as methyl, ethyl, isopropyl, allyl, t-butyl and octadecyl; and Y can be any aliphatic hydrocarbonoxy radical such as methoxy, ethoxy, butoxy, octadecyloxy, isopropoxy, allyloxy, or sec. amyloxy.

It should be understood that partial hydrolyzates of these beta-dicarbonyl compounds are also operative in this invention. These partial hydrolyzates may be prepared by partially hydrolyzing the composition so that some of the Y groups are removed and are replaced by oxygen forming a MOM or MOH linkage. For the pur-

pose of this invention the partial hydrolyzates are soluble in aliphatic or halo-aliphatic solvents.

The compositions of this invention in which (C) is the beta-keto complex compounds can be prepared in two ways. First the beta-keto complex zirconium or titanium compound can be prepared prior to mixing with siloxanes (A) and (B). The second method is that of mixing siloxanes (A) and (B) with a compound of the formula $M(OZ)_4$ in a mutual solvent and thereafter adding an appropriate amount of the defined beta-dicarbonyl compounds. Under these conditions reaction will occur spontaneously between the dicarbonyl compound and the $M(OZ)_4$ compound to produce the beta-carbonyl complexes. The presence of siloxanes (A) and (B) does not interfere with this reaction.

The leathers of this invention are excellent for use in shoes, belts, and other equipment which are subjected to weathering under moist conditions and to the effect of water-borne dehydrating agents such as calcium chloride or other salts.

Applicant has found that the synergistic effect obtained by first treating the leather with a water soluble zirconium salt followed by treatment with the siloxane compositions as defined herein is not obtained with other siloxane compositions. For example, there is no significant improvement if one employs a water soluble zirconium compound followed by treatment of the leather with a mixture of siloxanes (A) and (B) alone. This is also true when one first treats the leather with a water soluble zirconium compound followed by treatment with other types of siloxanes such as phenylsiloxane resins, methylsiloxane fluids, or with siloxane rubbers.

The following examples are illustrative only and should not be construed as limiting the invention which is properly delineated in the appended claims. All percents are by weight unless otherwise specified.

Example 1

Hides of fat liquored shoe upper leather were dried and then dipped into a 15% perchloroethylene solution of a siloxane composition consisting of A 33⅓% of a copolymer of trimethylsiloxane and SiO_2 having an average of 1 methyl radical per silicon, B 33⅓% of a fluid copolymer of dimethylsiloxane and trimethylsiloxane and C 33⅓% of tetra-2-ethylhexyltitanate. The hide was then dried at room temperature and cut into six samples.

Another portion of the same fat liquored shoe upper leather was immersed in a solution having a concentration of 364 g. of zirconium acetate per 5 gallons of water. The leather and the solution were rotated together in a drum for 30 minutes at 120° F. The pH during this treatment was 4.6. Sodium bicarbonate was added to the solution to adjust the pH to 5.4, and the mixture was tumbled for 25 minutes longer. The zirconium pickup was 1.7% by weight zirconium based on the dry weight of the leather. The leather was then dried at room temperature and thereafter dipped in a 15% by weight perchloroethylene solution of the siloxane composition of the preceding paragraph.

Another portion of the fat liquored shoe upper leather was tumbled in a drum with a solution having the concentration of 105 g. of zirconium oxychloride in 5 gallons of water at a temperature of 120° F. for 40 minutes. Sodium bicarbonate was then added to adjust the pH to 7.5 and the mixture was tumbled for 20 minutes longer. The leather was then dried at room temperature, dipped into the 15% perchloroethylene siloxane solution of the first paragraph of this example and then dried at room temperature.

The leather from each of the three treatments was split into 6 samples and the number of flexes required for water penetration was determined on the Sylflex leather tester as described above. The results of these tests are shown below.

Treatment	Siloxane pickup in percent by weight based on leather	Number of flexes before failure	Average
Siloxane alone	14.6	18,363	
	16.1	11,002	
	13.8	33,930	
	14.0	27,704	
	15.3	14,584	
	14.8	14,975	
			20,093
Zirconium acetate plus siloxane	14.8	100,000+	
	15.6	100,000+	
	15.6	100,000+	
	16.0	100,000+	
	14.8	100,000+	
	14.0	100,000+	
			100,000
Zirconium oxychloride plus siloxane	14.7	19,965	
	12.2	100,000+	
	14.1	100,000+	
	14.0	55,085	
	13.0	26,407	
	12.9	84,824	
			64,380

Example 2

The above procedures are repeated except that instead of dipping the leather in a solution of the siloxane composition, each leather sample was coated from a roller with a solvent-free mixture of the siloxane composition of Example 1. Each leather sample was then tested as described in Example 1 and the results are shown in the table below.

Treatment	Siloxane pickup in percent by weight based on leather	Number of flexes before failure	Average
Siloxane alone	5.5	6,822	
	5.6	5,329	
	5.2	5,916	
	5.1	4,705	
	5.3	3,547	
	6.5	20	
			4,388
Siloxane plus zirconium acetate	5.4	34,162	
	5.5	28,164	
	5.5	26,391	
	5.7	45,384	
	4.5	6,893	
	4.7	5,520	
			24,419
Siloxane plus zirconium oxychloride	4.4	22,685	
	5.9	59,984	
	6.5	10,455	
	7.1	10,460	
	7.3	22,488	
	5.6	39,821	
			27,648

Example 3

Six hides of shoe upper leather were fat liquored by drumming them with a mixture of 3.76 lbs. of H and H 1012W and 19 gallons of water for 30 minutes at 140° F. The fat liquor H and H 1012W is an emulsion of a mixture of sulfonated sperm oil, red oil and 20° raw neat's-foot oil which contained 1.5% KOH. One-half of the hides were dried at room temperature and then dipped in 15% by weight perchloroethylenet solution of the siloxane composition of Example 1. They were thereafter dried at room temperature and tested as shown below.

The other half of the hides were then drummed with a solution having the concentration of 645 g. of zirconium oxychloride in 14 gallons of water for 30 minutes at 130° F. The solution was treated with sodium bicarbonate to bring the pH to 5.3 and the mixture was drummed for 15 minutes longer. The hides were dried at room temperature and then dipped in a 15% by weight perchloroethylene solution of the siloxane of Example 1 and thereafter dried at room temperature. Three samples were checked

from each of these treatments and the results are shown in the table below.

Treatment	Siloxane pickup in percent by weight based on leather	Number of flexes before failure	Average
Siloxane only	10.2	618	
	12.6	1,956	
	13.8	1,591	
			1,388
Siloxane plus zirconium oxychloride	11.1	20,000	
	11.4	15,082	
	11.4	13,355	
			16,145

Example 4

Hides of fat liquored shoe upper leather were treated with zirconium acetate according to the procedure of Example 1. The dried hides were then dipped into a composition comprising a 15% by weight solution in perchloroethylene of a siloxane composition comprising A 33⅓% of a copolymer of trimethylsiloxane and SiO_2 having an average of 1.2 methyl groups per silicon, B 33⅓% of a fluid copolymer of dimethylpolysiloxane and trimethylpolysiloxane, and C 33⅓% by weight n-octyl ziraconate. The leather was then removed from the solution and air dried. The flex was obtained on 4 samples of this leather and was found to be as follows:

Treatment	Flex	Average
Zirconium acetate treated leather	111,066	
	104,139	
	7,763	
	103,430	
		81,599
Siloxane alone	28,966	
	13,389	
	7,592	
	2,066	
		13,003

Example 5

Equivalent results are obtained when the following siloxane compositions are employed in the procedure of Example 1:

Mixture No.	Composition of mixture in percent by weight [1]		
	A	B	C
1	5	75	20
2	50	33.3	16.7
3	33.3	16.7	50
4	10	50	40

[1] A, B and C each have the compositions shown in Example 1.

Example 6

Equivalent results are obtained when any of the following are employed for C in the procedure of Example 1:

Tetramethyl titanate,
Tetradodecyl titanate,
$Ti(OCH_2CH_2CH_2CH{=}CH_2)_4$,
Octylene glycolyl titanate,
Tetrapentenyl zirconate,
Tetradodecyl zirconate, and
Hydrocarbon soluble partial hydrolyzates of each of these compounds.

Example 7

Equivalent results are obtained when the following siloxanes are substituted for B in the procedure of Example 1:

A 100,000 cs. phenylmethylsiloxane or ethylvinylsiloxane fluid.

Example 8

Equivalent results are obtained by the procedure of Example 4 when 2 mols of ethylacetoacetate per mol of zirconium is added to the siloxane composition of that example, prior to treatment of the leather.

Example 9

Equivalent results are obtained when leather is treated in accordance with the procedure of Example 4 with the following composition: 33⅓% by weight of siloxane A,[1] 33⅓% by weight of siloxane B and 33⅓% by weight of

$$Zr[OC(CH_3){=}CHC{=}OCH_3]_4$$

Example 10

Equivalent results are obtained when a composition is prepared by mixing 33⅓% by weight of siloxane A,[1] 33⅓% by weight of siloxane B and 33⅓% by weight of 2-ethylhexyl titanate and the mixture is then heated at 200° C. until 75% by weight of the 2-ethylhexyloxy groups are removed in the form of dimethyl-di-2-ethylhexoxysilane and the resulting product is employed as the siloxane composition in the process of Example 1.

That which is claimed is:

1. A method of rendering leather water-resistant comprising treating leather with (1) a dispersion of a water soluble zirconium salt in amount such that the zirconium pickup in the leather is at least .5% by weight based on the dry weight of the leather, (2) drying the leather and (3) thereafter applying to the leather at least 2% by weight based on the weight of the leather, of a material consisting essentially of (A) from 5 to 70% by weight of a methylpolysiloxane resin composed of trimethylsiloxane units and SiO_2 units in such proportion that the ratio of methyl to silicon atoms is from .6:1 to 1.8:1, (B) from 15 to 80% by weight of polysiloxanes having the general formula

$$X_zSiO_{\frac{4-z}{2}}$$

where X is selected from the group consisting of alkyl and alkenyl radicals of less than 6 carbon atoms and monocyclic aryl radicals and z has an average value from 2 to 2.9 inclusive and (C) from 15 to 50% by weight of a compound selected from the group consisting of $M(OZ)_4$

$$\left[\begin{array}{l} RC(=O)-O- \\ R'C \\ R''C(=O) \end{array}\right]_n MY_{4-n}$$

and aliphatic hydrocarbon soluble partial hydrolyzates thereof, in which compounds M is selected from the group consisting of zirconium and titanium, Z is selected from the group consisting of aliphatic hydrocarbon radicals of less than 13 carbon atoms and hydroxylated aliphatic hydrocarbon radicals of less than 13 carbon atoms and containing less than 4 hydroxy groups, R is an aliphatic hydrocarbon radical, R′ is selected from the group consisting of aliphatic hydrocarbon radicals and hydrogen atoms, R″ is selected from the group consisting of aliphatic hydrocarbon radicals and aliphatic hydrocarbonoxy radicals, n has a value from .75 to 4 inclusive and Y is an aliphatic hydrocarbonoxy radical.

2. The method of claim 1 wherein (B) is

$$(CH_3)_zSiO_{\frac{4-z}{2}}$$

where z has an average value from 2 to 2.9 inclusive and

[1] A and B each have the composition shown in Example 1.

(C) is $Ti(OZ)_4$ in which Z is an aliphatic hydrocarbon radical of less than 13 carbon atoms.

3. The method of claim 1 wherein (B) is

$$(CH_3)_zSiO_{\frac{4-z}{2}}$$

in which z has an average value from 2 to 2.9 inclusive and (C) is $Zr(OZ)_4$ in which Z is an aliphatic hydrocarbon radical of less than 13 carbon atoms.

4. An article of manufacture comprising a leather article of improved water resistance which has been prepared by the method of claim 1.

References Cited in the file of this patent

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