United States Patent [15] **3,645,775**

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[54] PROCESS FOR PRODUCTION OF AN ARTIFICIAL LEATHER AND PRODUCT

[72] Inventors: **Helmut Schulze,** Bodelschwingstr. 34; **Gerhard Seibert,** Bergweg 13, both of Erlenbach, Germany

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**......................................**D06n 3/00,** B32b 27/40

[58] **Field of Search**...................117/135.5, 161 KP, 161 ZA, 117/63; 161/DIG. 2; 260/824 R, 858

[56] **References Cited**

UNITED STATES PATENTS

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Primary Examiner—Murray Katz
Assistant Examiner—Ralph Husack
Attorney—Johnston, Root, O'Keeffe, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

Process of producing an artificial leather by coagulating or hardening a polyurethane gel applied to a substrate into a microporous layer which is permeable to water vapor, wherein a silicone oil is added to the initial gelable solution of the polyurethane in an organic solvent.

7 Claims, No Drawings

PROCESS FOR PRODUCTION OF AN ARTIFICIAL LEATHER AND PRODUCT

As is well known, a synthetic or artificial leather can be produced from a nonwoven web or fleece which has been bonded with a polymeric elastomeric binder such as a polyurethane. Nonwoven webs or fabrics which have been treated in this way are generally capable of storing water vapor and then giving it off again at the surface of the web. This is of the greatest importance for an artificial leather which is to be used in the manufacture of shoes because the upper leather of a shoe must absorb water vapor as perspiration from the foot and then pass it to the outside at the exposed surface. If the upper leather does not fulfill this function, the water vapor accumulates inside the shoe and causes discomfort to the wearer.

Nonwoven webs or fabrics treated in this way, however, are also highly porous and permeable to liquid so that, for example, rain water can enter the shoe from outside. The porous bonded web or fleece, also termed the substrate, must therefore be provided with a microporous covering layer which although permeable to water vapor is impermeable to liquid water. In addition, this covering layer must give the shoe material the appearance of a leather surface and a leathery handle. Properties such as compression strength, bending or flexing resistance, resistance to cold, scuff resistance and the like of the finished material also depend largely on the quality of this surface covering layer.

It is known to produce covering layers for an artificial leather from polyurethanes. These layers can be produced for example from solutions of polyurethanes in dimethylformamide or other suitable organic solvents, the polyurethane in the solution being converted into a gel by the addition of a nonsolvent such as water and the gel then being coated onto the bonded nonwoven web or fabric. After coagulation of the polyurethane, washing to remove the solvent and drying, polyurethane surface layers with improved permeability to water vapor are obtained. With previously known microporous polyurethane layers, however, various mechanical or physical properties still have not been fully developed to yield durable and dependable artificial leather products.

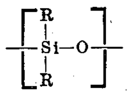
The general object of the present invention is to provide an initial gellable polyurethane composition and an improvement in the conventional process of providing a microporous surfacing of artificial leathers based on polyurethane whereby a number of important properties are enhanced in a relatively simple and economical manner. Specific objects and advantages of the invention are set forth in greater detail in the following disclosure.

It has now been found, in accordance with the invention, that an artificial leather with improved properties can be produced particularly advantageously by the application of a polyurethane layer to a substrate, if there is used a gellable solution of polyurethane in an organic solvent which contains about 1 to 10 percent and preferably 2 to 4 percent by weight of a silicone oil, based on the weight of the dissolved polyurethane. The organic solvent is preferably dimethylformamide.

Polyurethanes used in the process according to the invention are generally known. They may be obtained, for example, by reacting diisocyanates with polyethers or polyesters which contain terminal hydroxy groups to produce an NCO-containing prepolymer which may then undergo further reactions with chain lengthening agents such as diamines or glycols. A complete description of such polyurethanes and their preparation is set forth in numerous patents and other literature sources, e.g., U.S. Pats. No. 2,871,218 and No. 3,190,766, and standard references such as "Polyurethanes" by Dombrow, Rheinhold Publ. Corp. (1957), or "polyurethanes: Chemistry and Technology" by Saunders and Frisch, Interscience Publishers of John Wiley & Sons (1962). The polyurethane film-forming or coating material should be one which consists predominately of the polyurethane, preferably 65 percent by weight or more, and may contain one or more other film-forming thermoplastic organic polymers of the many polymers and copolymers known to be compatible with a polyurethane gel, preferably other elastomeric polymers. For example, it is known that polyvinyl chloride and various copolymers of vinyl chloride, e.g., with vinyl acetate or maleic acid anhydride, can be incorporated in minor amounts into the polyurethane film-forming composition. Other polymers include butadiene/acrylonitrile or butadiene/acrylonitrile/styrene interpolymers and also chlorinated rubber or nitrocellulose. These other polymers replace only a portion of the polyurethane in the composition, usually not more than 5 or 10 percent by weight thereof, and the total weight of such polymer mixtures is considered the weight of the polyurethane for purposes of the present invention.

The organic solvent normally used is dimethyl formamide but other well-known solvents for polyurethane are also suitable, for example dimethyl sulphoxide, dimethylacetamide and mixtures of such solvents. The quantity of the polyurethane in the solution may vary within wide limits in the process according to the invention. In general, concentrations of the polyurethane in the solvent of 15 to 40 percent by weight are found to be suitable. The polyurethane solution may also contain up to 30 percent by weight, based on the polyurethane, of other polymers such as polyvinyl chloride. Other additives such as stabilizers, pigments or dyes may of course also be included.

Silicone oils which may be used within the scope of the invention are generally known liquid substances. They are polymeric organosilicon compounds in which silicon atoms are linked together via oxygen atoms and the remaining valencies of the silicon atoms are saturated with hydrocarbon radicals. The preferred silicone oils have a predominately linear structure with recurring units of the formula



$$\left[-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O- \right]$$

sometimes expressed as —(SiR_2—O)—, in which the side groups R represent a hydrocarbon radical of one to 12 carbon atoms, preferably one to six carbon atoms, such as lower alkyl, e.g., methyl, or aryl, e.g., phenyl. Further details about silicone oils may be found in such references as "Chemical Encyclopaedia" by Hermann Römpp, 6th Edition, Frank'sche Verlagshandlung, Stuttgart, Germany. See also "Silicic Science" by Hauser, D. VanNostrand Co., Inc. (1955), Chapter XIII, pages 146–154. Commercially available silicone oils are generally quite similar in their chemical structure, corresponding to the above noted formula of the individual recurring unit in the polymer, although minor modifications can be made without affecting the essential properties of these silicone oils. Their viscosity is primarily determined by the chain length of the linear polyorgano-siloxane structure, although there may occasionally occur a cross-linking of individual chains by a silicon-oxygen-silicon linkage. Such minor variations of the well-known silicone oils are to be included within the scope of the invention.

Silicone oils which have a viscosity of 100 to 1,000 centipoise (cP) are found to be particularly suitable for purposes of the invention.

The silicone oils may be soluble or insoluble in the organic solvent such as dimethylformamide employed in the preparation of the polyurethane gel.

The silicone oil selected for purposes of the invention is added in a quantity of from about 1 to 10 and preferably about 2 to 4 percent by weight, based on the dissolved polyurethane. Addition of the silicone oil is best carried out when the polyurethane is already dissolved in the organic solvent. Care should be taken to ensure that the silicone oil is uniformly distributed in finely divided or finely dispersed form in the solution at the point where the dissolved polyurethane is converted into a gel, e.g., by the addition of a suitable non-solvent such as water. This uniform distribution is particularly applicable when using a silicone oil which is insoluble in the dimethylformamide or other solvent.

Working up the gel to produce a microporous covering layer or film coating is carried out in known manner. The gel can be applied to a porous nonwoven web or fleece, for example with the aid of a doctor blade, and is then coagulated, washed and dried. After drying, the microporous covering layer on the substrate preferably has a thickness of about 0.3 to 0.6 mm. and especially 0.3 to 0.4 mm.

The substrate itself is bonded with a polyurethane solution or any suitable elastomer solution by impregnating the nonwoven web or fabric and hardening the elastomeric binder in a conventional manner. A suitable nonwoven web can be obtained for example by the process according to British Pat. specification No. 1,017,023. Many techniques are known for the manufacture of nonwoven webs and their bonding into a flexible, porous substrate capable of providing the body or primary layer of an artificial leather, and the present invention is not limited to the use of any particular substrate.

It has been found, surprisingly, that the addition of a silicone oil according to the invention substantially improves the microporous covering or surface layers. Thus, it is possible by means of the silicone oil to substantially eliminate the tendency of certain polyurethanes, e.g., as obtained by the process according to French Pat. No. 1,546,169, to disintegrate when drying the covering layer so as to yield a film or surface layer which is nonporous and impermeable to water vapor. In addition, the covering layers obtained according to the invention are extremely stable.

Another advantage which was not expected is the fact that the process according to the invention permits the use of initial polyurethane solutions which contain a very high concentration of the polyurethane. By comparison, when using polyurethanes as disclosed in German Pat. specification No. 1,106,959, which in themselves are quite suitable for the production of microporous covering layers, it was not possible to work with solutions containing more than 30 percent of the polyurethane without taking special precautions during the gelling or precipitation step, e.g., a very long storage in a moist atmosphere. When a silicone oil has been added according to the present invention, a polyurethane solution having a concentration of over 30 percent, e.g., up to about 40 percent, can be used successfully without the necessity of taking any special precautions. The required microporous covering layers can therefore be rapidly obtained in a simple and effective manner.

Polyurethane solutions which contain 30 to 40 percent by weight of the polyurethane and about 1 to 10 percent by weight, based on the dissolved polyurethane, of a silicone oil therefore represent a preferred embodiment of the invention, these solutions being gelled and subsequently coagulated, washed and dried to yield the desired microporous layer.

The use of these more highly concentrated polyurethane solutions for the production of a microporous polyurethane layer is particularly advantageous because less solvent needs to be recovered. The microporous layers produced according to the invention can be easily washed out very thoroughly before they are dried and no residues remain which could subsequently cause difficulties, such as collapse of the microporous or fine cellular structure of the covering layer or discoloration of the polyurethane. Furthermore, covering layers with improved physical or mechanical properties are obtained when higher concentrations of the initial solution are used.

By using higher polyurethane concentrations, covering layers of higher density are obtained. A material with better surfacing properties is obtained, and in particular the scratch or scuff resistance is substantially increased.

The process according to the invention moreover makes it possible to produce colored surface coatings or layers in which a dye or pigment is very uniformly distributed. The patchiness frequently observed in the covering layers produced by previously known processes no longer occur. This greatly facilitates the finishing and final appearance of the coating or layer as an artificial leather.

The covering layers produced according to the invention are also notable for a very uniform pore structure and increased compressive strength. The bending resistance is also improved. Low-temperature mechanical properties, particularly the response to bending, are likewise superior in comparison to previous products.

Microporous covering layers produced according to the invention may be grained and provided with one or more coatings, e.g., an undercoat containing a polyurethane and a top lacquer containing nitrocellulose. The surface coatings which are applied when finishing the covering layer of the invention have a total thickness of only a few microns.

Although it is already known to use silicones in polyurethane-containing dressings or finishing agents for synthetic leather, the use of silicones in this limited way does not achieve the advantages of this invention. Moreover, it is extremely surprising that the use of silicone oils in the production of a microporous covering layer which is several hundred microns in thickness results in an artificial leather which has many improved properties.

The invention is further illustrated by the following examples.

EXAMPLE 1

5 grams of a commercial silicone oil (TEGO NV, available from Th. Goldschmidt AG, Essen, Germany) are added to 300 grams of a polyurethane solution which was prepared according to Example 3 of French Pat. specification No. 1,546,169, and 100 grams of a mixture of equal parts by weight of water and dimethylformamide are then added. A gel is thus formed which is centrifuged and then applied with a doctor blade to a substrate which has been produced from a nonwoven web according to British Pat. Specification No. 1,017,023. After coagulation with an aqueous solution of sodium chloride, the material is washed free from solvent with water and dried at 50° to 60° C. A product which has a stable microporous surface or covering layer is obtained.

The resistance of the product to bending stresses at −20° C. is above 100,000 but is only about 40,000 when no silicone oil is used. Flexing numbers of over 360,000 are obtained in a Bally Flexometer at a temperature of −5° C., whereas the same covering layer without the addition of silicone exhibits a flexing number of only about 180,000.

EXAMPLE 2

A 30 percent polyurethane solution in dimethyl formamide is initially prepared, wherein the polyurethane is obtained from a polybutylene adipate having a molecular weight of 1,000 and diphenylmethane-4,4′-diisocyanate in the molar ratio of 2:3 while providing a chain lengthening with diethanolamine and ethylene diamine in the molar ratio 0.15:0.70. This preparation corresponds to that disclosed in French Pat. specification No. 1,546,169. 3.7 grams of a commercial silicone oil (FF 400, available from Dow Corning Corp., Midland, Michigan, U.S.A.) followed by 100 grams of a mixture of equal parts by weight of water and dimethylformamide are then added to 300 grams of the initial 30 percent polyurethane solution with stirring. The gel which forms from the water addition is centrifuged off to remove excess liquid and is then applied to a substrate with a doctor blade as is customary for the production of synthetic leather. After coagulation in an aqueous solution of sodium chloride, the material is washed with water and dried at 50° to 60° C. Stable, microporous covering layers which have good bending and flexing numbers at −5° and −20° C. are obtained. The permeability to water vapor determined according to DIN 53 333 (German Industrial Standards) is 750 g./m.^{2} d.

If no silicone oil is added to the polyurethane, the covering layer collapses on drying to give a film or layer which is nonporous and impermeable to water vapor.

EXAMPLE 3

A 35 percent polyurethane solution in dimethylformamide is prepared in known manner from polyethylene adipate (molecular weight 2,000), diphenylmethane-4,4'-diisocyanate and ethylene glycol in the molar ratio of 1:4.3 : 3.3. 20.5 grams of water, 22.5 grams of dimethylformamide, 1.0 grams of a commercial metal complex dye consisting of equal parts of Savinyl dyes Brown GLS and Yellow RLS (Sandoz AG, Basle, Switzerland) and 2.2 grams of a commercial silicone oil (Getren 4, available from Th. Goldschmidt AG, Essen, Germany) are added successively to 207 grams of this polyurethane solution at 50° C. with stirring. The solution is homogenized, converted into a gel by cooling it to room temperature, and directly applied to a substrate which is permeable to water vapor to provide a surface layer having a thickness of 0.8 mm. The polyurethane layer is stored for 6 minutes at room temperature and 60 percent relative humidity and then coagulated in water at 20° C. and washed. When the polyurethane surface layer has been dried at 100° C., it is very smooth and of completely uniform color. The bending numbers of the product at −20° C. are higher than 300,000; in the flexometer at −5° C. and +20° C., the sample shows no damage after 1,000,000 flexes. If, however, a polyurethane surface layer is produced by the same process but without the addition of silicone oil, the resulting sample by contrast is uneven on its surface, i.e., it has a large number of pits and color patches. In the Bally flexometer, this sample is damaged after only 190,000 flexures, and it is broken after only 80,000 bendings at −20° C.

The silicone oils used in the preceding examples have the following characteristics:

TEGO NV:
Organopolysiloxane emulsion used as a release material.
Viscosity: 2,100 cP

FF400:
Water-soluble polydimethylsiloxane, containing polyglycol side chains. Used as fiber finish.
Viscosity: 490 cP

Getren 4:
Water-soluble organopolysiloxane, a release material for the rubber and plastic industry. Used for special release problems.
Viscosity: 1,300 cP

The invention is hereby claimed as follows:

1. In a process for the production of an artificial leather wherein a solution of polyurethane is an organic solvent is gelled, the gel is applied to a substrate and is converted into a microporous layer by coagulation, washing to remove the solvent and drying, the improvement which comprises:

   adding to the initial polyurethane solution about 1 to 10 percent by weight, with reference to the dissolved polyurethane, of a silicone oil, said oil being uniformly distributed in finely dispersed form in said solution at the point where the dissolved polyurethane is converted into a gel.

2. A process as claimed in claim **1** wherein the amount of silicone oil is about 2 to 4 percent by weight, with reference to the dissolved polyurethane.

3. A process as claimed in claim **1** wherein organic solvent is dimethyl formamide.

4. A process as claimed in claim **1** wherein said solution contains from 30 to 40 percent by weight of polyurethane.

5. A process as claimed in claim **4** wherein the organic solvent is dimethyl formamide.

6. A process as claimed in claim **1** wherein the silicone oil has a viscosity of about 100 to 1,000 centipoise.

7. The artificial leather product obtained by the process of claim **1**.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,645,775 Dated February 29, 1972

Inventor(s) Helmut Schulze and Gerhard Seibert

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

First page, left-hand column, seventh line, insert
-- [73] Assignee: Glanzstoff AG, Wuppertal, Germany --.

Column 1, line 28, "surface covering" should read -- surface or covering --; line 70, "polyurethanes" should read -- Polyurethanes --.

Signed and sealed this 10th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents