

PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Improvements relating to Surface Treatments for Porous Plastics Materials.

We, PORVAIR LIMITED, formerly Porous Plastics Limited, a Company registered under the Laws of Great Britain, of Dagenham Dock, Essex, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to surface treatments for porous plastics materials. It is concerned particularly, but not exclusively, with treatments which give an artificial material a surface appearance resembling natural leather.

According to the present invention a method of modifying the surface of a body having a surface zone of porous polymeric plastics material comprises bringing a solvent for the plastics material into a finely divided state and bringing the solvent in the said finely divided state into contact with the said surface under such conditions as to impart a grain leather-like appearance to the said surface without significantly affecting the structure of the remainder of the body.

The solvent may be brought into a finely divided state and into contact with the surface by spraying the surface with the solvent or solvent composition.

The body preferably comprises a water vapour permeable base zone and a microporous surface zone of polyurethane material, and the microporous surface zone is preferably one which has been made from a solution of the polyurethane by coagulation with a non solvent, for example the surface zone may be made from a solution of polyurethane having dispersed there-

through three parts by weight of removable filler per part of polyurethane, the said polyurethane being coagulated to microporous form by treatment with a non-solvent for the polyurethane which removes the solvent and the filler.

In one form of the invention a method of imparting a grain leather-like appearance to a surface of a flexible water vapour permeable body including a microporous surface zone of soluble polymer substantially all of the said pores opening through the said surface having no dimension in the plane of the surface greater than 100 microns, comprises depositing solvent for the polymer on the said surface in finely divided liquid form and heating the said surface preferably by directing a stream of heated air on to the said surface to produce a water vapour permeable material having an increased resistance to the ingress of liquid water through the treated surface. The stream or current of air may be blown across the surface between the surface and the source of the spray. Desirably the conditions, and in particular the degree of subdivision of the solvent, the rate of application of the solvent to the surface, the air flow, air temperature and air direction, are selected so that the gas permeability of the treated surface is still appreciably greater than that of the polymeric material when in a non porous state.

Preferably the spray of the said solvent is directed at the said surface and traversed back and forth across the surface whilst the surface moves transversely to the direction of spraying.

The source of the spray may be a spray-gun utilizing air under pressure for example

[Price 5s. 0d.]

between 15 and 30 pounds per square inch, to form and propel the spray.

In one form of the invention the body may be made by a method, which will be referred to as a dunking method, which includes forming a mixture comprising the plastics material dissolved in a solvent, shaping the mixture, for example by shaping it into a layer, treating the shaped mixture with an inert liquid so as to cause the plastics material to come out of solution, and removing the solvent and the inert liquid so as to form a porous body. The mixture may include a removable solid filler and the inert liquid may be a non solvent for the plastics material and may be used to remove the solvent and the solid filler and may then be itself removed by heating.

In another form of the invention the body may be made by a method which includes forming a mixture comprising the plastics material dissolved in a solvent and a removable solid filler which is insoluble in the solvent, shaping the mixture, heating the shaped mixture to remove the solvent, treating the dried shaped mixture with a solvent for the filler which is not a solvent for the plastics materials so as to remove the filler, and drying the resultant shaped porous body, and the treatment solvent may contain a minor proportion of a polymeric plastics material, the lacquer working material.

In another form of the invention the body may again be porous and may be made by a method as disclosed in British Patent Specification (Serial No. 1,166,994).

The surface may comprise a polyurethane and the treatment solvent may be dimethylformamide (referred to hereinafter as DMF).

The current of air may be heated, for example to between 40° and 100°C.

The term polyurethane is to be understood in its broadest sense and includes any material derived from the reaction, or a reaction product of a reaction, between a polyisocyanate, such as a di-isocyanate, and a molecule, which will be called the polyurethane precursor, which should generally be a polymeric molecule, containing at least two groups, such as hydroxyl, amido, or amino groups, which contain hydrogen atoms capable of reaction with an isocyanate group. The polyurethane precursor may be a polyester derivative, or a polyether diol, or a polyester amide.

The polyurethane used as the working material may be a thermoplastic elastomer having a low degree of cross-linking and thus may be a predominantly linear polymer. The molecular weight may be in the range 20,000 to 300,000.

The polyurethane may be derived from a polyester such as the proprietary material supplied by the B. F. Goodrich Chemical Company under the name Estane or by

Elastomer Products Limited (Elastollan Limited) under the name Elastollan (Trade Mark). An example of another suitable polyurethane is the proprietary material supplied by Monsanto Chemicals Limited under the name Texin (Trade Mark).

Polyurethanes of the type disclosed and claimed in British Patent Specification No. 1,035,172 are particularly suitable.

Each of the polyurethanes referred to are derived from an essentially linear polyester containing hydroxyl groups. The polyester is produced by reacting together adipic acid and ethylene glycol and preferably has a molecular weight of approximately 2000. The polyurethane is derived from the polyester by reacting a major proportion by weight of the polyester with a minor proportion by weight of 1:4 butylene glycol at an elevated temperature, both the polyester and the glycol being dehydrated before being reacted together. The mixture of polyester and 1:4 butylene glycol is reacted with sufficient isocyanate to produce an essentially linear polyurethane, the isocyanate being 4:4' diphenyl methane di-isocyanate and the reaction being carried out at elevated temperatures.

When the porous plastics material is one in which substantially all of the pores opening through the surface have a maximum dimension in the plane of the surface of less than 100 microns, the treatment solvent is preferably caused to impinge on the surface in a finely divided form so that substantially all of the droplets have a diameter between 1 and 30 microns when they impinge on the surface. When between 60% and 70% of the droplets have diameters in the range 1 to 10 microns useful deepening in colour and embossing effects tend to occur, so that the material takes on an appearance resembling natural calf grain leather.

The invention may be put into practice in various ways but three specific embodiments will be described by way of example.

In the examples all parts are parts by weight.

The letters W.V.P. stand for water vapour permeability and the results are expressed in grams/sq. metre/24 hours and are determined by the method described in British Standard Specification No. 3177/1959 but carried out at 38°C with a nominal humidity gradient of 100% relative humidity.

The hydrostatic head values are determined by the method described in British Standard Specification No. 2823. Nominal pore sizes are expressed in microns and are determined by the method described in British Standard Specification No. 1752/1963 using n-propyl alcohol. Abrasion resistance, and flex life are measured by conventional methods.

In each example a replacement leather

material suitable for use as a grain leather and made as described below has one surface treated in accordance with the present invention.

- 5 The replacement leather material has a fibrous base layer, a tie layer in accordance with British Patent Specification (Serial No. 1,148,711) and a surface layer.

The fibrous base layer

- 10 This is made from a felt made from staple nylon fibres by mechanical entangling involving a needle punching process but no shrinking stage. This is impregnated with a linear polyester based polyurethane
- 15 (Elastollan TN61 EH90AK) (Trade Mark) as a 12% by weight solution in N.N. dimethyl formamide (DMF). The impregnated felt is immersed in water at 20°C. for approximately one minute. The impregnated felt
- 20 with the polyurethane precipitated throughout its structure is left immersed in the water which is pumped past the impregnated felt so that the felt is continuously contacted with fresh water for two hours. The product emerges substantially free of all DMF
- 25 and is dried at 90°C to produce a satisfactory supple product.

The felt before impregnation has the following properties:

- 30 Thickness—4.3 mms
Weight in grams/metre²—653
Weight in grams/metre²/mm. thickness—141
Density—0.9 grams/cc

- 35 The following properties are all measured on a Hounsfield Tensometer.

Tensile strength extension percent and initial modulus are measured in a continuous test on a single sample.

- 40 The material to be tested has an L direction, the direction of travel of the material during its formation, and an X direction, the direction at right angles to the L direction. For each material separate tests are made in the L and X directions.

- 45 These are done on two samples 6" long and 1/2" wide cut from the material to be tested with the lengths of the samples parallel to the L and X directions of the material respectively.

- 50 The samples are mounted in the tensometer with their ends gripped in the jaws of the machine. The samples are then loaded to produce a constant rate of extension of 4 inches per minute.

- 55 The term Initial modulus (felt) used herein, is defined as the load in lbs/inch width of the sample/mm. thickness required to produce a 10% extension in length under these loading conditions.

- 60 The term Tensile strength used herein, is defined as the load in lbs/inch width/mm.

thickness at which the sample ruptures under these loading conditions.

The term Extension percent as used herein, is defined as the % increase in length of the sample at the time of rupture.

Tear strength is measured on a specially shaped sample. As for the other three properties the samples are 6" long and 1/2" wide and are cut with their lengths in the L and X directions respectively. In addition a small notch is cut at the mid point of one side and a small corresponding bulge is formed opposite the notch and extending outwards from the other side. The samples are in fact punched out of the material to be tested.

The notch propagates a tear in the test and the term Tear strength used herein is defined as the load in lbs/mm. thickness required to rupture the sample.

Initial modulus (felt) — L 1.13 × 0.56
Tensile strength — L 24.6 × 55.0
Extension percent — L 125 × 100
Tear strength — L 8.9 × 14.6

The tie layer

The fibrous base zone is split to 1 mm thick sheets with a band knife. The smooth surface thus produced is doctor knife coated with a layer of the following mixture using a gap setting of 0.015 inches.

Tie layer working material ... 25

A thermoplastic polyester based polyurethane, the proprietary material sold by B. F. Goodrich Chemical Company under the name ESTANE 5701 FI

Solvent—cyclohexanone ... 75

Removable filler—sodium chloride ground to a particle size range of 5—25 microns 75 100

Pigment ... 0.6
The layer is then dried at 100°C

The Surface Layer

The dried surface of the tie layer is doctor knife coated with a layer of the following mixture using a gap setting of 0.040 inches.

Surface working material ... 25 110

A thermoplastic polyester based polyurethane, the proprietary material sold by Elastollan Limited under the name Elastollan TN 61 EH 98 AK (Trade Mark)

Solvent—DMF ... 75 115

Removable filler—sodium chloride ground to a particle size range of 5—25 microns 75

Pigment ... 1.25

The composite material is then immersed in water at 20°C for 20 minutes and then washed with water at 80°C for two hours. The sheet is then dried at 100°C.

5 This sheet has the following properties:

WVP	—	3500
Nominal pore size	—	7.2 microns
Hydrostatic head	—	40 mm. Hg
Abrasion resistance	—	poor
10 Flex life	—	good

Example 1

The replacement leather material in the form of a long roll is supported on a stainless steel conveyor with its surface layer uppermost and carried at 2 ft/minute past a suitable spray-gun. The spray-gun is vertically above the sheet and points vertically downwards. The nozzle is 6" from the sheet. The spray-gun is arranged on a transverse slide and oscillated from side to side of the sheet at 80 passes per minute.

20 The treatment solvent, dimethyl-formamide (referred to hereinafter as DMF), is supplied to the spray-gun at a rate such that approximately 1 ml. per square foot of surface is used. Air at 16 p.s.i. is also supplied to the spray-gun.

30 Air is blown by suitable means counter current to the direction of travel of the sheet between the sheet and the spray-gun and generally parallel to the surface of the sheet. The velocity of the air adjacent the spray is 800 cu. ft/minute and the air is heated to 60°C.

35 The sheet after passing the spray-gun immediately enters an oven where it is heated at 120°C, to completely dry it.

The sheet has the following properties:

WVP	—	2900
40 Nominal pore size	—	4.0 microns
Hydrostatic head	—	120 mm. Hg.
Abrasion resistance	—	good
Flex life	—	good

Example 2

45 This is the same as Example 1 except that the treatment solvent, DMF, has lacquer working materials dissolved in it.

The treatment solvent has the following composition.

50 Treatment solvent—DMF 380

Lacquer working material—a polyurethane lacquer composition sold by I.C.I. Limited under the Trade Name Daltosec 258 (Trade Mark) 16
55 a polyurethane lacquer composition sold by I.C.I. Limited under the Trade name Daltosec 158 (Trade Mark). 4

The materials referred to as Daltosec 158

and 258 are 50% by weight solutions of a moisture curing urethane prepolymer dissolved in a mixture of butyl acetate and Pent-oxone. Daltosec 158 has a viscosity of 2.5 poise at 25°C. and an isocyanate value determined as NCO of 2.5%. Daltosec 258 has values of 7.5 poise and 4.5% for the same two properties.

The sheet has the following properties:

WVP	—	2600
Nominal pore size	—	3.4 microns
Hydrostatic head	—	140 mm. Hg.
Abrasion resistance	—	good
Flex life	—	good

Example 3

The sheet is first treated identically to Example 1. 75

The treated sheet is then retreated under the same conditions as Example 1 except that the treatment solvent, DMF, is replaced by cyclohexanone containing lacquer working materials. This treatment solvent has the same composition as that used in Example 2, the DMF being replaced by cyclohexanone. 80

The sheet has the following properties: 85

WVP	—	2700
Nominal pore size	—	2.1 microns
Hydrostatic head	—	180 mm. Hg.
Abrasion resistance	—	good
Flex life	—	good

It will be observed from the results given that materials in accordance with the present invention when compared with the untreated material have the following advantageous properties: 95

- an increased resistance to the ingress of liquid water through the treated surface.
- the treated surface has an increased abrasion resistance. 100
- the treated surface has a reduced pore size, reducing the soiling tendency of the material.
- In Addition
- the colour of the surface darkens and becomes less matt in appearance and may even achieve a glossy appearance and 105
- a leather-like "break" is achieved. By this is meant the appearance of the surface when the sheet is bent with the surface zone innermost a large number of fine lines being temporarily formed. 110

By varying the spraying conditions and the treatment solvent for any particular porous plastics material the surface appearance can be selected to range from a smooth glossy finish to a mottled appearance. 115

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It has been found that when the porous plastics material has been made by a melt roll coating process as disclosed in British Patent Specification (Serial No. 1,166,994) or by a dunking method, and in particular by the method described in the examples, by selecting the spraying conditions a surface finish closely approximating the surface finish, the so called hair cell pattern, of natural calf leather can be obtained.

It will be appreciated that the smaller are the spray droplets produced by the spraygun when they impinge on the surface the finer will be the indentations produced by them in the surface and the smoother the finish.

In this connection high speed photography has revealed that when Example 1 is carried out so that, of the droplets impinging on the surface, 67% have a diameter between 1 and 10 microns, 28% have a diameter between 10 and 20 microns, and 5% have a diameter between 20 and 25 microns a very satisfactory product is obtained. The colour changes from light grey to a deep black and the surface takes on an appearance closely resembling that of a good quality calf grain leather.

An air pressure of 18 p.s.i. in Example 1 is found to produce these droplet size values and distributions when a Binks Bullows spray gun automatic type L 500 is used with an air nozzle Type A1S, a material nozzle Type A28 having a 28 thou. bore and a needle Type 28 occupying the bore.

If too low an air pressure is used, although the colour change occurs the surface does not take on the desired grain appearance since the droplets coalesce and large uneven indentations are produced.

Thus, if an air pressure of 5 p.s.i. is used, of the droplets impinging on the surface, none have a diameter between 1 and 10 microns, 65% have a diameter between 10 and 20 microns, and 35% have a diameter between 20 and 30 microns, and the surface does not resemble a grain leather.

If too high an air pressure is used, whilst the colour change may occur, the surface does not take on the desired grain appearance since insufficient indentation or embossing of the surface occurs.

Thus if an air pressure of 50 p.s.i. is used, of the droplets impinging on the surface, 79% have a diameter between 1 and 10 microns, about 20% have a diameter between 10 and 20 microns, and less than 1% have a diameter between 20 and 30 microns, and the surface once more does not resemble a grain layer, though the colour change may be useful in achieving other finishes.

The proprietary material referred to above under the trade name ELASTOLLAN TN61 EH 98AK is a polyurethane derived

from a linear polyester containing hydroxyl groups which is produced by reacting adipic acid with ethylene glycol. This polyester has a molecular weight of approximately 2000, a hydroxyl index around 50 and an acid number of 1. This polyester (1000 grams) is heated to approximately 120°C. with 1, 4-butylene glycol (90 grams). Both the polyester and the glycol are adequately dehydrated before being reacted together. Solid 4-4'-diphenyl-methane-diisocyanate (400 grams) is added to the heated mixture with vigorous stirring, which is continued until the solid has dissolved, the temperature reaching about 100°C. After about two minutes the liquid is poured on to plates preheated to approximately 110°C to 130°C. After approximately ten minutes the mass is stripped from the plates, allowed to cool to room temperature, and granulated in a conventional granulating machine. This material has a Shore hardness of 98 on the A scale at 25°C. A 10% by weight solution in dimethyl formamide at 25°C. has a viscosity of the order of 15 to 30 centipoise.

By varying the spraying conditions and the treatment solvent for any particular porous plastics material the surface appearance can be selected to range from a smooth glossy finish to a mottled appearance.

To obtain the effects described herein some experimentation will generally be needed, since the rate of application of solvent, spraying pressures, type and positioning of equipment, etc. will affect the character of the product. For instance, it is obviously possible, by applying sufficient solvent, to dissolve the entire microporous layer so that a non-porous film remains on evaporation of the solvent, or to entirely collapse the porous structure throughout the microporous layer, rather than partially collapse it at the surface. With the teachings herein of the effects to be attained, those skilled in the art will have no difficulty in making the simple trials, with appropriate equipment needed to determine the best spraying conditions for that particular equipment and for the particular microporous sheet material and particularly solvent which is used.

The application of a stream of hot air to the solvent sprayed sheet has been found to make it much easier to obtain a high quality, generally finer grained, surface. One possible explanation for this is that the heat causes surface fusion of the solvent-carrying surface (which has, of course, a lower fusion temperature than the solvent-free material) and that the evaporation occasioned by the high velocity air stream keeps the solvent from penetrating into the microporous material so that the solvent affects only the surface; this occurs even though the temperature is, as will be evident, well below the boiling point of the solvent.

**WHAT WE CLAIM IS:—**

1. A method of modifying the surface of a body having a surface zone of porous polymeric plastics material which comprises bringing a solvent for the plastics material into a finely divided state and bringing the solvent in the said finely divided state into contact with the said surface under such conditions as to impart a grain leather-like appearance to the said surface without significantly affecting the structure of the remainder of the body.
2. A method of imparting a grain leather-like appearance to a surface of a flexible water vapour permeable body including a microporous surface zone of soluble polymer substantially all of the pores opening through the said surface having no dimension in the plane of the surface greater than 100 microns, the said method comprising depositing solvent for the polymer on the said surface in finely divided liquid form and heating the said surface to remove the deposited solvent to produce a water vapour permeable material having an increased resistance to the ingress of liquid water through the treated surface.
3. A method as claimed in Claim 1 or Claim 2 characterized in that the solvent is brought into a finely divided state and is brought into contact with the surface by spraying the surface with the solvent or solvent composition.
4. A method as claimed in Claim 3 in which the spray of the said solvent is directed at the said surface and traversed back and forth across the surface whilst the surface moves transversely to the direction of spraying.
5. A method as claimed in Claim 3 or Claim 4 characterized in that during the spraying a current of air is blown across the surface between the surface and the source of the spray.
6. A method as claimed in Claim 5 in which the current of air is heated to between 40°C and 100°C.
7. A method as claimed in any one of the preceding claims characterized in that the surface comprises microporous polyurethane and the solvent comprises N,N'-dimethylformamide.
8. A method as claimed in Claim 7 in which the surface is coloured and substantially all of the pores opening through the surface have a maximum dimension in the plane of the surface of less than 100 microns, and the treatment solvent is brought into contact with the surface in a finely divided form so that substantially all of the droplets have a diameter between 1 and 30 microns when they contact the surface, and the colour of the said surface is darkened and made less matt by the treatment.
9. A method as claimed in Claim 8 in which between 60% and 70% of the droplets have diameters in the range 1 to 10 microns.
10. A method as claimed in Claim 9 in which the spray is formed by means of air under a pressure between 15 and 30 pounds per square inch.
11. A method as claimed in any one of the preceding claims in which the body comprises a water vapour permeable base zone and a microporous surface zone of polyurethane material.
12. A method as claimed in Claim 11 in which the microporous surface zone has been made from a solution of the polyurethane by coagulation with a non solvent.
13. A method as claimed in Claim 12 in which the surface zone has been made from a solution of polyurethane having dispersed therethrough three parts by weight of microscopic removable solid filler per part by weight of polyurethane, the said polyurethane being coagulated to microporous form by treatment with a non-solvent for the polyurethane which removes the solvent and the filler.
14. A method of imparting a grain leather-like appearance to at least one surface of a body of which at least the surface being treated consists of porous polymeric plastics material substantially as described herein with reference to the Examples.
15. A body having a grain leather-like surface appearance produced by a method as claimed in any one of the preceding claims.

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