PRODUCTION OF A MICROPOROUS ARTIFICIAL LEATHER COATING

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18 Claims

ABSTRACT OF THE DISCLOSURE

Process for making a microporous artificial leather coating by converting a polyurethane gel on a substrate, precipitating the gel at 5–80° C. with an aqueous electrolytic solution having a pH-value of 3–9 and a concentration of the electrolyte of at least 15% by weight, and then washing and drying the gel to form a leather-like microporous structure. Metal salts such as sodium chloride or potassium nitrate are useful as the electrolyte.

This invention is concerned with a process for producing leather-like layers or coatings of polyurethane, preferably on a fibrous substrate so as to achieve an extremely fine pore structure as the outer surface layer of the finished article. This fine pore structure as a cover layer must be microporous in size and open-channeled to provide good air and vapor permeability while preventing the passage of liquid water.

It is known that leather-like flat shaped structures can be produced from a textile substrate in which an elastomeric binding agent is uniformly distributed. In preparing the textile base layer or substrate, it is preferable to use non-woven fibrous sheets or mats as a felt-like material although it is also possible to use woven or knitted fibrous textiles or even several layers of woven and/or non-woven sheets may also be used. As the elastomeric binding agent, various polymers have been used, for example: polyurethane, polyvinyl chloride and butadiene/ acrylonitrile copolymers. These polymers are generally sprayed onto the textile substrate in the form of solutions or are applied by dipping, impregnating or doctoring onto the substrate.

Up to the present time, the best results have been achieved by treating the impregnated substrate with a non-solvent which can be at least partially mixed with the solvent which has been used for the applied elastomeric binding agent. Then, after impregnating and precipitating or coagulating the elastomer, both the solvent and non-solvent are washed out and the resulting structure is dried. While these textile base layers having an elastomeric binding agent exhibit some leatherlike qualities or characteristics, it is still necessary to apply an additional cover layer or coating onto the base layer in order to improve the surface structure and appearance and also to obtain a waterproof article, i.e. to prevent the passage of liquid water.

A number of processes have become known for obtaining such cover layers or coatings which are preferably applied to a leather-like, elastomer-bound textile substrate. In these processes, one generally proceeds by first converting polyurethane or mixtures of polyurethane with polyvinyl chloride into their gel form in a suitable solvent, and then precipitating the gel on the textile base layer by treatment with a non-solvent, preferably water. In preparing the gel, the polymer is first dissolved in a solvent, e.g. dimethyl formamide being especially useful as the solvent for polyurethane, and a non-solvent such as water or alcohol is incorporated into this polymer solution. The quantity of the non-solvent is added or dosed in an amount which is just sufficient to gel the polymer. Such a gel can be considered as a two phase system in which at least one substance is uniformly dispersed in another substance, both the dispersed substance and the dispersing medium being continuous or coherent phases which penetrate one another. (See, for example, J. Stauff, "Kolloidchemie," Springer-Verlag, 1961, p. 666.) After application of the polymer gel onto the textile layer or substrate, water or mixtures of water with dimethyl formamide are used as the coagulating or precipitating bath. The polymer as the dispersed phase thereby hardens or coagulates and the dispersing medium as the second phase can then be removed from the solidified structure by washing, thereby leaving an open-channeled or interconnected porous solid structure.

In following such known procedures, however, it was learned that surface structures or layers are rarely produced so as to be completely free of macro pores. Another disadvantage of known methods for producing such layers resides in the fact that the dosage rate at which non-solvent and solvent are added is quite critical and must be precisely controlled. Relatively small deviations in the amount or rate of this dosage during the process results in a gel structure having very undesirable characteristics, either in its pore structure or a non-homogeneous gel.

The "macropores" are defined as pores in the hardened or solidified gel which are so large in size as to be visible with the naked eye down to smaller sizes which are still visible or recognizable as small vacuoles on a photographic cross-section of the porous layer enlarged on a scale of approximately 1:100. These macro pores generally lie close to or directly at the surface of the cover layer and are covered by an extremely thin film of the solid polymer or are separated from one another by such a thin film or membrane. This not only has a very unfavorable effect on the air permeability and water conductivity of the leather-like surface coating but also has a detrimental effect on its elastic qualities.

By contrast, "micropores" are defined as those pores in the leather-like coating or surface structure which are sufficiently small in size so that no vacuoles can be seen in a cross-sectional photographic enlargement of 1:100. Thus, in a perfectly microporous surface layer, a cross-sectional enlargement of 100 times actual size will not show any evidence of vacuoles or bubbles which are usually covered or separated by a thin film of polymer.

One object of the present invention is to provide a process for making a microporous leather-like polyurethane coating or layer which is substantially free of macro pores and exhibits improved elastic properties. Another object of the invention is to provide a process by which the desired microporous structure can be formed under conditions which are more easily controlled. These and other objects and advantages are more fully explained in the following detailed description.

It has now been found, in accordance with the present invention, that one can achieve a leather-like microporous
coating, film, or sheet material which is substantially free of macropores if a polyurethane gel initially applied to a substrate is coagulated or hardened by treatment at about 5 to 80°C, with an aqueous electrolytic solution having a pH-value between 3 and 9, preferably about 4.5 to 8, and a concentration of the electrolyte of at least 15% by weight, preferably more than 20% by weight, up to the saturation point of the electrolyte in the aqueous solution. i.e. up to the point at which the electrolyte forms a saturated solution in water at the coagulation temperature. Thereafter, the coagulated gel is washed and dried in conventional manner to remove the liquid portion thereof and the electrolyte, i.e. the soluble salt content of the gel.

The polyurethane gel can be applied to many different substrates depending upon the particular use of the final leatherlike film, sheet or cover layer, and in most instances is applied onto a fibrous substrate, e.g. woven and non-woven fiber-containing fabrics, fleeces or similar textile materials which may or may not be impregnated with a suitable binding agent. Paper sheets composed of natural, artificial and/or synthetic organic fibers may also be used as a substrate, or one can even produce a microporous sheet or film by using a substrate from which the coagulated gel can be easily removed by stripping or peeling. In any fiber treated in accordance with the process of this invention. The invention is especially applicable, however, in providing an improved microporous surface coating on a fibrous non-woven fleece which has been impregnated with an elastomeric polymer to provide a leather-like, fiber-reinforced base layer. The gel can be prepared and applied according to conventional processes, e.g. by spreading, brushing, extrusion, coating with a doctor blade or the like.

Polyurethanes which are suitable as a film-forming or coating material on a flat substrate to provide a porous elastomeric polymer surface layer are generally quite well known in this art. For purposes of the present invention, the desired elastomeric layer should consist predominately of a suitable polyurethane but may also contain a minor proportion of one or more other film-forming thermoplastic or organic polymers of the many polymers and copolymers which are known to be compatible with a polyurethane gel sterically. For example, one can use a mixture of polymers in which the polyurethane content is at least 50% by weight and preferably about 65% by weight or more.

Generally speaking, polyurethanes are produced by reacting a diisocyanate with one or more organic compounds or substrates which contain terminal hydroxyl groups or reactive hydrogen atoms, especially with such polymers as polyesters, polyethylenes or polystyrenes, often with the further interaction of diamines, water or glycols. For purposes of the present invention, the polyurethane must be soluble in organic solvents suitable for gel formation and also should be capable of being coagulated or solidified from the gel so as to provide a porous structure which is insoluble in water. Suitable polyurethanes of this type, including compositions containing minor amounts of other film-forming thermoplastic polymers are disclosed in such references as U.S. Pat. No. 2,871,218 and No. 3,190,766.

For example, in preparing the polyurethane, it is quite common to use such diisocyanates as tolylene-2,4- or 2,6-diisocyanate, diphenylmethane-4,4-diisocyanate, hexamethylene diisocyanate, naphthalene disocyanates or various other alkylene and/or alylene disocyanates. Examples of preferred types of polyurethanes which can be reacted with the diisocyanate in forming the polyurethane include the following: polyethers such as polyethylenes other glycols, polypropylene ether glycols, polyhexamethylen ether glycols and the like; polyesters such as tetramethylene glycol adipate, hexamethylene glycol adipate, hexamethylene glycol terephthalate and the like; and polystyrenes which are the amides of the previously noted polyesters. There may also be reacted with the diisocyanate and the linear polymer any number of reactive hydrogen atoms including: glycols such as ethylene glycol, tetramethylene glycol, hexamethylene glycol; diamines such as ethylene diamine, phenylene diamine and dimethyl piperazine; or even small amounts of diethylene diamine.

In most cases, it is essential to avoid extensive cross-linking in the initial polyurethane to be formed into a gel so that substantially linear polyurethanes are especially desirable, and in general such preferred polyurethanes should have a relative viscosity of about 20 to 100 poise as measured in a 20% dimethyl formamide solution at 20°C. (i.e. 20% by weight of the polyurethane being dissolved in the solvent).

It will be apparent from the foregoing description of polyurethanes or their combination with other film-forming or elastomeric polymers that when referring to a polyurethane gel, a polyurethane polymer or a polyurethane elastomer, the present invention is concerned with a relatively broad and well known class of polymers or polymer mixtures used in the preparation of porous surface structures from a gel. In many cases, however, the amount of polymers other than the polyurethane polymer does not exceed 5 to 10% by weight and for practical purposes may be considered as being essentially a linear polyurethane composition. This is also true with respect to the addition of small amounts of so-called chain extenders or even small amounts of a cross-linking agent, it being understood that those skilled in this art can readily prepare substantially linear polyurethanes and their gels within the scope of such minor modifications.

Good results have been achieved by preparing a polyurethane gel which contains about 15-55% by weight of the linear polyurethane, 0 to 15% by weight of one or more of the other film-forming thermoplastic polymers, 5 to 30% by weight of a non-solvent for the polyurethane and 20 to 80% by weight of a solvent for the polyurethane in which the non-solvent is at least partially soluble or miscible. Especially preferred proportions of the gel components are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane</td>
<td>20-30</td>
</tr>
<tr>
<td>Other polymers</td>
<td>0-10</td>
</tr>
<tr>
<td>Non-solvent</td>
<td>5-15</td>
</tr>
<tr>
<td>Solvent</td>
<td>45-75</td>
</tr>
</tbody>
</table>

Particularly suitable polymers other than polyurethanes contained in the gel composition include, for example: polyvinyl chloride; various copolymers of vinyl chloride, especially vinyl chloride/maleic acid anhydride or vinyl chloride/vinyl acetate copolymers; and butadiene-acrylonitrile and/or -styrene inter polymers. Chlorinated rubber or nitrocellulose are likewise especially useful. The nitrocellulose preferably has a nitrogen content of about 10.8 to 14% by weight. As additional examples of a number of suitable copolymers which can be at least partially mixed into the gel-forming composition containing polyurethane, the following table provides a further illustration of the additional film-forming thermoplastic polymers. All percentages are by weight with reference to the total weight of the copolymer so as to indicate the approximate proportions of the monomers.

### TABLE I

<table>
<thead>
<tr>
<th>(A) Vinylchloride copolymers</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 80% vinyl chloride+10% ethyl maleate, 10% methyl maleate;</td>
<td></td>
</tr>
<tr>
<td>(2) 80% vinyl chloride+20% methyl acrylate;</td>
<td></td>
</tr>
<tr>
<td>(3) 80% vinyl chloride+10% methyl acrylate, 10% iso-butyl maleate;</td>
<td></td>
</tr>
<tr>
<td>(4) 87% vinyl chloride+13% vinyl acetate;</td>
<td></td>
</tr>
<tr>
<td>(5) 80% vinyl chloride+20% ethyl maleate;</td>
<td></td>
</tr>
<tr>
<td>(6) 85% vinyl chloride+15% vinylidene chloride;</td>
<td></td>
</tr>
<tr>
<td>(7) 80% vinyl chloride+20% maleic acid anhydride;</td>
<td></td>
</tr>
<tr>
<td>(8) 70% vinyl chloride+30% vinylisobutylether,</td>
<td></td>
</tr>
</tbody>
</table>
(B) Butadiene/acrylonitrile copolymers

(9) 72% butadiene+28% acrylonitrile;
(10) 10% butadiene+90% acrylonitrile;
(and all proportions of butadiene and acrylonitrile falling within these limits).

(C) Styrene/butadiene copolymers

(11) 80% styrene+20% butadiene.

(D) Vinylidene chloride/acylonitrile/methacrylate copolymers

(12) 80% vinylidene chloride+10% acrylonitrile, 10% methyl methacrylate.

Regardless of whether the gel-forming composition consists essentially of a polyurethane or contains admixed therewith a relatively substantial amount of another film-forming, water-insoluble polymer, the procedure for producing the gel is generally well known. The polymer or polymer mixture is dissolved in a suitable solvent, preferably dimethyl formamide although dimethyl acetamide is also quite useful. Other well known solvents for polyurethanes include dimethyl sulfoxide, tetrahydrofuran, gamma-butyrolactam, gamma-butyrolactone and epsilon-caprolactam. In general, the polyurethane gel utilized in the present invention is most conveniently prepared with dimethyl formamide as the solvent.

In order to precipitate the gel from the polymer solution (which may also be considered a colloidal solution or suspension of the polymer in the solvent), it is necessary to add a suitable non-solvent up to the point where gel formation takes place or just slightly beyond this point. Suitable non-solvents for the preparation of polyurethane gels include water or lower alkanols such as methanol and ethanol. While the non-solvent is usually a liquid in which the polyurethane elastomer is insoluble, it is also feasible to use ammonium nitrate as a precipitating agent in the form of a solid non-solvent or else ammonium nitrate dissolved in dimethyl formamide or other suitable solvent for the polyurethane can be used as a liquid non-solvent medium. In either case, the non-solvent should be at least partially soluble or miscible in the dimethyl formamide or other suitable solvent. The gels prepared for use in this invention contain as the preferred non-solvent about 5-10% water or 5-30% by weight of ammonium nitrate.

In applying the gel to the substrate, e.g. a fibrous fleece or non-woven textile base layer, regardless of the particular technique used such as spraying, dipping or doctoring, it is usually most desirable to provide a layer thickness of about 0.4 to 1.5 mm. In the case of the treated product is to have the surface appearance and characteristics which stimulate natural leather. Of course, the applied gel may also contain pigments or dyes, and one can also add inert thickening agents, fillers or extenders in a conventional manner.

The novel and critical step essential for achieving the improved results of the present invention is the coagulation or hardening of the applied polyurethane gel by treatment with the prescribed electrolytic solution. The following details of this step are therefore quite important and should be carefully observed in order to obtain the desired product.

The treatment with the aqueous electrolytic solution takes place in the usual form of a liquid bath although it is also feasible to spray or flow the treating solution onto the gel-coating provided that the temperature is maintained within the range of approximately 5 to 80 °C, preferably 15-60 °C.

The electrolytic solution is essentially an aqueous solution of a water-soluble metal salt in a concentration of at least 15% by weight and generally more than 20% by weight. The upper limit of concentration is not critical since saturated solutions of the metal salt at the coagulation temperature, i.e. between 5 and 80 °C are quite suitable. Both inorganic and organic metal salts, i.e. the metal salts of inorganic and organic acids are useful provided that the resulting solution in the prescribed concentration yields a pH-value of 3-9 and preferably from about 4.5 to 8. Mixtures of salts can also be used as the electrolyte provided that the mixture is soluble in water in the required concentration. Furthermore, it has been found that it is quite advantageous to add a small amount of dimethyl formamide to the electrolytic solution, e.g. up to 15% by weight and preferably about 5-10% by weight of dimethyl formamide with reference to the total weight of the electrolytic bath.

The aqueous electrolytic solution can be prepared by dissolving in water any metal salt which will yield the desired pH and concentration required for the treatment bath. For example, one can select any number of suitable salts of the metals of Groups I and II of the Periodic Table, preferably the alkali metal and alkaline earth metal salts. Ammonium and zinc salts are also quite useful for purposes of the present invention. There can be used salts of mineral acids such as the phosphates, sulfates, chlorides and nitrates, or the salts of organic acids such as the acetates and formates. From readily available data or by a simple preliminary test, it can be determined whether any particular salt will meet the pH and concentration limitations of the method of the invention.

For convenience, the following table lists a number of salts which can be used as the electrolyte according to the invention together with their solubility in water at 20 °C. This table is intended as being illustrative only.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Solubility in H₂O at 20 °C (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>26.4</td>
</tr>
<tr>
<td>NaN₃</td>
<td>46.8</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>27.1</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>65.2</td>
</tr>
<tr>
<td>KCl</td>
<td>25.6</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>62.9</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>43.0</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>43.0</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>73.2</td>
</tr>
</tbody>
</table>

The precipitation, coagulation or hardening of the elastomer gel by the electrolytic solution requires the bath to be in intimate contact with the gel under controlled temperature conditions, but the time required to complete the coagulation is not critical. In general, the duration of the bath treatment need not exceed 15 minutes and shorter periods of time are usually quite suitable. The reaction time required for coagulation naturally depends upon the temperature of the coagulating bath. In the case of very hot baths of about 80 °C, the precipitation or coagulation of the gel can be substantially completed after only about one minute. In order to assure a uniform microporous structure of the coating or surface layer, it has been found advantageous to complete the precipitation of the gel with the electrolytic solution within a period of about 2 to 10 minutes.

After the polymer gel has been coagulated, it is washed with water in a conventional manner so as to substantially completely remove the solvent and non-solvent components of the original gel and especially to remove the water-soluble salts. After washing, the coagulated gel is dried in the usual way, e.g. by using heat. The use of salt solutions as an electrolytic bath does not prolong the time normally required for washing the coagulated gel since the water-soluble salts used as the electrolyte are more easily extracted than the solvents such as dimethyl formamide.

The following examples will serve to further illustrate the invention:
EXAMPLE 1

According to known procedures, there was first produced a fibrous fleece by carding polyamide (nylon) and regenerated cellulose (rayon) fibers of a conventional staple length, and this carded fleece was impregnated with a linear polyurethane corresponding to that to be applied subsequently as a surface coating. After hardening the polyurethane to form an elastomeric binder for the fleece and washing and drying the resulting fibrous sheet, a polymer gel was applied by means of a doctor blade to a thickness of 1.1 mm. The polymer gel consisted of 20% by weight of a linear polyurethane, 4% by weight of polyvinyl chloride, approximately 6% by weight of ammonium nitrate and approximately 70% by weight of dimethyl formamide.

The textile base layer or substrate coated with this gel was then conducted through an aqueous coagulating bath consisting of an aqueous solution of 20% by weight NaCl at a bath temperature of 20°C. After a reaction period or time of treatment of five minutes, the coagulated gel was washed with water and dried.

The resulting product exhibits a surface layer having a highly uniform microporous structure. Pores with a diameter of 10 microns or more could not be observed, most of the micropores being much smaller. The finished article exhibited a permeability to water vapor of 650 g/m²/day. In a comparative test wherein the same procedures were followed except that pure water was used in coagulating the applied gel, the finished article had a surface coating in which there were dispersed a large number of macropores with a diameter above 20 microns.

EXAMPLE 2

As described in Example 1, the fiber fleece sheet material was coated with a surface layer of the polymer gel. However, in order to coagulate the gel, an electrolyte bath was used which contained 10% by weight dimethyl formamide as well as the 20% by weight NaCl. The treatment with this bath took place at a temperature of 50°C. The resulting leather-like product has an extremely fine pored surface structure. In testing for water vapor permeability according to DIN 53333 (German Industrial Standard), the finished article exhibited a value of 750 g/m²/day.

EXAMPLE 3

The same procedure was followed as in Example 1 except that the coagulating bath consisted of a 50% by weight solution of MgCl₂ in place of the sodium chloride solution. The polyurethane surface coating was again found to be substantially free of macropores while exhibiting a uniform distribution of micropores.

EXAMPLE 4

By following exactly the same procedure as in Example 1 but using a 50% by weight sodium acetate solution in water as the aqueous coagulating bath to precipitate the gel coating, it was again possible to obtain a uniform microporous surface structure substantially free of macropores.

EXAMPLE 5

A non-woven fibrous fleece in the form of a sheet was produced in the usual manner on a paper-making machine from staple lengths of polyamide (nylon) and regenerated cellulose (rayon) fibers. The fibrous sheet was then impregnated with an elastomeric binder consisting of a linear polyurethane in admixture with polyvinyl chloride, and this binder was then hardened, washed with water, and dried to form a textile base layer. Onto this base layer there was applied a surface coating or layer of 0.8 mm. thickness of a polymer gel having approximately the following composition: 25% by weight of polyurethane; 5% by weight of a copolymer of 80 parts by weight of vinyl chloride to 20 parts by weight of maleic acid anhydride; 10% by weight of water and 60% by weight of dimethyl formamide.

The coagulating bath was then conducted through a coagulating bath of water containing 52% by weight of KNO₃ as the electrolyte while maintaining the bath temperature at 65°C. The coated substrate had a residence time of 3 minutes in this bath. Subsequently, the coagulated coating was washed with water and dried to yield a very fine and uniform porous surface structure substantially free of macropores.

EXAMPLE 6

The procedure of Example 5 was repeated except that the coagulating bath consisted of an aqueous 19% by weight solution of KNO₃. With this lower concentration of the electrolyte, a few macropores appeared in the otherwise microporous coating.

EXAMPLE 7

As described in Example 5, the polymer gel was applied to the non-woven fibrous substrate impregnated with the elastomeric binder. The polymer gel had the same composition as described in Example 5 except that the vinyl chloride/maleic acid anhydride copolymer was replaced by nitrocellulose in the same quantity, i.e. 5% by weight with reference to the total weight of the gel.

In order to coagulate or precipitate the polymer gel as a surface coating, the coated substrate was conducted through a 50% by weight NH₄NO₃ solution in water, the bath temperature being maintained at 23°C, for a total residence time in the bath of 8 minutes. After washing with water and drying, a flat surface coated microporous structure resembling leather was obtained. This finished product remained undamaged after 500,000 flexures during a test of its flexing or bending strength carried out in accordance with JUP 20 by means of a Bally flexometer.

EXAMPLE 8

The procedure of Example 7 was repeated except that the concentration of the NH₄NO₃ in the coagulating bath was varied in a series of tests in which this concentration was reduced from 50% to 10%. At a concentration of 25% by weight of NH₄NO₃ some macropores can be observed which increase in size and number as the concentration of the salt in the coagulating bath decreases. During these tests the bath had a pH-value of between about 5 and 6.

EXAMPLE 9

Using a polyurethane impregnated fibrous fleece for the textile base layer as in the preceding examples, a polymer gel coating was applied on the surface thereof to a thickness of 0.5 mm. This polymer gel contained approximately the following amounts of individual components: 24% by weight of a linear polyurethane; 6% by weight of ammonium nitrate and 70% by weight of dimethyl formamide. In order to coagulate the gel coating, it was conducted on the substrate through an aqueous electrolytic solution consisting of 22% by weight of a mixture of 70 parts by weight NaCl to 30 parts by weight KCl. The temperature of the solution was maintained at 30°C. During the bath treatment. After washing with water and drying, a very fine-pored surface structure was obtained. By photographing a cross-section of this surface coating and enlarging in a ratio of 1:100, no macropores could be observed and the product exhibited a highly uniform microporous structure.

In each of the foregoing examples, the linear polyurethane used to form the surface layer or coating on the textile substrate was prepared as described in U.S. 2,871,218 from polybutyladipate (molecular weight of 1000), diphenyl-methane-4,4-diisocyanate and a small amount of butanediol as a chain extender. This is the polyester type
of polyurethane and has a solution viscosity of 50–70 poise when measured as a 20% solution in dimethyl formamide at 20° C. This same linear polyurethane can be used to impregnate the fibrous substrate as an elastomeric binding agent, preferably in admixture with polyvinyl chloride as pointed out in Examples 1 and 5. However, the particular substrate is not critical, the examples herein using an impregnated fibrous fleece as an illustration of a preferred sweater knit product.

The aqueous electrolytic solution employed as the coagulating bath in each of the foregoing examples exhibited a pH-value ranging between about 3 and 9 depending upon the particular electrolyte used in each case. One should avoid using salts which result in an excessively low pH-value, e.g., iron chloride or aluminum chloride, because the polymer coating then tends to become shriveled or exhibit a wrinkled or puckered surface. The minimum concentration of the electrolyte will tend to vary to some extent, but it has been found that more than 20% by weight is usually required, and the formation of macro pores can be eliminated in any case by simply increasing the concentration up to the saturation value of the electrolyte in water at the coagulation temperature.

In addition to an excellent microporous structure, the coating or covering layer produced according to the invention has a distinctly better resistance to bending, i.e., a higher flexing life, than coatings which still contain macro pores. Where the polymer surface structure contains such macro pores, the thin film of polymer above or between the visible bubbles or vacuoles break or tear during a repeated flexural stress test. Once this break takes place, the crack in the surface coating continues to tear very quickly and extends through the rest of the structure. In comparative tests according to IUP 20 on a Bally flexometer (Messrs. Bally A. G., Schoenenwerd, Switzerland), cover layers or coatings containing such macro pores are destroyed, on an average, after about 10,000 flexures, while the microporous coatings produced according to the present invention remain undamaged up to about 200,000 flexures or more.

The polyurethane polymer coatings or flat surface film structures of the present invention are thus distinguished not only by their excellent microporous structure but also by their resistance to bending or flexing. Since artificial leather products are often subjected to such stress, for example when used in footwear or the like, an increased flexing life is a very substantial advantage. At the same time, a uniform microporous structure contributes to the desired air and water vapor permeability of the artificial leather product.

The invention is hereby claimed as follows:

1. A process for the production of a microporous artificial leather coating which comprises: applying to a porous substrate a polyurethane gel containing a solvent for said polyurethane, coagulating the applied gel at a temperature of about 5 to 80° C. with an aqueous electrolytic solution having a pH-value between 3 and 9 and a concentration of a water soluble or ammonium salt electrolyte of at least 15% by weight up to the saturation point of the electrolyte in said aqueous solution, and subsequently washing and drying the coagulated gel to form a microporous coating.

2. A process as claimed in claim 1 wherein the polymer of said gel consists essentially of a linear polyurethane having a relative viscosity of 20 to 100 poise measured in a 20% dimethyl formamide solution at 20° C.

3. A process as claimed in claim 1 wherein said gel contains 15 to 35% by weight of a linear polyurethane, up to 15% by weight of at least one other film-forming thermoplastic polymer, 5 to 30% by weight of a non-solvent for polyurethanes and 20 to 80% by weight of a solvent for polyurethanes in which said non-solvent is at least partially soluble.

4. A process as claimed in claim 1 wherein said gel contains 20 to 30% by weight of a linear polyurethane, up to 10% by weight of at least one other film-forming thermoplastic polymer, 5 to 15% by weight of a non-solvent for polyurethanes and 45 to 75% by weight of a solvent for polyurethanes in which said non-solvent is at least partially soluble.

5. A process as claimed in claim 3 wherein the polymer content of said gel consists essentially of a linear polyurethane having a relative viscosity of 20 to 100 poise measured in a 20% dimethyl formamide solution at 20° C. and at least one other polymer selected from the class consisting of polyvinyl chloride, vinyl chloride/maleic anhydride copolymers, vinyl chloride/vinyl acetate copolymers, and copolymers of butadiene with at least one of the monomers acrylonitrile and styrene.

6. A process as claimed in claim 3 wherein the polymer content of said gel consists essentially of a linear polyurethane having a relative viscosity of 20 to 100 poise measured in a 20% dimethyl formamide solution at 20° C. and nitrocellulose.

7. A process as claimed in claim 3 wherein water is used as the non-solvent in an amount of about 5 to 10% by weight with reference to the total weight of the gel.

8. A process as claimed in claim 3 wherein ammonium nitrate is used as the non-solvent in an amount of 5 to 30% by weight with reference to the total weight of the gel.

9. A process as claimed in claim 3 wherein said solvent is dimethyl formamide.

10. A process as claimed in claim 1 wherein said coagulation of the applied gel is carried out at a temperature of about 15 to 60° C. with an aqueous electrolytic solution having a pH-value of about 4.5 to 8 and a concentration of the electrolyte of at least about 20% by weight up to the saturation point of the electrolyte in said aqueous solution at the coagulation temperature.

11. A process as claimed in claim 10 wherein said electrolytic solution contains approximately 5 to 10% by weight of dimethyl formamide with reference to the total weight of the solution.

12. A process for the production of a microporous artificial leather film layer which comprises: applying to a porous substrate a polyurethane gel containing about 15 to 35% by weight of a linear polyurethane having a relative viscosity of about 20 to 100 poise measured in a 20% dimethyl formamide solution at 20° C. and from 0 up to 15% by weight of another film forming thermoplastic polymer, about 5 to 30% by weight of a non-solvent for polyurethanes and about 20 to 80% by weight of a solvent for polyurethanes in which said non-solvent is at least partly soluble; coagulating the applied gel at a temperature of about 5 to 80° C. by treatment thereof with an aqueous solution of at least about 25% by weight of a water soluble electrolyte selected from the class consisting of the salts of alkali metals, alkaline earth metals, zinc and ammonium, said electrolyte being sufficient to provide an electrolytic solution with a pH-value of about 3 to 9; and subsequently washing the coagulated gel to form a microporous layer substantially free of macro pores.

13. A process as claimed in claim 12 wherein said solvent for polyurethanes is dimethyl formamide.

14. A process as claimed in claim 12 wherein said said electrolyte has an anion selected from the class consisting of sulfate, phosphate, chloride, nitrate, formate and acetate.

15. A process as claimed in claim 12 wherein said electrolyte is an alkali metal salt.

16. A process as claimed in claim 12 wherein said other thermoplastic polymer is selected from the class consisting of polyvinyl chloride, vinyl chloride copolymers, and copolymers of butadiene with at least one of the monomers acrylonitrile and styrene.

17. A process as claimed in claim 12 wherein said other thermoplastic polymer is nitrocellulose.
18. A process as claimed in claim 12 wherein said coagulating treatment is carried out for a period of about 1 to 15 minutes.

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