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[54] **PRODUCTION OF POLYURETHANE FILM/SPLIT LEATHER LAMINATE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 659,101, Aug. 8, 1967, abandoned, and Ser. No. 737,116, June 14, 1968, abandoned.

[52] **U.S. Cl.** **156/246,** 156/247, 156/289, 156/331, 161/226, 156/302

[51] **Int. Cl.**.....**B29c 19/00**

[58] **Field of Search**.....156/302, 246, 247, 289, 331; 161/247, 226

[56] **References Cited**

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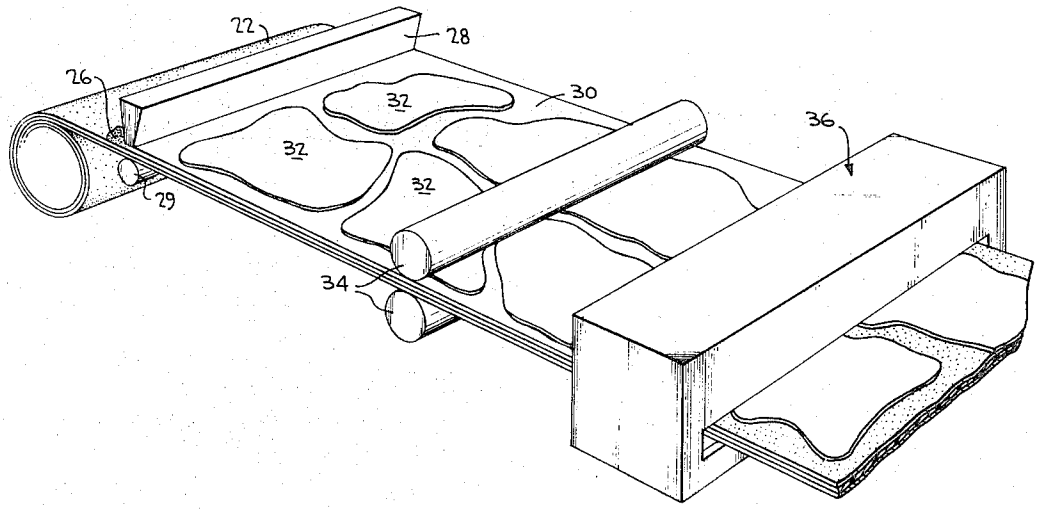
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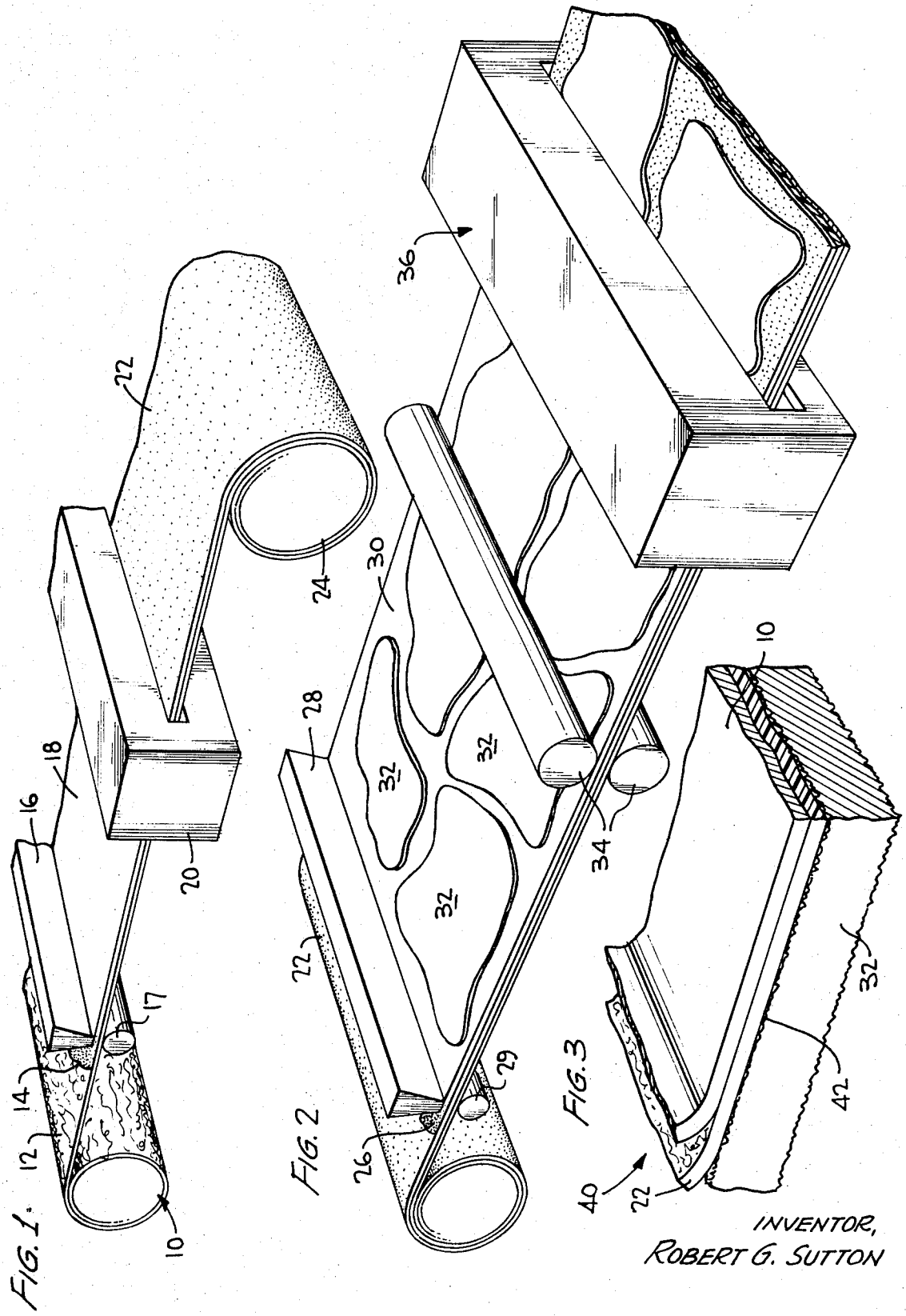
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[57] **ABSTRACT**

Production of laminated articles by casting and drying a layer of a fully-reacted polyurethane material on a release treated carrier in a manner to form a moisture vapor-permeable and moisture-impermeable film, one or more hides of split leather being bonded to the supported film through a moisture vapor-permeable tie-coat of a compatible adhesive, and the carrier then being removed. The resultant split leather/polyurethane film product has the appearance and other properties of top-grain leather.

4 Claims, 3 Drawing Figures





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PRODUCTION OF POLYURETHANE FILM/SPLIT LEATHER LAMINATE

This application is a continuation-in-part of applications Ser. Nos. 659,101 and 737,116, filed Aug. 8, 1967 and June 14, 1968, respectively, both now abandoned.

This invention relates to the production of laminated articles and relates more particularly to the production of laminates from a pre-cast, fully reacted polyurethane film bonded to split leather through a discontinuous tiecoat of a compatible adhesive material.

The long-established art of tanning leather is well documented. Top-grain leather is a veneer of the hide which, after removal, leaves a great deal of leather known as "split leather." Thus, the term "split leather" as used herein and in the appended claims, is intended to define the material remaining in a leather hide after removal of the top-grain veneer as well as reconstituted leathers made from such materials by well-known techniques, and is intended to exclude such materials as the top grain veneer itself and synthetic poromeric products, such as "Corfam." The term "hide" is intended to apply to the remaining leather portion from an entire animal or any portion thereof.

The instant inventive concepts are applicable to split leathers from the skins of various animals, including, for example, cattle, goats, calfs, sheep and horses, regardless of the method of tanning, whether the same be chrome-tanned, zirconium-tanned, vegetable-tanned or tanned by synthetic tanning agents.

Since tanning techniques and procedures for the production of reconstituted leather are well known in the art, and since these concepts do not form a part of the instant invention, further details regarding same are not necessary herein.

Split leather has not found a sizable market, other than in buffed, dyed, "reverse," or suede leather products. Due to the porosity of split leather, it cannot be finished in the same manner as top-grain leather, since the solution coatings conventionally used with top-grain leather will penetrate split leather, resulting in a boardy product with no actual top finish.

It has now been found that pre-cast, fully reacted polyurethane films can be adhesively bonded to split leather, resulting in a finish which is actually far superior to conventionally finished top-grain leather. Since split leather is, for certain purposes, a superior part of the hide, the polyurethane film / split leather products of this invention have softer hand, better drape, significantly improved abrasion resistance and flex-fold characteristics than top-grain leather. The products of this invention have all of the advantages of leather, since they are formed primarily of natural leather as contrasted with such synthetic poromeric materials as "Corfam" which, while porous, do not satisfactorily absorb moisture.

It is important in leather products used, for example, in shoe uppers, that the interior thereof absorb moisture from the foot while moisture is desirably precluded from passing from the exterior to the interior. Yet, while passage of moisture is undesirable, passage of moisture-vapor, that is moisture-vapor permeability or "breathability," of the shoe upper is recognized to be a necessary characteristic of such materials. Solution or liquid coating of porous material such as split leather, while precluding moisture

passage, also precludes passage of moisture vapor, rendering coated products moisture vapor-impermeable.

It is an important object of the instant invention to provide for the production of split leather laminates which, when used as shoe uppers, provide an interior moisture-absorbing material, that is, the split leather itself, with a moisture-proof exterior, while the entire product is moisture-vapor permeable or "breathable."

Another important and basic object of this invention is the provision of a simple and inexpensive procedure for the upgrading of split leather to a product having all of the advantageous characteristics of top-grain leather.

Yet another object of this invention is the provision of techniques for forming laminated products in a continuous manner even though the split leather hides being processed are non-uniform in size and shape and, are therefore difficult to handle in a continuously-operating production line.

Other and further objects hereof will be obvious from the following detailed description which makes reference to the attached drawing wherein:

FIG. 1 is a schematic illustration of the first step of forming products according to this invention;

FIG. 2 is a schematic illustration of further steps according to the process of this invention; and

FIG. 3 is an enlarged fragmentary perspective view of a portion of a product according to the instant inventive concepts prior t removal of the release papers therefrom.

Like reference characters refer to like parts throughout the several views of the drawing.

It has been found that the foregoing objects can be satisfied by bonding a pre-cast, fully reacted moisture vapor-permeable and moisture-impermeable polyurethane film in a manner so as to render the same moisture-vapor permeable. This is preferably accomplished by casting a fully reacted polyurethane composition on a release paper in a limited thickness and drying the film to remove solvent therefrom, resulting in a film having minute pin holes which render the same moisture-vapor permeable, but moisture-impermeable. Casting of a film of this nature, particularly considering the preferred thicknesses set forth hereinafter may be readily accomplished by those skilled in the art.

The release paper acts as a carrier for the film which is provided with a tie-coat of a compatible adhesive into which are laid the split leather hides, permitting continuous manufacture of the laminated products. Additionally, the release paper can also be used to provide the outside surface of the film with a desired decorative design and degree of gloss.

It is also important, in order to insure "breathability" in the final product, that the adhesive layer be thin enough that the rough surface or "nap" of the split leather penetrates the same during lamination to render the tie-coat discontinuous and permit moisture vapor passage therethrough in the resultant laminates.

In practicing the invention, a layer of a fully reacted polyurethane elastomer solution is first applied to release casting papers by standard techniques of knife-over-roll or reverse-roll coating equipment. Then the "-wet" layer is carried through an oven to dry by solvent evaporation to a continuous film on the release paper

and the dried film and the paper with which it is in intimate contact may be wound on a core for subsequent use in the laminating process. The supported film, on the release paper, is then bonded to the split leather substrate through a discontinuous tie-coat of a compatible adhesive material which may preferably be of the same composition as the film. A layer of the adhesive is applied to the dried plastic film while it is still on the release paper, using knife-over-roll or reverse-roll coating equipment of the like, to provide a controlled thickness of wet bonding agent on the film. At this point, the split leather hides are laid onto the wet tie-coat. The entire assembly is nipped to a controlled degree to bond the split leather hides to the film, using the release paper as a carrier for one or more of the split leather hides.

Depending upon the adhesive material used, various techniques are required to dry the same. The nipping pressure is such as to render the tie-coat discontinuous by partly pressing the surface of the split leather therethrough, whereby the vapor-permeability of the product is insured. Finally, the release paper is removed to produce the finished leather product.

One known process for finishing leather is to solution-coat the tanned hide on a top-grain surface with various lacquers and/or polymer solutions. Only top-grain leather can be finished using this process due to the tightness of the grain which holds the solution on the surface for subsequent drying and recoating. Curtain coating of patent finish on top-grain leather requires several applications of solutions with drying required between applications. This long-established process is time-consuming and costly. In addition, it can only be utilized on whole or top-grain leather. Split leather cannot be finished using solution-coating techniques because split leather is very porous and would absorb the solutions, rendering the same vapor-impermeable. As a result, there is little use made of split leather in finished products. Suede leather products have been the only significant use made of split leather to date. However, the instant invention of laminating a pre-cast, fully reacted polyurethane film to split leather results in a finished product which can be utilized in any application where finished top-grain leather products are presently being utilized.

Referring now to the drawing and more particularly to FIG. **1**, a roll of conventional release paper is shown at **10** as having a textured surface **12** which provides a similar surface on the polyurethane film cast thereon. A fully reacted polyurethane composition **14** is cast on the release paper **10** with a knife **16** over roll **17** or the like metering the thickness of the layer **18** formed thereon. The cast layer **18** supported by the release paper **10** is then passed through an oven or the like **20** to dry the film by evaporating the solvent therein, resulting in a vapor-permeable cast film **22** which may, for convenience, be rolled on a core as shown at **24**.

The roll of supported polyurethane film **24** may then be used as shown in FIG. **2** for production of the final product. A quantity of a compatible adhesive material **26** is metered as by a knife **28** over roll **29** or the like to form a layer **30** thereof on the polyurethane film surface. One or more split leather hides **32** are laid on the adhesive layer **30** and pressed into the adhesive layer as by nip rolls **34**, the pressure being sufficient to insure that the rough surface or "nap" of the split leather hides **32** are pressed into the adhesive **30** to render the same discontinuous, whereby the moisture vapor-permeability of the final product is insured. The thus-formed laminate may then be passed through an oven or the like **36** to dry the adhesive material **20**.

Referring now to FIG. **3** an enlarged fragmentary view of the resultant product is designated generally by the reference numeral **40** and comprises the split leather **32** as a substrate intimately bonded to the pre-cast, fully reacted, polyurethane film **22** by the adhesive material, the roughened surface of the split leather **32**, schematically illustrated at **42**, being pressed into and through the adhesive layer so as to render the same discontinuous. The release paper **10** may then be removed to form the final product which is moisture-permeable on the split leather surface, moisture-impermeable on the polyurethane film surface, and moisture vapor-permeable throughout. From the illustrative dimensions to be given hereinafter for the film thickness and the thickness of the layer of adhesive, it will be readily recognized that the showing in FIG. **3** is exaggerated in order to facilitate an understanding of the instant inventive concepts. The laminae **22**, **32** are shown as separated for illustrative purposes only, although it is understood that in the final product, they will be bonded together over their interfacial contact areas through the discontinuous tie-coat of adhesive material.

As indicated, the release paper **10** may be embossed on its contact surface to provide a desired pattern on the contacted face of the polyurethane film. Additionally, the release paper may be of various degrees of gloss depending on the desired gloss on the surface of the polyurethane film in the final product.

While one form of coating equipment has been illustratively shown in the drawings, it will be understood that other conventional types of equipment, such as reverse-roll coaters may similarly be used. Any device which will supply a controlled thickness of polyurethane material and of adhesive material will be suitable.

Although "free" films of fully reacted polyurethane may be laminated to split leather according to this invention, supported films can similarly be used. Supported films may comprise a film of polyurethane material bonded to, for example, paper, nonwoven fabrics or a textile material, through a discontinuous layer of tie coat, a further discontinuous layer of tie coat then bonding the supported film to the split leather substrate. Thus, the use of the term "pre-cast, fully reacted, polyurethane film" as used herein and in the appended claims is intended to cover such films, whether they be "free" or "supported".

The preferred technique of this invention is to precast the fully reacted polyurethane material onto the release paper and dry the film by oven heating or the like, resulting in a continuous, moisture vapor-permeable film of from 0.5–5.0 dry mil thickness, preferably 1.5–4.0 mil, and most preferably 1.5–3.0 dry mil. A film of this thickness can be readily formed having satisfactory moisture vapor-permeability properties by evaporation of the solvent during the drying procedure. It is preferred to use a pigmented polyurethane material in order to produce a surface layer on the final product of a desired color.

After the film has been dried in intimate contact with the release paper, the adhesive material may be applied thereto as shown in FIG. 2. It is preferred to use an adhesive material identical with the material used in the formation of the pre-cast film itself, although other compatible adhesive materials may be used as explained in more detail hereinafter. The thickness of the tie-coat will depend on the material used, its percent solids, the solvents used, etc. A thickness of from 0.5–3.0 dry mils, preferably 0.5–1.5 dry mils has been found suitable to insure that the roughened of the split leather substrate will penetrate the same during the lamination procedure. Again, depending upon the nature of the tie coat, particularly the percent of solids, an initial layer of 2–8 wet mil may be applied which will be reduced in thickness on drying.

After laying the split leather hides onto the wet tie-coat, the entire assembly is then nipped under pressure as shown in FIG. 2 and the tie coat dried either in an oven, or at ambient temperatures, depending upon the nature of the adhesive material. The nipping pressure is not critical so long as sufficient pressure is applied to penetrate the wet tie-coat by the nap of the split leather. Once the tie-coat is dried, the resultant laminate may be cut to eliminate the web of release paper between the hides and the release paper may then be stripped from the laminates resulting in a surface polyurethane film, finished in the desired pattern color and gloss. Alternatively, the release paper may be removed prior to cutting the laminate into the final desired shape.

It is also possible, if desired, to print or postemboss the resultant laminates to produce a further design depending upon the aesthetics of the final products. Release papers can also be printed in a known manner with a pattern or design which becomes an integral part of the polyurethane film surface when the release paper is removed from the film. It is also possible to print the polyurethane film on the laminating side with various designs and colors while the film is on the release paper.

The wet tie-coat can be pigmented to colors different from the polyurethane film resulting in a multitude of patterns, designs and colors. This technique would produce a pattern which is protected by a layer of polyurethane film above the color design.

Thermosetting polyurethane resins are the preferred materials used in the process of the instant invention, although thermoplastic resins are satisfactory for some applications. The thermosetting materials lend themselves to shoe fabrication where high heat is used to smooth the leather on the last. Polyurethane films have far superior abrasion resistance to other finishes and can be made breathable due to the minimum thickness required for the final product. The process of this invention also results in a bond of the polyurethane film to split leather which is several times as great as conventional finishes used.

As pointed out previously, the use of a pre-cast, fully reacted polyurethane film is critical to the production of a laminate with split leather. Since split leather is porous, it cannot be finished using conventional solution coating techniques.

Although it is believed that the instant inventive concepts can be readily understood from the foregoing, the following specific Examples are set forth to further illustrate the same:

EXAMPLE 1

A layer of a thermosetting, fully reacted, polyurethane resin is cast onto release paper using a knife-over-roll coater and passed through an oven at about 100°C for about 4 minutes to dry the same and form a film of about 3 dry mil thickness. The polyurethane resin is a polyurea-polyurethane in dimethyl formamide. The resin is made by conventional reactions of diisocyanates with glycols which produces an isocyanate terminated prepolymer. The prepolymer is chain extended using aliphatic and/or aromatic diamines and terminated to form a fully reacted resin by using alcohol or other conventional means. The glycols may be either a polyester or a polyether depending on the desired properties of the end product.

The dried polyurethane film is in intimate and tenacious contact with the release paper. A wet laminating compound, preferably of the same composition as used for the polyurethane film, is doctored onto the dried film using the same type of coating equipment, to form a layer of about 2–8 wet mil thickness, depending on the roughness of the split leather surface.

The split leather hides are laid onto the wet tie-coat and the entire assembly is passed through a nip at a fixed pressure. The laminate is passed into an oven at about 100° C for about 2 minutes to dry the tie-coat to a thickness of about 1 mil and the release paper is stripped from the film.

Excellent interfacial bonding between the polyurethane film and the split leather results from the aforementioned technique. The laminate produced can be utilized in any application where conventionally finished top-grain leather has been used heretofore.

The resulting product when tested in accordance with the applicable ASTM test method at 100° F and 92 percent R.H. has the following water vapor transmission rate in grams/cm²/24 hours:

Finished side as face	438–428
Unfinished side as face	473–526

EXAMPLE 2

A 3 mil polyurethane film is cast on embossed release paper from a solvent-based system and dried at about 100° C for about 4 minutes.

On this dry polyurethane film is cast a 2.0 mil water emulsion adhesive. The split leather hides are then laid on the wet adhesive and the assembly placed in an oven at about 100° C. for about two minutes to dry the adhesive. The release paper is then stripped from the polyurethane film.

Again, excellent interfacial bonding between the polyurethane film and the split leather results and the laminates resulting therefrom can be used to produce finished leather products where only conventional top-grain leather has been used heretofore.

Drying of the polyurethane film and the adhesive material can be accomplished with ordinary heated ovens or by the use of dielectric heating.

While thermosetting polyurethane films are desired, thermoplastic materials may also be used. Similarly, although it is preferred to utilize a release paper in the manufacture of laminates according to this invention, other conventional casting techniques may be readily substituted therefor. For example, the fully reacted polyurethane material may be cast on a highly polished,

continuously moving belt, the surface of which has been treated with a conventional release agent. Moreover, the polyurethane film can be cast on non-embossed, embossed, or patent-finish release paper to obtain the desired finish on the film itself. Post-embossing the laminated product can also be accomplished by conventional embossing techniques. Various designs can be produced in situ on the polyurethane film by printing the release paper with the desired pattern prior to solution casting the film. When the dried film is stripped from the printed paper, the design is transferred to the film and is actually an integral part of the film itself. As indicated, it is also possible to print the polyurethane film with any desired pattern. However, the former technique results in a durable print without the use of top coating for protection against abrasion and moisture resistance.

With regard to the specific materials utilized for the formation of the polyurethane film/split leather products of this invention, the film is preferably precast from a solvent-based urethane elastomer in thicknesses as indicated previously, drying of the same occurring at temperatures on the order of 100°–105°C for from about 2–5 minutes. As is well known, polyurethanes are ordinarily formed from organic isocyanates and polyhydric compounds which may include linear or branched-chain polyesters, polyethers, or the like.

Among the various isocyanates are both aliphatic and aromatic isocyanates, such as ethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, diphenylmethylene-4,4'-diisocyanate, 1,5-naphthylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1-chlorophenylene-2,4-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, 4,4'-diphenyl diisocyanate, 3,5-tolyl diisocyanate, 2,4-tolylene diisocyante, 3,3'-dimethyl-4,4'-diphenylene diisocyanate, 3,3'-dimethoxy-4,4'-diphenylene diisocyanate, triphenylmethane triisocyanate and the like.

Various polyhydric compounds, generally in liquid form, are conventionally used to react with the organic isocyanates to produce the polyurethane resins. For example, commercially available "Carbowax", polyalkylene glycols having an average molecular weight of from about 300 to about 750 may be used. Other common materials include butylene glycol-2,3', butylene glycol-1,3, 2-methylene pentanediol-2,4', styrene glycol decamethylene glycol, and the like. Broadly, various polyesters and/or polyester amides may be utilized, including those obtained by condensing polybasic (preferably dibasic carboxylic) organic acids, such as adipic, sebacic, phthalic, isophthalic, tetraphthalic, oxalic, malonic, succinic, maleic, cyclohexylene-1,2-dicarboxylic, cyclohexylene-1,4-dicarboxylic, polyacrylic, naphthalene-1,2-dicarboxylic, fumaric, itaconic, glutaric, pimelic, suberic, azaleic, and the like, with polyalcohols, such as ethylene glycol, diethylene glycol, glycerol, sorbitol, triethanolamine, di-(β-hydroxyethyl)ether, and the like, and/or amine alcohols such as ethanolamine, 3-aminopropanol, 4-aminopropanol, 5-aminopentanol-1, 6-aminohexanol, 10-aminodecanol, 6-amino-5-methylhexanol-1, p-hydroxy-methylbenzylamine, and the like, and with mixtures of the above polyalcohols and amines and/or amino-alcohols and the like. In the esterification, the acid per se may be used for condensation or, where desirable, equivalent compounds, such as the acid halide or anhydride may be used.

Generally, an excess of the polyisocyanate is used in preparing a cross-linked polyurethane, and various cross-linkers and conventional polyurethane modifiers may be included in the composition. The term "fully reacted" as used herein and in the appended claims with reference to the material from which the polyurethane film is cast is to be understood to indicate that the polyurethane has no reactive isocyanate groups, the reaction being terminated in a conventional manner prior to casting to preclude further cross-linking.

The deposition of the polyurethane is generally preferably accomplished from a solution or dispersion of the same and a suitable solvent, such as, inter alia, methylethylketone, methylenechloride, xylene, toluene, and lower alkylene alcohols, dimethylsulfoxide, dimethylformamide and methylpyrrolidone.

The aforementioned materials are not intended to be all-inclusive, but do provide a comprehensive list of conventional reactants utilized in the manufacture of polyurethanes suitable for this invention. The specific polyurethane chosen is not critical, nor is the processing thereof, so long as sufficiently thin films are cast in order to form a water vapor-permeable and preferably water-impermeable film. Using the thicknesses discussed above, such properties can readily be provided.

Many adhesive materials may be used to bond the polyurethane film to the split leather, water emulsions, solvent solutions, or solids of natural and synthetic resins, such as natural and synthetic rubbers, epoxies, such as Armstrong Epoxy J–1148, asphalts, oleoresins such as Armstrong F–1450, polyamides, hot melts, neoprenes, polyesters, polybutanes, polyarylethers, polysulfones, polyvinylbutynes, nitriles, acrylics, particularly high temperature curing acrylic emulsions, dextrines, acetoxylated polyethylene, phenolics, copolymer emulsions such as Airco Chemical 400, polyurethane polymers such as Bostik 7070, or any polymer of the above. The choice of adhesive depends upon the end use of the polyurethane film/split leather laminate, solvent effect on the polyurethane film, curetime of the adhesive, flammability hazards, ease of application, and cost.

With the above considerations in mind, it has been found that film-forming water emulsion adhesives are preferred, although solvent-based urethanes have proven equally successful. Since many solvents may swell the polyurethane film, the water emulsions eliminate this possible drawback. The water emulsion viscosity can be controlled for ease of application, there is no health or fire hazard due to solvents, and rapid drying is easily accomplished. Drying is usually accomplished in 2 to 3 minutes at 110° C. Longer drying times or higher temperatures may have detrimental effects on the split leather. The film thickness of the dried adhesive layer is completely dependent on the quality of the split leather and on the end use of the laminate. The mil thickness is usually in the range of 1–3 mils.

Again, the aforementioned materials are not intended to be all-inclusive, but merely to provide a comprehensive list of commercially available, conventional adhesives which may be utilized to bond the polyurethane film to the split leather according to this invention. It is only important to select an adhesive which is compatible with the polyurethane film and the split leather, a selection which is well within the skill of the art. Preferably, as indicated, the adhesive may be of the same composition as the material used in formation of the polyurethane film.

Since many variations of the foregoing concepts may be contemplated, it is to be understood that all matter herein is to be interpreted merely as illustrative and not in a limiting sense.

What is claimed is:

1. A process of finishing split leather comprising the steps of

casting a layer of a fully reacted polyurethane material on a carrier treated with a release agent,

drying said layer to form a moisture vapor-permeable film,

applying a layer of wet adhesive material to said dried film,

placing at least one soft, supple, moisture vapor-permeable split leather hide on said adhesive material layer,

pressing the split surface of said split leather hide into said adhesive material layer to render said adhesive material layer discontinuous and moisture vapor-permeable,

drying said adhesive material, and

removing said carrier.

said layer of adhesive material being insufficient to impregnate said split leather to any substantial extent thereby producing a laminated product which is moisture vapor-permeable and which retains a soft and supple nature.

2. The process of claim 1 wherein said adhesive material is polyurethane.

3. The process of claim 1 wherein a plurality of individual split leather hides of irregular size and shape are successively fed onto the wet layer of adhesive material in juxtaposed relationship, whereby said carrier acts as a continuous support for said film with said adhesive material and plurality of split leather hides superimposed thereon.

4. The process of claim 3 wherein said plurality of split leather hides is fed with their major surface horizontally onto said adhesive material layer.

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