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

(71) We, PORVAIR LIMITED, formerly
POROUS PLASTICS LIMITED, a Company re-
gistered under the Laws of Great Britain, of
Estuary Road, North Lynn, King's Lynn,
5 Norfolk, formerly of Dagenham Dock,
Essex, England, do hereby declare the in-
vention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particu-
larly described in and by the following state-
ment:—

This invention relates to the making of
water vapour permeable flexible porous sheet
materials, more especially microporous
15 materials, particularly, though not exclu-
sively, man-made leather-like materials, and
is an improvement in or modification of the
invention set forth in the present applicants'
British patent specification Serial No.
20 1,122,804.

In the methods described in that specifica-
tion water vapour permeable flexible sheet
material is made by forming a mixture in-
cluding a synthetic polymeric plastics work-
ing material in a solvent having distributed
25 through it a removable solid filler, shaping
the mixture and treating the shaped mixture
with a coagulating agent which is not a sol-
vent for the working material but is at least
30 partially miscible with the solvent so as to co-
agulate the working material into a sheet,
and removing the filler by treating the shaped
mixture with the same coagulating agent or
another coagulating agent which is also not a
35 solvent for the working material, the choice
of coagulating agent and time of treatment
being selected to ensure that substantially
all the filler is removed. The mixture may
40 comprise a polyurethane working material,
N,N-dimethyl formamide (DMF) as the sol-
vent, and sodium chloride as the filler, whilst
the coagulating agent or agents may be water.

The filler may have a substantial number of
particles whose diameters fall within the
range 7 to 25 microns.

The above specification envisages a wide
range of ratios of filler from 0.5 parts by
weight to 6 parts by weight of filler to 1 part
of working material but all the embodiments
specifically described employ a ratio of 3 to
1 or more.

It has now been found that by selecting
certain lower ratios of filler to working ma-
terial in conjunction with certain values of
the ratio of working material to solvent (re-
presented by a certain area of a graph re-
lating these parameters) materials can be ob-
tained having certain desirable properties dif-
ferent from those represented by other areas.

The materials corresponding to the se-
lected area, have a structure which may be
termed "cellular", comprising a micro-
porous matrix having interconnected micro-
pores providing permeability, and a number
of much larger pores, which will be called
macropores, which do not extend from face
to face of the sheet and are of such size as
to be visible to the unaided eye when a cross
section of the sheet is viewed in normal day-
light.

In another structure, of the materials of
the parent specification which may be termed
the "non-cellular" structure, on the other
hand, there are no or only a relatively few
macropores and the microporous structure is
more nearly homogeneous. A method of
forming other materials having a "non-cellu-
lar" structure is disclosed in British Patent
Specification No. 1608/67 (Serial No.
1,217,341).

Although in general the "cellular" struc-
ture tends to be weaker and less tough at a
given permeability than the "non-cellular"
structure, this may not be important for cer-

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tain applications, either because a lower strength may be tolerated or because a backing may be provided. On the other hand it tends to possess a cushion-like feel, or plump handle, which is particularly desirable for certain purposes, for example in upholstery materials, and in certain instances shoe upper materials.

Thus according to the present invention a method of making a water vapour permeable flexible sheet material which comprises treating with a coagulating liquid a continuous layer on a temporary backer of a mixture comprising a solution of a film-forming flexible synthetic thermoplastic elastomeric polymeric working material in a solvent having distributed through it microscopic removable solid filler particles, preferably ground to a narrow range of particle sizes, the coagulating liquid being a non-solvent for the working material but a solvent for the removable filler and at least partially miscible with the solvent for the working material, so as to coagulate the working material into a sheet, and removing substantially all the solvent and the removable filler by washing the material with a coagulating liquid, is characterised in that the ratio in parts by weight of filler to working material and the percentage ratio in parts by weight of working material to working material and solvent fall within the area defined by the closed figure A-B-C-A in Figure 1, of the accompanying drawings.

The temporary backer is one to which the polymer solution adheres but from which the polymer layer can be stripped after it has been coagulated and is so stripped. The coagulated polymer layer may be dried on the backer.

The washing of the material to remove the solvent and the filler may be merely immersing the material in coagulating liquid or may be washing with fresh coagulating liquid or continuing the treatment with the liquid used to achieve the actual coagulation.

Such materials are likely to have a "cellular" structure as defined above and this likelihood can be increased by suitable selection of the parameters of the thickness of the layer, the temperature at which the coagulation is carried out, and the filler particle size.

Preferably the ratio in parts by weight of filler to working material and the ratio in parts by weight of working material to solvent in the mixture fall within the area defined by the closed figure D-E-C-D in Figure 1, of the accompanying drawings.

Materials which have a high degree of cellularity in the sense of having a large number of macropores may be obtained by using a ratio in parts by weight of filler to working material of about 0.5:1 and a ratio in parts by weight of working material to sol-

vent in the range 30:70 to 37.5:62.5.

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 Ltd. 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.

The precise ratio of working material to working material and solvent and of filler to working material at which macropores occur depends to some extent on the particle size of the filler, and if the particle size of the filler is reduced the area of ratios within which macropores are found to occur will be reduced. Thus the preferred average particle diameter is 13 microns. Preferably the mixture used to form the layer is applied in a single coating step in such a way as to achieve a leached and dried porous product whose thickness is greater than 1 mm, and preferably is in the range 1.2 to 1.6 mm. Mixtures otherwise identical tend to produce less cellular materials when applied as thinner coatings. Preferred working materials are polyurethanes derived from polyesters, polyethers and polycaprolactones. Examples of polyester-based resins are those sold under the trade marks ELASTOLLAN TN61 EH98AK 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.

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.

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.

A preferred working material is a thermoplastic elastomeric polyurethane derived from a polyester by reaction with a diol and a diisocyanate, 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 very slight molar excess. Part of the ethylene glycol may be replaced by 1,4-butylene glycol.

A preferred coagulating liquid is water.

The temporary backer is preferably a sheet of porous synthetic plastics material, which may 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" $\pm$.004" thick, has a permeability of 18 $\pm$ 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/cm.² and an elongation at break less than 25%.

An example of such a material is that sold under the trade mark VYON. 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 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 dimethyl-formamide, and the mixture is formed by dissolving the polyurethane in the dimethyl formamide 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 layer is knife coated onto the backer as it passes around a roll the layer being applied to the backer between a doctor knife which is preferably vertical and an upstream inclined backing plate located before the doctor knife from the point of view of the movement of the backer.

It appears that if the moisture content of the sodium chloride is very much lower than 0.2—0.4% w e.g. 0.05% w or much greater e.g. 0.5% w the tendency for macropores to occur is increased. This tendency does not appear very clear cut and it is thus preferred to use salt with a moisture content of about 0.2—0.4% w and ratios in the area D-E-C-D. Similarly the results obtained under milling

conditions more humid than 50% RH at 25°C seem to indicate a tendency for increased occurrence of macropores with increased humidity but once again the tendency is not clear cut and it is thus preferred to use milling conditions of about 50% RH at 25°C. It is also desirable for the milling to be very thorough to ensure that the dispersion of the salt in the polyurethane solution is homogeneous since although formulations which are not sufficiently milled have increased numbers of macropores they are of less regular size and distribution.

Increasing the coagulation temperature for example to 80°C also appears to increase the number of macropores but once again their size and distribution is less regular than when lower coagulating temperatures are used with ratios in the range D-E-C-D. Thus preferably the coagulation is carried out by immersing the layer on the backer 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 removed to an adequate level by mangling the material in heated coagulating liquid, for example at 60°C, which is passed in countercurrent to the material.

It will be noted that the lower limit of the ratio of working material to solvent in the area referred to above is set at about 25:75. Thus if this ratio is further reduced, that is to say if the proportion of solvent is increased, the effect is somewhat similar to that of increasing the ratio of filler to working material above 3:1 in giving a more open and weaker structure. As regards the upper limit of this ratio, this is set by the practical question of providing sufficient solvent to form a mixture capable of being formed in a continuous layer.

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

Figure 1 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. Those samples which were "cellular" are represented by circles, while those which were "non-cellular" are represented by crosses; and

Figure 2 is a flow diagram of the process for the preparation of a single layer or substrate material.

General description of the process

Referring to Figure 2 the main stages of

the process are numbered 32 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 stage of the process consists of preparing a substrate paste containing a solution of a polyester based polyurethane dissolved in dimethyl formamide, and finely divided sodium chloride. These are stages 32 and 35. The substrate paste is used to form the materials in accordance with the present invention which find particular uses as substrates for man-made leather-like materials. Optional additional coatings may be formed on the material in accordance with the present invention, or it may be provided merely with a surface finish.

A layer of the substrate paste is spread on the backer. This is stage 40.

The coated backer, held under suitable tension throughout this stage of the process, is smoothly immersed, coated face down, in water and washed with water (for example at 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 (for example to 60°C) and the material dried with the layer uppermost, care being taken that the heating does not warp the backer. Twenty minutes in an oven at 120°C is suitable. These are stages 60 and 65.

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 surface which was in adherence with the backer.

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.

The material is then inspected and tested, stage 75, and if it comes up to specification may optionally be given further coatings as mentioned above and/or 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 surface of the material. It may also be given other optional treatments mentioned below.

Detailed description of the process.

Stage 20 Grinding the filler

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 re-circulating 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 50% of the total mass is returned for regrinding. The grinder may be of the type comprising a pair of coaxial 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 range.

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 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.

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/ft.².

Stages 30 to 36 Preparing the substrate paste

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 dimethyl formamide 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-butylene glycol so that the basic polyester is in fact a copolymer of two diols.

The material may also contain conventional stabilisers.

Stage 32 of Figure 2, 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 dimethyl formamide (less than 0.01% of moisture, supplied by I.C.I. Ltd. in accordance with their specification for dry dimethyl formamide) 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 dimethyl formamide 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.

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 and 15 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 a Torrance triple roll mill to produce a homogeneous dispersion. Two passes through the mill produce a dispersion which, when tested with a Hegman gauge, is indicated by a reading of 6.5 to 7 to have present no particles greater than 14 microns in diameter. This dispersion, the substrate paste, is stored under dry conditions.

To summarise the substrate paste may have the following composition:—

EXAMPLE 1

Polyurethane (15—30 centipoise at 25°C) 30 parts by weight
Ground sodium chloride (average particle diameter 13 ± 4.5 microns (one standard deviation)) 15 parts by weight
Dimethyl formamide 70 parts by weight

Stage 40 Forming the layer.

The backer which has been stored under dry conditions is passed round an 18" diameter ground steel spreading roll underneath a doctor knife blade and down under a guide roll into a coagulating tank.

The substrate paste is mixed to eliminate any settling of the sodium chloride and deaired under vacuum in a mixer and then supplied to the doctor knife.

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

Stage 50 coagulating the layer

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

The backer with the layer 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 layer is 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 layer.

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

The channels 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 at the centre of the tank. The water is maintained at 20°C by a steam

jacket at the bottom of the tank and plastic balls floating on and covering the surface of the water.

5 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 backer rising or being forced through the polyurethane layer thus forming bubbles or macropores.

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

20 Stage 55, leaching out the dimethyl formamide, is carried out as follows. The material is wound up on a roll which is transferred to a static cold water holding tank 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.

30 *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 countercurrent to the material. This takes about four hours. The water is heated at 60°C. This removes sufficient sodium chloride to result in a satisfactory product.

40 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 layer and thus does not interfere with the solvent spraying, stage 80.

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

Stage 70 Stripping the material from the backer

50 The material is separated from the backer, taken round a 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 material goes to Stage 75, inspection and testing. The material may then be given further coatings and/or be spray finished as mentioned above.

60 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.

The sheet was 1.2 mm. thick and was "cellular". 65

The water vapour permeability of the product was measured by the dessicant method and by the control dish method (as described below) figures of 935 g/m²/24 hours and 94.9 mm. respectively being obtained. The product had a plump handle making is particularly suitable for use as an upholstery material. 70

EXAMPLE 2 75

The procedure of Example 1 was repeated for a formulation having a working material to solvent ration of 25:75 and a filler to working material ratio of 1/2:1.

A coagulating temperature of 20°C was used and the sheet when dried was 1.59 mm. thick and was "cellular". 80

The water vapour permeability of the product was measured by the dessicant and the control dish methods, figures of 2950 g/m²/24 hours and 15.5 mm. being obtained. The product has a plump handle making it particularly suitable for use as an upholstery material. 85

The dessicant method referred to above for determining water vapour permeability is as described in BSS 3177/1959 but is carried out at 38°C with a nominal humidity gradient of 100% relative humidity. 90

The control dish method of measuring water vapour permeability is described in The Textile Research Journal Volume XXV No. 3 pp 197 to 205, March 1966, and in D.R.M.L. No. 121-3, (P.C.C. Project No. D 49-75-70-12) issued by the Defence Research Medical Laboratories P.O. Box 62 Postal Station K Toronto Canada dated January, 1959, on The Measurement of the permeability of Clothing Materials to Water Vapour. 100 105

EXAMPLES 3 to 19

The procedure of Example 1 was followed but with the following different formulations:—

Example	filler:working material ratio	working material:solvent ratio	
3	0.5:1	40:60	
4	0.5:1	37.5:62.5	
5	0.4:1	35:65	
6	0.5:1	35:65	115
7	0.6:1	35:65	
8	0.7:1	35:65	
9	0.8:1	35:65	
10	0.5:1	32.5:67.5	
11	1.0:1	32.5:67.5	120
12	1.0:1	30:70	
13	1.0:1	25:75	
14	1.5:1	25:75	

Example	filler:working material ratio	working material: solvent ratio
15	2.0:1	25:75
16	1.0:1	37.5:62.5
17	1.2:1	35:65
18	1.5:1	32.5:67.5
19	1.5:1	30:70

These examples are plotted in Figure 1. Those samples which were cellular are represented by circles, while those which were non-cellular are represented by crosses.

Alternatively or in addition the material can be lacquered.

The material can alternatively be supplied by known techniques with one or more additional coatings, which may then be spray finished and/or lacquered.

WHAT WE CLAIM IS:—

1. A method of making a water vapour permeable flexible sheet material which comprises treating with a coagulating liquid a continuous layer on a temporary backer of a mixture comprising a solution of a film-forming flexible synthetic thermoplastic elastomeric polymeric working material in a solvent having distributed through it microscopic removable solid filler particles, the coagulating liquid being a non-solvent for the working material but a solvent for the removable filler and at least partially miscible with the solvent for the working material, so as to coagulate the working material into a sheet, and removing substantially all the solvent and the removable filler by washing the material with a coagulating liquid, characterised in that the ratio in parts by weight of filler to working material and the percentage ratio in parts by weight of working material to working material and solvent in the mixture fall within the area defined by the closed figure A-B-C-A in Figure 1, of the accompanying drawings.

2. A method as claimed in Claim 1 in which the ratio in parts by weight of filler to working material and the percentage ratio in parts by weight of working material to working material and solvent in the mixture fall within the area defined by the closed figure D-E-C-D in Figure 1, of the accompanying drawings.

3. A method of making a water vapour permeable flexible sheet material as claimed in Claim 2 characterised in that the ratio in parts by weight of filler to working material is about 0.5:1 and the percentage ratio in parts by weight of working material to working material and solvent is in the range 30:70 to 37.5:62.5.

4. A method as claimed in any one of the preceding claims in which the filler is ground so that more than 50% of the particles have a diameter within the range 4 to 20 microns.

5. A method as claimed in Claim 4 in which the average diameter of the particles is in the range 10 to 14 microns.

6. A method as claimed in any one of the preceding claims in which the mixture used to form the layer is applied in a single coating step in such a way as to achieve a leached and dried porous product whose thickness is greater than 1 mm.

7. A method as claimed in Claim 6 in which the thickness is in the range 1.2 to 1.6 mm.

8. A method as claimed in any one of the preceding claims in which the working material is a polyurethane derived from a polyester, a polyether or a polycaprolactone.

9. A method as claimed in Claim 8 in which the polyurethane is derived from a polyester by reaction with a diol and a di-isocyanate.

10. A method as claimed in Claim 9 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 iso-cyanate is used in very slight molar excess.

11. A method as claimed in Claim 10 in which part of the ethylene glycol is replaced by 1,4-butylene glycol.

12. A method as claimed in any one of the preceding claims in which the temporary backer is a sheet of porous synthetic plastics material.

13. A method as claimed in Claim 12 in which the temporary backer is formed by sintering powdered thermoplastic polymer.

14. A method as claimed in Claim 13 in which the thermoplastic polymer is a high density polyethylene.

15. A method as claimed in Claim 14 in which the backer is .067" $\pm$.004" thick, has a permeability of 18 $\pm$ 4 cubic ft/min air at a pressure of 8" static water gauge and weighs 114 grams/sq. ft.

16. A method of making a water vapour permeable flexible sheet material as claimed in any one of the preceding claims in which 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 mixture is 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.

17. A method as claimed in Claim 16 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.

18. A method as claimed in any one of

Example	filler:working material ratio	working material: solvent ratio
15	2.0:1	25:75
16	1.0:1	37.5:62.5
17	1.2:1	35:65
18	1.5:1	32.5:67.5
19	1.5:1	30:70

These examples are plotted in Figure 1. Those samples which were cellular are represented by circles, while those which were non-cellular are represented by crosses.

Alternatively or in addition the material can be lacquered.

The material can alternatively be supplied by known techniques with one or more additional coatings, which may then be spray finished and/or lacquered.

WHAT WE CLAIM IS:—

1. A method of making a water vapour permeable flexible sheet material which comprises treating with a coagulating liquid a continuous layer on a temporary backer of a mixture comprising a solution of a film-forming flexible synthetic thermoplastic elastomeric polymeric working material in a solvent having distributed through it microscopic removable solid filler particles, the coagulating liquid being a non-solvent for the working material but a solvent for the removable filler and at least partially miscible with the solvent for the working material, so as to coagulate the working material into a sheet, and removing substantially all the solvent and the removable filler by washing the material with a coagulating liquid, characterised in that the ratio in parts by weight of filler to working material and the percentage ratio in parts by weight of working material to working material and solvent in the mixture fall within the area defined by the closed figure A-B-C-A in Figure 1, of the accompanying drawings.

2. A method as claimed in Claim 1 in which the ratio in parts by weight of filler to working material and the percentage ratio in parts by weight of working material to working material and solvent in the mixture fall within the area defined by the closed figure D-E-C-D in Figure 1, of the accompanying drawings.

3. A method of making a water vapour permeable flexible sheet material as claimed in Claim 2 characterised in that the ratio in parts by weight of filler to working material is about 0.5:1 and the percentage ratio in parts by weight of working material to working material and solvent is in the range 30:70 to 37.5:62.5.

4. A method as claimed in any one of the preceding claims in which the filler is ground so that more than 50% of the particles have a diameter within the range 4 to 20 microns.

5. A method as claimed in Claim 4 in which the average diameter of the particles is in the range 10 to 14 microns.

6. A method as claimed in any one of the preceding claims in which the mixture used to form the layer is applied in a single coating step in such a way as to achieve a leached and dried porous product whose thickness is greater than 1 mm.

7. A method as claimed in Claim 6 in which the thickness is in the range 1.2 to 1.6 mm.

8. A method as claimed in any one of the preceding claims in which the working material is a polyurethane derived from a polyester, a polyether or a polycaprolactone.

9. A method as claimed in Claim 8 in which the polyurethane is derived from a polyester by reaction with a diol and a di-isocyanate.

10. A method as claimed in Claim 9 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 iso-cyanate is used in very slight molar excess.

11. A method as claimed in Claim 10 in which part of the ethylene glycol is replaced by 1,4-butylene glycol.

12. A method as claimed in any one of the preceding claims in which the temporary backer is a sheet of porous synthetic plastics material.

13. A method as claimed in Claim 12 in which the temporary backer is formed by sintering powdered thermoplastic polymer.

14. A method as claimed in Claim 13 in which the thermoplastic polymer is a high density polyethylene.

15. A method as claimed in Claim 14 in which the backer is .067" $\pm$.004" thick, has a permeability of 18 $\pm$ 4 cubic ft/min air at a pressure of 8" static water gauge and weighs 114 grams/sq. ft.

16. A method of making a water vapour permeable flexible sheet material as claimed in any one of the preceding claims in which 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 mixture is 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.

17. A method as claimed in Claim 16 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.

18. A method as claimed in any one of



- the preceding claims in which the layer is knife coated onto the backer as it passes around a roll the layer being applied to the backer between a doctor knife and an upstream inclined backing plate located before the doctor knife from the point of view of the movement of the backer.
19. A method as claimed in any one of the preceding claims in which the coagulation is carried out by immersing the layer coated face downwards on the backer in water at 20°C.
20. A method 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 removed to an adequate level by mangling the material in heated coagulating liquid, which is passed in countercurrent to the material.
21. A method of making a water vapour permeable flexible sheet material as specifically described herein with reference to the drawings and any one of Examples 1 to 15.
22. A water vapour permeable flexible sheet material whenever made by a method as claimed in any one of the preceding claims.
23. A man-made leather-like material consisting of or including a material as claimed in Claim 22.

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