

PATENT SPECIFICATION

(11) 1220 218

DRAWINGS ATTACHED

- (21) Application No. 1611/67 (22) Filed 11 Jan. 1967
 (23) Complete Specification filed 10 Jan. 1968
 (45) Complete Specification published 20 Jan. 1971
 (51) International Classification B 32 b 5/32
 (52) Index at acceptance

B2E 170 173 17Y 203 20Y 210 225 22Y 237 23Y 257 302
 308 331 339 361 368 372 380 383 38Y 413
 41Y 420 435 43Y 447 449 44Y 467 498 549
 568 569 570 571

D1L 23A

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NATIONAL REFERENCE
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 AND INVENTION

(54) IMPROVEMENTS RELATING TO WATER VAPOUR PERMEABLE FLEXIBLE SHEET MATERIALS

(See *Exhibition*)

(71) We, PORVAIR LIMITED, formerly Porous Plastics Limited, a Company registered under the Laws of Great Britain, of Estuary Road, North Lynn, King's Lynn, Norfolk, England, formerly of Dagenham Dock, Essex, 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:—

This invention relates to the making of water vapour permeable flexible porous sheet materials, more especially microporous materials, particularly, though not exclusively, man-made leather-like materials, by methods of type comprising forming a spreadable mixture comprising a solution of a film forming flexible synthetic polymeric plastics working material in a solvent, forming a continuous layer of the mixture on a temporary backer or support, treating the layer on the support with a coagulating liquid, which is a non solvent for the working material, but is at least partially miscible with the solvent for the working material, so as to coagulate the working material into a microporous sheet, and washing with fresh coagulating liquid or continuing the treatment until substantially all the solvent has been removed. Thereafter the resultant sheet material may be dried and torn or stripped from the temporary support.

The invention is concerned with such methods in which, for one reason or another, the material is made in two superimposed layers. There may be various reasons for making the material in two layers. For example natural leather comprises a main fibre layer and a surface layer termed the grain layer, and in making an artificial

leather it is often thought desirable to provide two layers having rather different properties to simulate these two layers of natural leather. In other cases the purpose of the exposed layer may be merely to give a pleasing appearance or a desired colour whilst employing for the greater part of the thickness a material having other desirable qualities such as strength or toughness, or cheapness. Again it may be desirable that the exposed layer should be waterproof whilst the other layer may have a degree of water absorbency.

In certain known processes the difficulty has arisen that when the mixture for the second layer is applied to the already formed first layer, the solvent in the former partly dissolves the surface of the latter and adversely affects its structure, for example by collapsing its micropores and lowering its water vapour permeability. To overcome this difficulty it has been proposed to interpose a third or tie layer between the other two layers, the solvent for each layer being chosen so as not to dissolve or adversely affect the preceding layer. Naturally this adds considerably to the complexity of the method.

It has now been found that if the second layer mixture is deposited on the first layer mixture before coagulation of the latter, the two layers can be coagulated simultaneously and the difficulties referred to above do not arise.

Thus according to the present invention a method of making a water vapour permeable flexible sheet material includes forming a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, forming a continuous layer of the mixture on a temporary support,

[Price 5s. 0d. (25p)]

and, before the solvent is removed, forming a second layer also of a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, on the surface of the first layer, treating both layers on the support with a coagulating liquid which is a non solvent for the working material, but is at least partially miscible with the solvent for the working material of both layers, and removing substantially all the solvent by washing the material with a coagulating liquid. Thereafter the sheet material may be dried and stripped from the temporary support. The term washing includes merely immersing the material in a coagulating liquid.

Preferably the viscosity of the mixture forming the first layer is greater than the viscosity of the mixture forming the second layer. The viscosity of the first layer mixture may be greater than 700 poise, measured at 25°C.

In some cases it may be desirable to include in the mixture of either or both layers a removable solid filler ground to a narrow range of particle sizes, the filler being insoluble in the solvent for the working material but preferably soluble in the coagulating liquid, thus enabling the filler to be removed during or after the coagulation of the working material merely by continuing the treatment with the coagulating liquid.

A preferred process in accordance with the present invention comprises providing a first spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microporous particles of removable filler dispersed therein, providing a second spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microscopic particles of removable filler dispersed therein, said first and second spreadable mixtures being of different composition, forming a continuous layer of said second spreadable mixture in face to face adherent contact with a continuous layer of said first spreadable mixture on a temporary support and coagulating both said contacting layers with non solvent for the polymeric material of said layers, which non solvent is miscible with the solvent material of said layers, and removing substantially all the solvent by washing the coagulated contacting layers with none solvent for the polymeric material, and leaching said removable filler from said coagulated contacting layers, to form a microporous material having two superimposed adherent layers of different properties. Preferably the said two mixtures differ in their removable filler: polymer weight ratios. Also preferably neither of the said two layers is

less than 0.3 mm thick, measured after said coagulation and leaching and after removal of liquid. Further neither of the said two contacting layers, prior to said coagulation preferably contains more than 4 parts of solvent per part of polymeric material.

The said layer of the said first mixture is conveniently formed on a temporary support to which the said layer adheres, the said layer of the said second mixture is formed over the said first layer, and the said layers on the said support are treated with liquid non solvent to effect the said coagulation on the said support, the resulting composite of adherent coagulated layers being then stripped from the said support.

Both of the said mixtures may have microscopic sodium chloride particles dispersed therein and the said non solvent may be aqueous.

Preferably the filler is ground so that more than 50% of the particles have a diameter within the range 4 to 20 microns. The average diameter of the particles may be in the range 10 to 14 microns, and is preferably 13 microns; the standard deviation on either side of the average being 4.5 microns. This particle size will be referred to as 13 ± 4.5 microns (one standard deviation) in the rest of the specification. A suitable filler material is sodium chloride. These particle sizes are as measured by means of a Photo-extinction Sedimentometer manufactured by Evans Electro Selenium Limited, Model No. 41 used in accordance with the manufacturers' instructions based on papers by H. E. Rose in "Engineering" of 31st March and 14th April 1950 and "Nature" of 1952 Volume 169 p. 287.

The mixture used to form the second layer may contain an amount of removable solid filler such that the ratio of filler to working material in the mixture is in the range 0.5:1 to 6:1 in parts by weight, and preferably 3:1 to 6:1. The mixture used to form the first layer may contain an amount of removable solid filler such that the ratio of the filler to working material is in the range 0.5:1 to 3:1 in parts by weight, and preferably 1.78:1.

In addition to simplifying the process the invention has or may have certain other advantages. Thus the simultaneous coagulation of the two layers tends to produce greater lamination strength, that is to say greater resistance to tearing apart of one layer from the other. In addition it is found that certain formulations have a tendency to produce what may be termed a "cellular structure" comprising a number of relatively large cells, or macropores big enough to be seen by the naked eye, in a microporous matrix, and this structure tends to have reduced toughness, wear resistance, or resistance to tear propagation. It is found that certain formulations

which produce this cellular structure in the layers when made individually do not do so when the layers are simultaneously coagulated in accordance with the present invention.

5 In the mixture for the first layer the ratio of working material to solvent may be in the range 25:75 to 35:65 in parts by weight, and preferably 30:70.

10 In the mixture for the second layer, the proportion of working material to solvent may be in the range 20:80 to 30:70 in parts by weight, and preferably 25:75.

15 In the mixture used to form the first layer the ratio of filler to working material and working material to solvent may fall within the area defined by the closed figure DQLMD, for example AKLMA, preferably RSTUR, in the diagram, Figure 5, of the accompanying drawings.

20 Provided that the ratios fall within the area R-S-T-U-R macropores are unlikely to be produced in the substrate. However in the case of the particle sizes of the sodium chloride being at the low end of the range quoted above the tendency of sodium chloride to absorb moisture is increased and care must be taken to ensure that the preferred moisture content of 0.2-0.4% w for the sodium chloride mentioned below is not exceeded and the milling conditions are such as to achieve homogeneous dispersions. In addition the coagulation temperature should be kept down if macropores are to be avoided.

25 Preferably in the said first mixture the ratio of removable filler to polymer is in the range 0.6:1 to 2.5:1 and the polymer concentration based on polymer and solvent is in the range 25% to 37.5% and these ratios and concentrations also fall within the area defined by the closed figure DQLMD in the diagram, figure 5 of the accompanying drawings and in which, in the said second mixture, the ratio of removable filler to polymer is about 3 to 1 and the polymer concentration based on polymer and solvent is in the range 20% to 30%.

30 Preferably the mixture used to form the first layer has a ratio of filler to polymeric working material of about 1.78:1 parts by weight and the mixture used to form the second layer has a ratio of filler to polymeric working material of about 3:1 and the filler is ground to an average particle diameter of 10 to 14 microns.

35 The mixture forming the first layer is preferably applied in such a way as to achieve a layer which has a thickness in the range 1.1 to 1.3 mm. The mixture used to form the second layer is preferably applied in such a way as to achieve a composite finished leached and dried microporous product whose overall thickness is in the range 1.6 to 1.8 mm. Both layers may be applied by knife coating.

The preferred working materials are polyurethanes derived from polyesters, polyethers or polycaprolactones.

40 Examples of polyester-based resins are those sold under the trade names ELASTOLLAN TN61 EH98AK (Trade Mark) and TEXIN. A suitable polyether-based resin is that sold as ELASTOLLAN TN63 PA98AK. A suitable caprolactone-based polyurethane is that sold as ELASTOLLAN TN65 EN98AK.

The solvent in the said second mixture maybe a solvent for the polymer of the said first mixture.

45 Solvents for the working material which may be employed include dimethyl formamide, dimethyl sulphoxide, N-methyl pyrrolidone and dimethyl acetamide, but the actual solvent chosen will depend on the working material employed. Thus for ELASTOLLAN TN61 EH98AK, dimethyl formamide is preferred.

50 Dimethyl formamide can be diluted with other cheaper solvents such as toluene and methyl ethyl ketone which although not solvents for the polyurethane on their own do not act as non solvents when mixed with dimethyl formamide.

55 A preferred working material for both layers is a thermoplastic elastomeric polyurethane derived from a polyester by reaction with a diol and a di-isocyanate, and in particular one in which the polyester comprises the condensation reaction product of adipic acid and ethylene glycol, the diol comprises 1,4 - butylene glycol and the di-isocyanate comprises 4,4' - diphenylmethane di - isocyanate, and the isocyanate is used in molar excess preferably a very slight molar excess. Part of the ethylene glycol may be replaced by 1,4-butyleneglycol.

60 A preferred coagulating liquid is water, but other solvents, for example organic solvents, or mixtures of other solvents with water, may be used.

65 The temporary backer is preferably a sheet of porous synthetic plastics material, which may conveniently be formed by sintering powdered thermoplastic polymer. The thermoplastic polymer may be a high density polyethylene. One particular such backer which has been found suitable is .067" ± .004" thick, has a permeability of 18 ± 4 cubic ft./min. air at a pressure of 8" static water gauge and weighs 114 grams/sq.ft.

Desirably the backer has an ultimate tensile strength greater than 115 Kg/cm² and an elongation at break less than 25%.

70 An example of such a material is that sold under the trade name VYON (Trade Mark). Such a material is formed by spreading an even layer of Ziegler high density polyethylene powder on a smooth metal surface and then placing the smooth metal surface and the layer in a suitably heated oven to

cause the particles to sinter. The surface of the resultant sintered sheet which was in contact with the smooth metal surface is smoother than the other face and it is on this smoother face that the layer is formed.

In a preferred form of the invention for both layers the filler is sodium chloride, the working material comprises thermoplastic elastomeric polyurethane derived from a polyester by reaction with a diol and a di-isocyanate, the solvent comprises dimethylformamide, and the mixtures are formed by dissolving the polyurethane in the dimethylformamide and then milling dried sodium chloride into the solution under conditions of low humidity until a homogeneous dispersion is obtained. Preferably the moisture content of the sodium chloride is not greater than 0.2—0.4% by weight and the milling conditions are not more humid than 50% RH at 25°C. In this form of the invention the viscosity of the first layer mixture is greater than that of the second layer mixture and layers are knife coated onto the backer as it passes around a roll the first layer being applied to the backer between a first knife preferably vertical and an upstream inclined backing plate located before the first knife from the point of view of the movement of the backer and the second layer is applied between the first knife and a second knife located downstream from the first knife, the second layer thus being applied immediately on top of the first layer.

Preferably the coagulation is carried out by immersing the support, coated face downwards in water at 20°C. Conveniently the material is immersed in the cold, for example at 20°C, in the coagulating liquid until insufficient solvent remains to cause collapse of the porous structure on heating and then the filler is substantially removed by callendering the material in heated coagulating liquid, for example at 60°C, which is passed in countercurrent to the material.

The surface of the second layer of the leached and dried microporous product may be sprayed with a solvent for the working material so as to partially collapse the microporous structure of the surface whilst leaving the gas permeability of the treated surface still appreciably greater than that of the working material when in a non porous state. This treatment imparts a grain leather like appearance to the material and enables it to be used as a calf grain leather like man made material for example as a shoe upper material.

This treatment is in accordance with the invention claimed in British Patent Specification Serial No. 1,190,551.

A typical product made in accordance with the invention as hereinafter specifically described, apart from the thicknesses of the substrate and top coat, and coagulating temperatures of 25—30°C and leaching tempera-

tures 70—80°C has a substrate thickness of 0.95 mm, a top coat thickness of 0.75 mm and a weight per unit area of 747.6 g/m². Its breathability is indicated by a water vapour permeability of 1455 g/m²/24 hours (measured by the desiccant method), whilst its resistance to the ingress of liquid water is indicated by a hydrostatic head of 9 cm.Hg. The material is suitable for use as a shoe upper material.

The desiccant method for determining water vapour permeability is as described in B.S.S. 3177/1959 but carried out at 38°C with a nominal humidity gradient of 100% relative humidity.

Hydrostatic head is measured by the method described in B.S.S. 2823.

The invention may be put into practice in various ways but one specific process embodying the invention will be described by way of example and with reference to the accompanying diagrams in which:—

Figure 1 is a flow diagram of the process;

Figure 2 is a diagrammatic side elevation of a two head coating arrangement and a coagulating tank 500 used to form a layer of substrate paste on the backer and a layer of top coat paste on top of the layer of substrate paste and to coagulate both layers, stages 40, 41 and 50 respectively in Figure 1;

Figure 3 is a diagrammatic plan view of the two head coating arrangement shown in Figure 2;

Figure 4 is a diagrammatic cross-sectional view of the entry end of the coagulating tank 500 taken on the line IX—IX in Figure 2;

Figure 5 is a graph with ratios in parts by weight of working material to solvent expressed as percentages of working material as abscissae, and the corresponding ratios in parts by weight of filler to working material as ordinates.

General description of the process

Referring to Figure 1 the main stages of the process are numbered 31 to 80. There are two ancillary stages, those of grinding the sodium chloride to a narrow range of fine particle sizes, stage 20 and manufacturing the backer, stage 25. The backer is a sheet of porous sintered high density polyethylene and is formed by spreading an even layer of Ziegler high density polyethylene powder on a smooth metal conveyor belt, passing the layer on the belt through a suitably heated oven to cause the particles to sinter, cooling the sintered sheet and stripping it from the belt. The surface of the resultant sintered sheet which was in contact with the smooth metal surface is smoother than the other face, and it is on this smoother surface that the mixture is spread.

In general terms the main stages of the

process consist of preparing two different pastes containing a solution of a polyester based polyurethane dissolved in dimethyl formamide, finely divided sodium chloride, and carbon black pigment, the first (or substrate paste) having more polymer, less salt, less pigment, and a higher viscosity than the second (or top coat) paste. These are stages 31 to 36.

10 A first layer of the first paste is spread on the backer and then immediately a thinner layer of the other paste is spread on top of the first layer. These are stages 40 and 41.

15 The coated backer, held under suitable tension throughout this stage of the process, is smoothly immersed, coated face down, in cold water and washed with cold water (20°C) until the polyurethane has all been precipitated out of solution and all the dimethyl formamide has been removed. These are stages 50 and 55. The remainder of the sodium chloride is then removed by leaching with water heated at 60°C and the material dried with the top coat uppermost, care being taken that the heating does not warp the backer. 25 Twenty minutes in an oven at 120°C is suitable. These are stages 60 and 65.

30 After being dried it is carefully stripped from the backer. This is stage 70. It may be easier to do this whilst the material is still hot. This process imparts a fibrous or flesh surface appearance to the substrate surface which was in adherence with the backer. 35 The backer is then treated to enable it to be reused if possible and returned to stage 25 of the process for reuse or recovery.

40 The material is then inspected and tested, and if it comes up to specification is given a surface finishing treatment by spraying with dimethyl formamide and drying. This procedure may be in accordance with the invention disclosed in British patent specification Serial No. 1,190,551. This is stage 80. This imparts a high quality calf grain appearance to the top coat surface. 45

Stage 20 grinding the salt

Satisfactory results are obtained when the majority of the particles are between 4 and 20 microns in diameter, the preferred average particle diameter being 13 ± 4.5 microns (one standard deviation). The particle size of the salt is measured on a Photo-extinction Sedimentometer manufactured by Evans Electro Selenium Limited, Model No. 41 used in accordance with the manufacturers' instructions based on papers by H. E. Rose in 'Engineering' of 31st March and 14th April, 1950 and 'Nature' of 1952. Volume 169 page 287. Care must be taken to ensure that the particles in the test suspension have not agglomerated and this can be achieved by applying ultrasonic vibrations to the test suspension, these of course must be such as not to break up the individual particles but

merely any agglomerates. The grinding is performed by recirculating the sodium chloride between a grinder producing particles somewhat on the coarse side and a classifier which separates the particles that are too coarse and returns them to the grinder. Typically approximately 60% of the total mass is returned for regrinding. The grinder may be of the type comprising a pair of co-axial discs which can be rotated at different speeds or in opposite directions, each disc having concentric rings of pegs projecting from it and lying between the rings of pegs of the companion disc.

The material which is ground consists of sodium chloride crystals having a moisture content not in excess of 0.2—0.4% w to which are added between 0.4 and 0.7% w of a co-precipitated lime and silica anti-caking agent for example that sold as Microcal 160 (Trade Mark) by Joseph Crossfield & Sons Ltd. The ground sodium chloride is sealed in cans and stored under dry conditions so that the moisture content of the ground salt does not exceed 0.2—0.4% w and is preferably about that value.

Stage 25 Manufacturing the backer

The temporary backer is a sheet of porous synthetic plastics material formed by spreading an even layer of Ziegler high density polyethylene powder on a smooth metal surface and then placing the smooth metal surface and the layer in a suitable heated oven to cause the particles to sinter. The surface of the resultant sintered sheet which was in contact with the smooth metal surface is smoother than the other face and it is on this smoother face that the layer is formed.

The material is 22" wide, $0.067'' \pm 0.004''$ thick, has a permeability of 18 ± 4 cubic ft./air/minute at a pressure of 8" static water gauge and weighs 114 gram./ft².

Stages 31 to 36 preparing the substrate and top coat pastes

The working material from which the man-made leather-like water vapour permeable flexible sheet material is made is a polyester based polyurethane which is made as follows.

The starting material is a linear polyester containing hydroxyl groups which is made from adipic acid and ethylene glycol, which has a molecular weight of approximately 2,000, a hydroxyl index around 50 and an acid number of 1. 1,000 g. of this polyester is heated to approximately 120°C with 90 g. 1,4-butylene glycol, both re-agents having been adequately dessicated beforehand. 400 g. of solid 4,4'-diphenylmethane di-isocyanate 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 between

110°C and 130°C. After about 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% w solution in dimethylformamide has a viscosity of the order of 15 to 30 centipoise at 25°C.

In a modification of this material part of the ethylene glycol is replaced by 1,4-butyleneglycol so that the basic polyester is in fact a copolymer of two diols.

The material may also contain conventional stabilizers.

Stage 32 of Figure 1, preparing the substrate solution, is carried out by weighing out 3 parts by weight of this polymer and dissolving this in 7 parts by weight of dry dimethylformamide (less than 0.01% of moisture, supplied by I.C.I. Ltd. in accordance with their specification for dry dimethylformamide) in a vertical mixer with a high rate of shear, e.g. a Silverson mixer. Care must be taken to keep the temperature below 40°C during mixing or degradation of the polyurethane is liable to occur. The substrate solution is stored under dry conditions.

Care must be taken when handling dimethylformamide solutions since the vapour is toxic and also hygroscopic. Thus when possible the mixing stages are enclosed and are kept at low humidity ideally less than 50% RH at 25°C.

Stages 31 and 33, blending and curing the top coat polyurethane and preparing the top coat solution are carried out in a ribbob blender and a Silverson mixer identical to that used for Stage 32.

The polymer of 15 to 30 centipoise viscosity at 25°C in 10% w solution is cured and blended dry.

The curing is carried out at 75°C under an inert atmosphere, e.g. of nitrogen until the viscosity of 10% w solution of the cured polyurethane has risen to 70 to 90 centipoise at 25°C.

1 Part by weight of the cured polyurethane is weighed out and mixed with 3 parts by weight of dry dimethylformamide in the same way as the substrate solution and stored under dry conditions.

The dimethylformamide is also stored under dry conditions.

Stage 34, preparing the pigment master batch, is carried out as follows. 60 parts by weight of top coat solution are filtered to remove any agglomerations or undissolved solids. The filtered solution is then placed in the pot of a five gallon paddle type mixer where it is mixed with 30 parts by weight of dry dimethylformamide and 10 parts by

weight of carbon black pigment of 20 microns average particle diameter. The mixture is then milled on a Torrance triple roll mill to produce a homogeneous dispersion and stored under dry conditions.

The milling is carried out in an air conditioned enclosure the filtered heated air taken in being kept at 25°C and a humidity of about 50% RH.

Stage 35, preparing the substrate paste, is carried out as follows. 100 parts by weight of filtered substrate solution are placed in a paddle type mixer, 1.5 parts by weight of the pigment master batch is added and 53.4 parts by weight of ground salt taken from sealed cans is added after being sieved through a 60 mesh British Standard screen in a vibratory sieve.

This is mixed in a paddle type mixer, and then milled on the triple roll mill to produce a homogeneous dispersion, which, when tested with a Hegman gauge gives a reading of 6.5—7 which is indicative that no particles greater than 14 microns in diameter are present. This dispersion, the substrate paste, is stored under dry conditions.

To summarise the substrate paste may have the following composition:

Polyurethane (15—30 centipoise at 25°C)	30 parts by weight	90
Polyurethane (70—90 centipoise at 25°C)	0.23 parts by weight	
Ground sodium chloride (average particle diameter 13 ± 4.5 microns (one standard deviation))	53.4 parts by weight	95
Dimethylformamide	71.13 parts by weight	
Carbon black pigment	0.15 parts by weight	100

It has a viscosity of the order of 1.51×10^6 centipoise at 25°C.

Stage 36, preparing the top coat paste, is carried out as follows. 100 parts by weight of filtered top coat solution is placed in the pot of a paddle type mixer, 12.5 parts by weight of the pigment master batch is added and 80.63 parts by weight of ground salt taken from sealed cans is added after being sieved through a 60 mesh British Standard screen in the vibratory sieve. This is mixed in the paddle type mixer and milled in the triple roll mill in exactly the same way as the top coat paste in stage 35, and the resultant top coat paste is stored under dry conditions.

To summarise the top coat paste may have the following composition:

- Polyurethane (70—90 centipoise at 25°C)
 26.86 parts by weight
 Ground sodium chloride (average particle
 diameter 13 ± 4.5 microns (one standard
 deviation))
 80.63 parts by weight
 Dimethylformamide
 84.38 parts by weight
 Carbon black pigment
 1.25 parts by weight

It has a viscosity of the order of 1.0×10^6 centipoise at 25°C.

The two-head coating arrangement and the coagulating tank 500 (Figures 2, 3 and 4)

The backer 403 which has been stored under dry conditions is mounted as a roll 401 on a braked wind off stand 402. The backer passes round an 18" diameter ground steel spreading roll 404 underneath the two head coating arrangement and down under a guide roll 405 into a coagulating tank 500.

The two head coating arrangement includes a first coating blade 406 located just to the right in Figure 3 of the centre of the roll 404 and adjustably mounted on the stand 407 which supports the roll 404. A trough 408 is formed by a backing plate 409 and cheek pieces 410 and 411 adjustably mounted on the stand 407. A second coating blade 412 is located at about 35° to the first blade 406 and is also adjustably mounted on the stand 407. A second trough 413 is formed between the first and second blades 406 and 412 by cheek pieces 414 and 415 adjustably mounted on the stand 407.

The blades 406 and 412 have chamfered trailing edges 416 and 417 and flat bases.

Stage 40, the formation of the layer of substrate paste on the backer, is carried out as follows:

The substrate paste from the tank is mixed to eliminate any settling of the sodium chloride and de-aired under vacuum in a mixer and then poured into the trough 408.

The blade 406 is set to provide a gap setting between the backer and the blade of 0.100" such that a 0.090" wet coating 18" wide is produced. This layer if leached and dried weighs 450 grams/m.² and is 0.050" or 1.2 mm. thick

Stage 41, the formation of the layer of top coat paste on the substrate layer, is carried out as follows. The top coat paste is mixed to eliminate any settling of the sodium chloride and de-aired under vacuum in a paddle type mixer and then poured into the trough 413.

The blade 412 is set at a total gap setting between the backer and the blade of 0.135" and produces a wet top coat 0.050" thick. The top coat when leached and dried weighs 200 grams m.².

As mentioned above the coated backer enters the tank 500 by passing under a guide 405. Located along the inside of the side walls of the tank 500 are horizontal channels 501 through which slide the uncoated edges of the 22" wide backer. The backer 403 emerges out of the tank around a guide roll 502 and through a constant speed wind up arrangement 503 driven by a variable speed motor and gearing and is fed on to a wind up roll 504.

Stage 50, coagulating both layers, is carried out as follows.

The backer with the two superimposed coats on it is run at 4'/minute into the tank of water maintained at 20°C with, it will be appreciated, its coated face downwards. The layers are thus immersed within about half a minute of being formed. The entry to the water is done as smoothly as possible so as to avoid the formation of ripples on the surface of the top coat.

Alternatively the coating may be passed through an atomised spray of water just before it is immersed.

The channels 501 and the tension in the backer hold it about 2" below the surface of the water. Fresh water is pumped into the tank from both ends and the level is maintained by an overflow 505 at the centre of the tank. The water is maintained at 20°C by a steam jacket 507 at the bottom of the tank and plastics balls 506 floating on and covering the surface of the water.

The material is passed into the 60 ft. long tank and the total immersion time is 45 minutes. This is to allow the microporous polyurethane which precipitates out of solution in a few minutes to harden off. The material is kept with the coated surface down during this stage to prevent any air in the polyurethane layers thus forming bubbles or backer rising or being forced through the macropores.

The layers of polyurethane contract during precipitation but the backer is tensioned and is such that warping and shrinkage in length or breadth does not occur to any disadvantageous degree.

Stage 55, leaching out the dimethylformamide, is carried out as follows. The material is wound up on a roll 504 which is transferred to a static cold water holding tank (not shown) where the coils of the roll are allowed to loosen slightly. The material is held in this tank until the amount of dimethylformamide left in the material is not sufficient to cause collapse of the porous structure on heating. About two hours are required for this stage.

Stage 60, leaching out the sodium chloride. The material from the holding tank is passed in loops and through mangles with loads of about 300 lbs. through a series of

leaching tanks arranged so that the water is fed in counter current to the material. This takes about four hours. The water is heated to 60°C. This removes sufficient sodium chloride to result in a satisfactory product.

5 Stage 65, drying the material, is carried out by passing the wet material, coated side uppermost through an oven at 120°C in twenty minutes. Any salt remaining tends to be deposited out in the backer rather than in the top coat, and thus does not interfere with the solvent spraying, stage 80.

This temperature and time in the oven does not cause the backer to warp.

15 Stage 70, stripping the material from the backer

The substrate and top coat material is separated from the backer, taken round the roll past circular edge trimming knives and wound up on a constant speed wind up roll, driven via a friction clutch so as to prevent undue stretching of the material. The backer is returned to the sintering plant for recovery or re-use and the substrate and top coat material goes to Stage 75, inspection and testing. The material may then be spray-finished as mentioned above.

25 The material produced by this process after spraying with the solvent has the appearance of a high grade calf grain leather and this man made leather-like material can be used as a replacement for such materials, for example as a men's shoe upper material.

35 Photomicrographs indicate that it has a fine even interconnecting pore structure.

WHAT WE CLAIM IS:—

1. A method of making a water vapour permeable flexible sheet material which includes forming a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, forming a continuous layer of the mixture on a temporary support and, before the solvent is removed, forming a second layer also of a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, on the surface of the first layer, treating both layers on the support with a coagulating liquid which is a non solvent for the working material, but is at least partially miscible with the solvent for the working material, so as to coagulate the working material of both layers, removing substantially all the solvent by washing the material with a coagulating liquid.

2. A process of making microporous flexible sheet material which comprises providing a first spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microscopic particles of removable filler dispersed therein, providing a

second spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microscopic particles of removable filler dispersed therein, said first and second spreadable mixtures being of different composition, forming a continuous layer of said second spreadable mixture in face to face adherent contact with a continuous layer of said first spreadable mixture on a temporary support and coagulating both said contacting layers with non solvent for the polymeric material of said layers, which non solvent is miscible with the solvent material of said layers, and removing substantially all the solvent by washing the coagulated contacting layers with non solvent for the polymeric material, and leaching said removable filler from said coagulated contacting layers, to form a microporous material having two superimposed adherent layers of different properties.

3. A process as claimed in Claim 2 in which the said two mixtures differ in their removable filler: polymer weight ratios.

4. A process as claimed in Claim 1, 2, or Claim 3 in which neither of the said two layers is less than 0.3 mm thick, measured after said coagulation and leaching and after removal of liquid.

5. A process as claimed in Claim 1 or Claim 2 or Claim 3 or Claim 4 in which neither of the said two contacting layers, prior to said coagulation contains more than 4 parts of solvent per part of polymeric material.

6. A process as claimed in any one of the preceding claims in which the said coagulation is effected by bathing the composite of the said contacting layers in liquid non solvent.

7. A process as claimed in any one of the preceding claims in which the said layer of the said first mixture is of such thickness that after the said coagulation and leaching and after removal of liquid there from it has a thickness in the range of 1.1 to 1.3 mm and the said layer of the said second mixture is of such thickness that after the said coagulation and leaching and after removal of liquid from the said layers the total thickness of the said two layers is in the range of 1.6 to 1.8 mm.

8. A process as claimed in any one of the preceding claims in which the said layer of the said first mixture is formed on a temporary support to which the said layer adheres, the said layer of the said second mixture is formed over the said first layer, and the said layers on the said support are treated with liquid non solvent to effect the said coagulation on the said support, the resulting composite of adherent coagulated layers being then stripped from the said support.



leaching tanks arranged so that the water is fed in counter current to the material. This takes about four hours. The water is heated to 60°C. This removes sufficient sodium chloride to result in a satisfactory product.

- 5 Stage 65, drying the material, is carried out by passing the wet material, coated side uppermost through an oven at 120°C in twenty minutes. Any salt remaining tends to be deposited out in the backer rather than in the top coat, and thus does not interfere with the solvent spraying, stage 80.

This temperature and time in the oven does not cause the backer to warp.

- 15 Stage 70, stripping the material from the backer

- The substrate and top coat material is separated from the backer, taken round the roll past circular edge trimming knives and wound up on a constant speed wind up roll, driven via a friction clutch so as to prevent undue stretching of the material. The backer is returned to the sintering plant for recovery or re-use and the substrate and top coat material goes to Stage 75, inspection and testing. The material may then be spray-

- 25 finished as mentioned above.
The material produced by this process after spraying with the solvent has the appearance of a high grade calf grain leather and this man made leather-like material can be used as a replacement for such materials, for example as a men's shoe upper material.

- 30 Photomicrographs indicate that it has a fine even interconnecting pore structure.

WHAT WE CLAIM IS:—

1. A method of making a water vapour permeable flexible sheet material which includes forming a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, forming a continuous layer of the mixture on a temporary support and, before the solvent is removed, forming a second layer also of a spreadable mixture comprising a solution of a film forming, flexible, synthetic, thermoplastic, elastomeric, polymeric working material in a solvent, on the surface of the first layer, treating both layers on the support with a coagulating liquid which is a non solvent for the working material, but is at least partially miscible with the solvent for the working material, so as to coagulate the working material of both layers, removing substantially all the solvent by washing the material with a coagulating liquid.
2. A process of making microporous flexible sheet material which comprises providing a first spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microscopic particles of removable filler dispersed therein, providing a

second spreadable mixture which is a solution of a film forming synthetic thermoplastic elastomeric polymer in a solvent therefor, said solution having microscopic particles of removable filler dispersed therein, said first and second spreadable mixtures being of different composition, forming a continuous layer of said second spreadable mixture in face to face adherent contact with a continuous layer of said first spreadable mixture on a temporary support and coagulating both said contacting layers with non solvent for the polymeric material of said layers, which non solvent is miscible with the solvent material of said layers, and removing substantially all the solvent by washing the coagulated contacting layers with non solvent for the polymeric material, and leaching said removable filler from said coagulated contacting layers, to form a microporous material having two superimposed adherent layers of different properties.

3. A process as claimed in Claim 2 in which the said two mixtures differ in their removable filler: polymer weight ratios.

4. A process as claimed in Claim 1, 2, or Claim 3 in which neither of the said two layers is less than 0.3 mm thick, measured after said coagulation and leaching and after removal of liquid.

5. A process as claimed in Claim 1 or Claim 2 or Claim 3 or Claim 4 in which neither of the said two contacting layers, prior to said coagulation contains more than 4 parts of solvent per part of polymeric material.

6. A process as claimed in any one of the preceding claims in which the said coagulation is effected by bathing the composite of the said contacting layers in liquid non solvent.

7. A process as claimed in any one of the preceding claims in which the said layer of the said first mixture is of such thickness that after the said coagulation and leaching and after removal of liquid there from it has a thickness in the range of 1.1 to 1.3 mm and the said layer of the said second mixture is of such thickness that after the said coagulation and leaching and after removal of liquid from the said layers the total thickness of the said two layers is in the range of 1.6 to 1.8 mm.

8. A process as claimed in any one of the preceding claims in which the said layer of the said first mixture is formed on a temporary support to which the said layer mixture is formed over the said first layer, and the said layers on the said support are treated with liquid non solvent to effect the said coagulation on the said support, the resulting composite of adherent coagulated layers being then stripped from the said support.

9. A process as claimed in any one of the preceding claims in which the solvent in the said second mixture is a solvent for the polymer of the said first mixture.

10. A process as claimed in any one of the preceding claims in which the polymer in each of the said mixtures is a thermoplastic elastomeric polyurethane and in which the solvent in each of the said mixtures is selected from the group consisting of dimethylformamide, dimethyl sulphoxide, N-methyl pyrrolidone and dimethyl acetamide.

11. A process as claimed in any one of the preceding claims in which both of the said mixtures have microscopic sodium chloride particles dispersed therein and the said non solvent is aqueous.

12. A process as claimed in any one of the preceding claims in which in the said first mixture the ratio of removable filler to polymer is in the range 0.6:1 to 2.5:1 and the polymer concentration based on polymer and solvent is in the range 25% to 37.5% and these ratios and concentrations also fall within the area defined by the closed figure DQLMD in the diagram, figure 5 of the accompanying drawings and in which, in the said second mixture, the ratio of removable filler to polymer is about 3 to 1 and the polymer concentration based on polymer and solvent is in the range 20% to 30%.

13. A process as claimed in any one of the preceding claims in which the polymer in each of the said mixtures is a thermoplastic elastomeric polyurethane derived from a polyester by reaction with a diol and a diisocyanate, the polyester comprising the condensation reaction product of adipic acid, part ethylene glycol and part 1,4-butylene glycol, the diol comprising 1,4-butylene glycol and the diisocyanate comprising 4,4'-diphenylmethane-di-isocyanate, the isocyanate being used in a molar excess.

14. A process as claimed in any one of the preceding claims in which the temporary support is a sheet of porous synthetic plastics material.

15. A process as claimed in claim 14 in which the temporary support is formed by sintering powdered thermoplastic polymer.

16. A process as claimed in Claim 15 in which the thermoplastic polymer is a high density polyethylene.

17. A process as claimed in Claim 16 in which the support is .067" $\pm$.004" thick, has a permeability of 18 ± 4 cubic ft/min. air at a pressure of 8" static water gauge and weighs 114 grams/sq. ft.

18. A process of making microporous flexible sheet material as claimed in any one of the preceding claims in which for both layers

the filler is sodium chloride, the polymer in each of the said mixtures comprises thermoplastic elastomeric polyurethane derived from a polyester by reaction with a diol and a diisocyanate, the solvent comprises dimethylformamide, and the mixtures are formed by dissolving the polyurethane in the dimethylformamide and then milling dried sodium chloride into the solution under conditions of low humidity until a homogeneous dispersion is obtained.

19. A process as claimed in Claim 18 in which the moisture content of the sodium chloride is in the range 0.2—0.4% by weight and the milling conditions are not more humid than 50% RH at 25°C.

20. A process as claimed in any one of the preceding claims in which the viscosity of the first layer mixture is greater than that of the second layer mixture and layers are knife coated onto the support as it passes around a roll the first layer being applied to the support between a vertical knife and an upstream inclined backing plate located before the vertical knife from the point of view of the movement of the support and the second layer is applied between the vertical knife and an inclined knife located downstream from the vertical knife, the second layer thus being applied immediately on top of the first layer.

21. A process as claimed in any one of the preceding claims in which the coagulation is carried out by immersing the support coated face downwards in water at 20°C.

22. A process as claimed in any one of the preceding claims in which the material is immersed in the cold in the coagulating liquid until insufficient solvent remains to cause collapse of the porous structure on heating and then the filler is substantially removed by callendering the material in heated coagulating liquid, which is passed in countercurrent to the material.

23. A process as claimed in any one of the preceding claims in which the surface of the second layer of the leached and dried microporous product is sprayed with a solvent for the working material so as to partially collapse the microporous structure of the surface whilst leaving the gas permeability of the treated surface still appreciably greater than that of the working material when in a non porous state.

24. A method of making a vapour permeable flexible sheet material as specifically described herein with reference to Figure 1 of the accompanying drawings.

25. A method as claimed in Claim 24 and as specifically described herein with reference to Figures 2 to 4.



26. A vapour permeable flexible sheet material made by a method as claimed in any one of the preceding claims.

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Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

