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[54] **PROCESS FOR THE PRODUCTION OF A LEATHER SUBSTITUTE**

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[51] **Int. Cl.** **B44c 1/02**

[58] **Field of Search** ..... 117/135.5, 10, 11, 117/65.2, 161 KP

[56] **References Cited**

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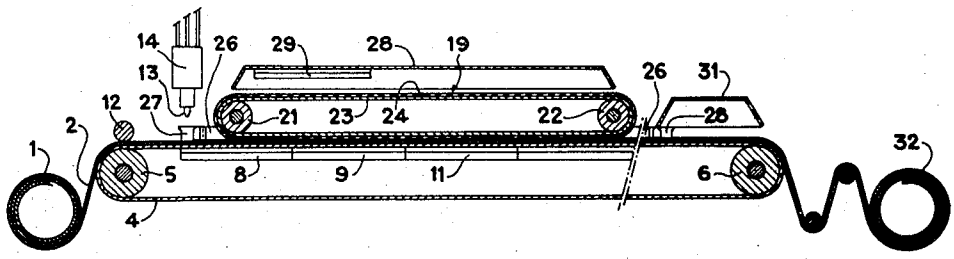
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Assistant Examiner—Theodore G. Davis
Attorney—Irwin S. Thompson and Robert J. Patch

[57] **ABSTRACT**

Supple and resistant material especially suited to be used as a leather substitute is produced by process wherein a cross-linkable coating composition of a microporous product is spread on a water vapor-permeable sheet and the coated sheet is maintained in contact with a belt applicator moving at the same speed and in the same direction as the coated sheet, the time of contact being sufficient to maintain the composition of the coated sheet in compression for at least a part of the cross-linking period.

3 Claims, 2 Drawing Figures



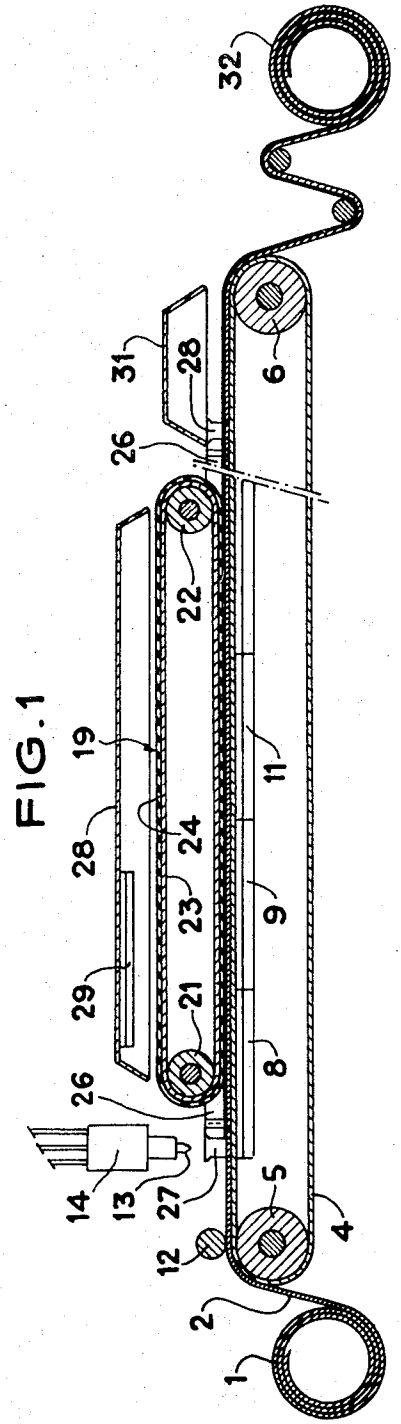

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FIG. 1

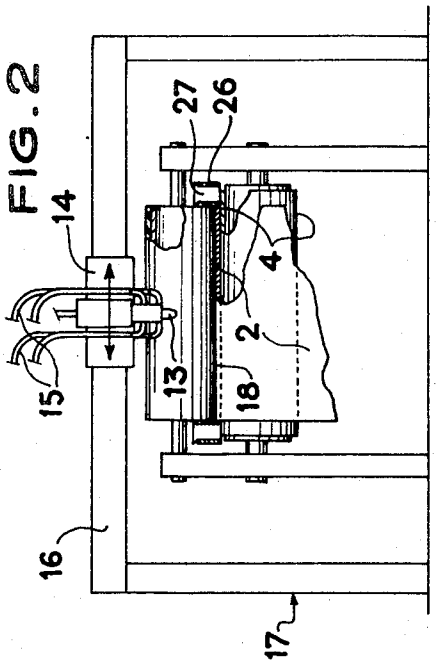

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FIG. 2

PROCESS FOR THE PRODUCTION OF A LEATHER SUBSTITUTE

The invention relates to a process for the production of a supple and resistant material which is permeable to air and water vapor, and more particularly to such a material which can be used as a leather substitute.

It is known to prepare such a material in the form of a product which is permeable to water vapor and air, but impermeable to water in the liquid state. This product is generally called a "poromer" and generally comprises:

1. a fibrous non-woven needled sheet, composed substantially of artificial fibers, especially polyester, impregnated with an adhesive having a low modulus of elasticity, said sheet corresponding to the back of the material, i.e., in the case of leather to the "flesh side,"
2. a surface coating corresponding to the "face side" of the leather, and consisting of a microporous layer of a polymer material having a low modulus of elasticity, generally polyurethane, and attached to the fibrous sheet by adhesion or coating,
3. a woven support inserted between the non-woven sheet and the coating layer, in order to give an adequate resistance to tension.

The microporous layer is obtained from a polymer solution to which is added a liquid which is a non-solvent for the polymer, but miscible with the solvent used for making the solution. A substantially colloidal dispersion is obtained which is applied as a thin layer, either to a temporary support or to the substrate formed by the combination of the fibrous sheet and the woven support. After partial gelation this layer is subjected to various treatments especially to immersions in liquids containing a certain proportion of a product which is a non-solvent for the polymer, but miscible with the solvent in the solution. As a result of the action of various successive baths, more and more rich in non-solvent maintained at appropriate temperatures, a microporous layer is obtained due to the extraction of the solvent by the non-solvent.

It is also known to obtain the surface coating by the method called sintering, according to which a continuous layer of fine powder of a linear polymer, especially polyurethane, generally containing a blocked isocyanate fraction, is formed. This layer is subjected to the action of both pressure and heat, without fusion of the polymer. The blocked isocyanate fraction is liberated and ensures the molecular bonds which improve the cohesion of the material.

It is also known to prepare the microporous surface layer applied to the substrate, by using a process called fibridation, using paper making techniques. The fibrids are prepared from a polyurethane prepolymer having a radial spreading rate of about 1 to 40 cm/sec. A polyurethane film is formed by adding the prepolymer solution to an amine solution containing a non-solvent for the prepolymer. The amine solution, called a chain extension solution, reacts with the interface of the prepolymer film, to form a polyurethane polymer, with recurrent polyurea configurations able to form fibrids. The film spread on the non-solvent amine solution is cut after reaction by a paddle-type mixer in order to obtain fibrids. The fibrids are filtered from the slurry according to paper making techniques, and poromeric microporous sheets are obtained which can be bonded to a non-woven substrate or the like, with a view to obtaining a leather substitute product.

These various processes are complicated and require high capital installation leading to a high manufacturing cost.

The invention envisages a process which, compared with the above-indicated processes, has the advantage of avoiding the coating in the solution or dispersion phase, does not have recourse to the so-called sintering or fibridation methods, which are too complicated industrially, and which in addition makes an insert support unnecessary during the manufacture of the poromeric material, and permits said manufacture to be performed continuously.

An object of the invention is a process for the production of a supple material, which is permeable to air and water vapor, characterised in that one prepares a sheet permeable to water vapor and moves the sheet beneath a belt applicator means, in the same direction and at the same speed as said means, whilst spreading on the sheet above said means a cross-linkable coating composition consisting of a microporous product, the belt applicator means having a sufficient length to maintain the composition in compression during at least part of the duration of the cross-linking.

The invention is particularly suited to the production of material which can be used as a leather substitute and therefore proposes a process for the production of said material wherein one prepares a sheet having a permeability to water vapor of at least 40 g/m²/h, moves the sheet beneath a belt applicator means in the same direction and at the same speed as said means, whilst spreading on the sheet above the belt applicator means a cross-linkable coating composition consisting of a microporous product containing 40 to 90 percent open cells, and a 6 mm thick sample which has a residual deformation of 15 to 35 percent at 20° C, for a 300 percent extension at a speed of 21 cm/min, the belt applicator means having a sufficient length to maintain the composition in compression during at least part of the cross-linking.

The invention includes as an important embodiment a substitute product for leather, comprising a sheet coated with a microporous polyurethane layer, characterised in that the sheet has a permeability to water vapor of at least 40 g/m²/h and the layer has 40 to 90 percent of open cells, a 6 mm thick sample thereof having a residual deformation of 15 to 35 percent at 20° C, for a 300 percent elongation at a speed of 21 cm/min.

The product obtained according to the invention has in particular the following characteristics:

a. the grain of a natural leather can be faithfully reproduced, which was not possible with the hitherto known processes;
b. the "touch" or "handle" of the product obtained is better than that of comparable known products;
c. it has a permanent deformability which in the important application of footwear manufacture makes it possible to give the footwear the desired contours, and when wearing the footwear ensures a conformation to the morphology of the foot, thus reproducing to a maximum the desired characteristics of natural leather, and giving the wearer the desired comfort.

The invention also has for its object apparatus for performing the process according to the invention.

The method of the invention will be described in further detail hereinafter, together with the characteristics of the products obtained, with reference to the accompanying drawings, wherein:

FIG. 1 is a schematic longitudinal view of an apparatus for the continuous manufacture of a leather substitute;

FIG. 2 is a schematic sectional view along the line 2—2 of FIG. 1;

The first stage of the process consists in preparing a sheet which is permeable to water vapor. To obtain a high quality material it is preferable that the permeability to water vapor of the sheet is at least 40 g/m²/h as measured by the method of Kanagy and Vickers described in the "Journal of the Leather Chemists Association," 45, 211 to 242, (Apr. 19, 1950).

For most uses and in particular for leather substitutes fibrous porous sheets are used. These sheets are for example woven fabrics, knitted fabrics such as jersey, felts, porous sheets impregnated with rubber or synthetic resins, such as vinyl halide polymers and even reconstituted leather. The choice of fibers is not critical; these sheets can be produced from polyamides, polyesters, polyesteramides, viscose rayon, wool, cotton, glass and their mixtures. It is also possible to use elastomeric fibers and elastic fabrics. Porous non-woven sheets, which are preferably heat-shrunk, of polyethyleneterephthalate fibrids impregnated with the above-indicated polymers, are particularly preferred in leather substitutes.

When non-woven fibers are used it is advantageous to aid interlacement by needling on a Hunter No. 9 loom for example, and by heat shrinkage of 5 to 25 percent.

While it is possible to use a non-woven fibrous sheet as such, it is also possible to impregnate it with 10 to 60 percent by weight of a bonding polymer placed in solution at a rate of 20 to 30 percent in an appropriate solvent. Depending on the type of polymer, it is possible to use as the solvent, especially ethyl acetate, methyl ethyl ketone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, chlorinated solvents, etc. The impregnating polymer can also be applied in the form of an aqueous emulsion, dispersion or latex. Advantageously the bonding polymer has a modulus of elasticity below 5 kg/mm².

It is also possible to use a polyester polymer having urethane segments, or polyether urethane or polyurea, a polyamide, a polyvinyl chloride or, in association with a polyurethane, an butadiene acrylonitrile elastomer in emulsion an elastomer latex, etc. The impregnating product can be applied to the non-woven sheet by immersion, with a doctor, using a roller or by pulverisation.

The sheet 2 forming the substrate, unwound from a reel 1, is forced to move horizontally on contact with the upper edge of a conveyor belt 4, formed by an endless compact flat metal lattice which passes around two drive rolls 5, 6, whereof the second 6 is subjected to the action of an actuator, not shown, ensuring the tension of the belt 4. The upper edge, on contact with which the substrate 2 is moved, is guided by sliding on the top of a table 7, having heating elements 8, 9, 11.

After passing beneath a pressure roller 12, located directly above the first roll 5, substrate 2 appears below a mixing head 13 carried by a carriage 14, caused to move transversely to and fro on the cross beam 16 of a gantry 17. This head supplies, in the form of a pasty liquid 18, a cross-linkable coating composition of a microporous product.

It is advantageous when the coating composition is cross-linked that it contains 40 to 90 percent of open cells. Excellent results are obtained when the composition is such that a 6 mm thick sample of the cross-linked composition, not applied to the substrate, has a residual deformation of 15 to 35 percent at 20° C for a 300 percent elongation at a speed of 21 cm/min.

Such results can be obtained by selecting as the base constituent of the coating composition a linear polyester or polyether, having a molecular weight between 1,000 and 5,000 and having at least two terminal hydroxy groups, and by reacting this constituent with a polyisocyanate, especially a diisocyanate. Chain extension then takes place with the formation of urethane groups.

Among suitable polyethers are especially the polyalkylene ethers of diols, particularly glycol, e.g., a glycol polyethylene ether, a glycol polypropylene ether, a glycol polytetraethylene ether, a glycol polyhexamethylene ether, a glycol polyoctamethylene ether, a glycol polynonamethylene ether, a glycol polydecamethylene ether, and mixtures thereof. It is also possible to use polyglycols containing several different radicals in the molecular chain, such as for example the compound $HO\ (CH_2—OC_2H_4O)_nH$, where n is an integer greater than one.

Polyesters which can be chosen to replace or be combined with the above polyethers are, for example, those formed by reacting carboxylic acids, esters or hydroxy acids with mono- or polyglycols, for example the condensation products of dicarboxylic acids, such as azelaic, suberic, adipic, sebacic acids and alkylene glycols such as ethylene glycol, propylene glycol or tetramethylene glycol.

As the diisocyanate can be used aromatic, aliphatic or cycloaliphatic diisocyanates or mixtures thereof. Such diisocyanates are for example tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, m-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, methylene bis-(4-phenyl-isocyanate) 4-chlorophenlene-1,3-diisocyanate, naphthalene-1,5-diisocyanate, tetramethylene-1,4-diisocyanate, decamethylene-1,10-diisocyanate, cyclohexylene-1,4-diisocyanate, etc.

Generally 0.5 to 2 molar parts of diisocyanate are used per molar part of the base constituent.

The polyaddition of the polyether or polyester and the diisocyanate can be effective prior to the operations which will be described hereinafter (operating method using the prepolymer) or at the same time.

Cross-linking is performed using a diol, especially glycol of the above-indicated type.

Generally 0.5 to 2 moles of dialcohol are used per mole of the addition product, of diisocyanate, polyether (or polyester).

Finally, to form the cells in the final material the cross-linking is performed in the presence of water. Water is used at the rate of 1.8 to 2.2 moles per mole of diisocyanate in excess in the reaction mixture, i.e., not used in the polyaddition reaction. The water reacts on the isocyanate groups and evolves carbon dioxide. It is thus possible to obtain 40 to 90 percent open cells by controlling the CO_2 formation rate in particular, the chain extension and its cross-linking, for example, by introducing an appropriate quantity of catalysts, which

aid these various reactions and by regulating the operating conditions, especially the temperature.

It is also possible to use an auxiliary porogenic agent, for example a halogenated hydrocarbon such as monofluorotrichloromethane, or methylene chloride. The auxiliary porogenic agent facilitates the bursting of the cells at the desired amount of the cross-linking phase by regulating the temperature of the belt. The proportion of this auxiliary porogenic agent is 0.03 to 0.8 percent relative to the total weight of the other constituents, so as to avoid the formation of macrocells. The main porogenic agent involved in the cross-linking reaction permits a cellular density gradient to be obtained without the formation of a compact surface skin, due to the fact that its action is relatively independent of the surface temperature of the belt applicator means.

The swelling agents, the action of which is caused solely by thermal dissociation, lead either to a compact skin if the shaping walls are below the critical temperature, or to a visibly porous structure. The actions of these two porogenic systems can thus be advantageously combined.

The coating composition **18,** can be prepared by any appropriate technique. The composition can especially be formed by the prepolymer operating method or by the one shot operating method.

After having been deposited on the substrate in such a way as to form a layer, the thickness of which is substantially defined by the speed of the carriage **14,** the flow of the constituents supplying the various tubes **15** of the head **13** and the linear speed of belt **4,** the composition **18** comes into contact with the lower edge of an endless applicator and impressing belt **19,** arranged above the conveyor belt **4** and approximately parallel to the latter, being driven by at least two rolls **21, 22,** which can be regulated in height independently of one another and which are supplemented by means ensuring the tension of belt **19.** The second roll **22** is normally regulated in height so as to be slightly higher than the first roll **21.**

The belt applicator means **19** comprises two superimposed belts **23, 24** the first of which **23** in direct contact with the drums **21, 22** is a metal lattice-like conveyor belt **4,** whilst the second belt **24** is preferably a silicone elastomer. The outer surface of this latter belt has a pattern which can be of any design, but in the example shown is the grain of the leather which it is desired to apply to the outer coating face of the artificial leather strip to be obtained.

The speed of the lower **4** and upper **19** belts is synchronised by a differential variator in such a way that the two edges, respectively in contact with the bottom of subtrate **2,** and the top of coating **18** have a strictly identical speed, in such a way that during the cross-linking which commences after passing over drum **21** and during the subsequent evolution of CO_2 and the expansion of the composition the pattern carried by belt **24** is constantly applied under pressure and without sliding on the coating **18** and is impressed thereon perfectly.

On the edges of substrate **2** the pasty material **18** can be retained by two endless belts **26** passing over rollers **27, 28** of vertical axis, whereof the former drives the belts **26** synchronously with the two belts **4, 19.**

The heating members **8, 9, 11** are supplemented by a tunnel **28** surmounting belt **19** and provided with infra-red radiation panels **29** to activate the cross-linking and maintain the equilibrium of the reaction leading to the formation of the desired open cells.

When the substrate leaves the belt applicator means, the cellular polymer coating is 80 to 90 percent cross-linked. Cross-linking is completed in a heating tunnel **31.** The final product which has a permeability to water vapor of 35 to 70 g/m²/h is wound onto reel **32.** The length of the conveyor belt is, for example, 8 metres, for a belt applicator means length of 4 metres. Instead of the endless belt **19** it is possible to use a paper strip or some other appropriate material unwinding from a reel and winding onto a reel-up drum.

The following examples illustrate the invention.

EXAMPLE 1

Operating method using a prepolymer

Firstly a prepolymer is prepared by reacting 13,000 g of poly(ethylene glycol adipate) having a hydroxy number of 1.76 and a molecular weight of 2,000 (viscosity 500 cp) dehydrated under 5 mm of mercury between 120 and 130° C, for 8 hours with 5,450 g of diphenylmethane-4,4′-diisocyanate whilst operating at 50° C accompanied by stirring for 6 hours. The prepolymer thus contains a certain number of free isocyanate groups such as determined by titration using dibutylamine (free NCO level 16).

The following mixture is prepared separately:

	Grams
Butane-1,4-diol	1300
Stannous octoate	40
Triethylene diamine (Dabco)	36
Surfactant (silicone DC 193) Houndry Process	10
W M emulsifier (Bayer)	10
SM-Dow Corning additive, 5% in water	40
Monofluorotrichloromethane	5

This cross-linking mixture and the prepolymer are brought to a temperature which can be regulated between 30° and 60° C in the mixing head **13** by pumps supplying a given ratio between the cross-linking mixture and the prepolymer.

The mixture is treated in the mixing head and a mixing screw rotating at a speed of 5 to 20,000 rpm.

The coloring agents (metallic or organic oxide in butyl dioctyl phthalate or in a polymeric plasticiser) are added either directly to one of the ingredients or admitted via a third pump in the mixing head in the same way as the auxiliary swelling agent.

As a variant to Example 1, and with the object of obtaining an approximately equal viscosity of prepolymer and cross-linking mixture so as to facilitate the homogenisation of the mixture, it is possible to add to the cross-linking mixture a polyester of the same type as that used for the prepolymer. In this case it is sufficient to increase the isocyanate excess in the prepolymer by a quantity corresponding to the stoichiometric ratio with the polyester added to the cross-linking mixture can thus be reduced from 2 : 1 to 1.1 : 1, expressed in moles.

The mixture of prepolymer and cross-linking mixture obtained in the mixing head is spread uniformly over the substrate.

EXAMPLE 2

Example 1 is repeated, but the poly(ethylene glycol adipate) linear polyester is replaced by a butane diol and ethylene glycol adipate, having a hydroxy number

of 1.76, an average molecular weight of 2,500 and a viscosity of 900 cp.

EXAMPLE 3

One shot operating method

The following polyol mixture is prepared:

Ingredients	Weight in grams
Polyester (butane diol and ethylene glycol adipate; average molecular weight 2,000)	11,000
Butane-1,4-diol	112
Stannous octoate	12
Triethylenediamine	32
Emulsifier	15
S M-Dow Corning additive, 5% in water	37
Monofluorotrichloromethane	5

The mixture is spread onto the belt via head **13** at the same time as 4,700 g of diphenylmethane-4,4'-diisocyanate.

The operations of Example 1 are then performed.

EXAMPLE 4

Example 3 is repeated, but the polyester is replaced by a polyoxyalkylene glycol polypropylene glycol of molecular weight between 1,500 and 3,000.

I claim:

1. Process for producing a leather substitute composite product comprising providing a composition which is cross-linkable into a microporous material and contains a base constituent selected from the group consisting of linear polyester and polyether and combinations thereof, diisocyanate, dialcohol, water and a porogenic agent, providing a water vapor permeable sheet, placing the sheet on a moving elongate support which is under tension, spreading the composition on the sheet at a thickness for subsequently producing a thickness of the finished composite product comprising said composition and said sheet which corresponds to the required thickness of leather to be imitated, moving a belt having on one face of the belt a surface pattern for reproducing by impression a leather grain in pressure-applying contact by said one face with the spread composition on said sheet at a distance from the support for producing said thickness of the finished composite product, the directions and speeds of the movements of the belt and support being identical, and heating the spread composition while it is located between the belt and the support, the length and duration of contact between the composition combined with the sheet and the belt and support being such that the composition is maintained in compression for at least a part of the cross-linking period while the face of the belt having said surface pattern impresses a leather grain into the adjoining composition, and removing the composite product obtained from the support and belt.

2. Process as claimed in claim **1**, wherein the sheet has a permeability to water vapor of at least 40 g/m²/h and the composition is such as to result in a microporous product containing 40 to 90 percent of open cells, a 6 mm thick sample of which product has a residual deformation of 15 to 35 percent at 20° C for an elongation of 300 percent at a speed of 21 cm/min.

3. Leather substitute composite product produced by the process of claim **1**, comprising a sheet coated with a microporous polyurethane layer, the sheet having a permeability to water vapor of at least 40 g/m²/h, and the layer containing 40 to 90 percent of open cells, a **6** mm thick sample of the layer alone having a residual deformation of 15 to 35 percent at 20° C for a 300 percent elongation at a speed of 21 cm/min.

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