

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Production of Microporous Polymeric Plastics Materials

We, POROUS PLASTICS LIMITED, a Company registered under the Laws of Great Britain, 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:—

The present invention relates to a method of making microporous polymeric plastics materials.

According to the present invention a method of making a microporous polymeric plastics material comprises:

- (a) forming a mixture comprising a solution of at least one synthetic polymeric plastics working material in an organic solvent, the said solution having evenly distributed through it solid particles of a powdered removable filler;
- (b) shaping the mixture, and
- (c) coagulating the working material by treating the shaped mixture with at least one leaching agent, which is at least partially miscible with the organic solvent, and either at the same time or afterwards leaching out substantially all the removable filler to leave the working material in a microporous solid form.

Preferably the following general solubility relationships exist between the various components. The working material should be substantially soluble in the organic solvent but substantially insoluble in all the leaching agents; the removable filler should be substantially insoluble in the working material,

should be substantially insoluble in the solvent, and should be substantially soluble in at least one of the leaching agents, the removable filler leaching agents; and at least one of the leaching agents, the solvent leaching agent should be substantially miscible with the organic solvent. Conveniently the removable filler is substantially soluble in the solvent leaching agent which is also used as the removable filler leaching agent.

Preferably the proportion of working material to solvent in the mixture is in the range of 10 to 70% of working material by weight.

The proportion of working material to organic solvent may be in the range 1 to 2 to 1 to 4 in parts by weight and the proportion of filler to working material may be in the range 3 to 1 to 5 to 1 in parts by weight.

The working material may comprise at least one of the following materials, plasticised polyvinyl chloride; a copolymer of vinyl chloride and vinylene chloride or a copolymer of vinyl chloride and vinyl acetate, a butadiene - styrene copolymer, a polyester, a polyamide for example nylon, a polyesteramide, a polyvinyl formal, a polyacrylate, for example polymethyl methacrylate, or a polystyrene.

The working material may also comprise a polyurethane.

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 an isocyanate such as a di-isocyanate and a molecule, which will be called the polyurethane precursor, contain-

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ing 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 should generally be polymeric for example a polyester derivative or a polyether diol, or a polyester amide.

The precursor may be reacted with an excess of a di-isocyanate to produce a polyurethane having a comparatively low molecular weight, for example of the order of 10,000, which will be called a polyurethane prepolymer, and which has isocyanate end groups. The prepolymer may then be chain-extended by reaction with a chain extending agent, for example a low molecular weight glycol (to produce a polyurethane polyurethane containing urethane linkages ($-\text{NH}-\text{CO}-\text{O}-$)), or a low molecular weight diamine (to produce a polyurea polyurethane containing urea linkages ($-\text{NH}-\text{CO}-\text{NH}-$)).

These chain-extended prepolymers may finally be cured. The curing process is believed to involve cross-linking and chain branching reactions between the unreacted isocyanate end groups and the active hydrogen containing groups in the polyurethane prepolymer chain.

The degree of cross-linking and chain branching may be controlled by varying the ratio of isocyanate groups to total active hydrogen containing groups and/or by the addition to the polymer during the curing stage of a molecule containing three groups containing active hydrogen, for example, a triol.

An increase in the degree of cross-linking modifies the plastic properties of the polyurethane producing a tendency for it to be thermosetting rather than thermoplastic. In certain applications of the present invention for example those relating to the production of an artificial leather it is desired that the polyurethane should have thermoplastic properties.

Thus the polyurethane precursor, the di-isocyanate, and the chain extending agent may be chosen to minimise any further reaction, for example cross linking or chain branching or the like, which could occur during any curing stage of the polyurethane.

For such uses the polyurethane is preferably a thermoplastic elastomer having a low degree of cross linking, and thus may be a predominantly linear polymer. The polyurethane may have a molecular weight in the range 20,000—300,000.

The working material may be a polyurethane derived from a polyester, as by reaction with a diol and a di-isocyanate for example the proprietary material supplied by the B. F. Goodrich Chemical Company under the trade name ESTANE, or the proprietary material supplied by Elastomer Products Limited (Elastollan Limited) under the trade

name ELASTOLLAN. An example of another polyurethane suitable also as a thermoplastic working material is the proprietary polyurethane material supplied by Monsanto Chemicals Limited under the Trade Mark TEXIN.

Preferably the removable particulate filler is a material in which substantially all the particles have diameters less than 100 microns, and more particularly falling within the range 7—25 microns.

Conveniently the removable particulate filler is water soluble, and is for example, a sugar or a salt.

The salt may be an inorganic salt for example sodium chloride or sodium sulphate.

However, other leaching agents and removable fillers may be used. Thus the removal of the removable filler from the mixture may involve chemical action, by at least one of the leaching agents or chemical action by a substance included in at least one of the leaching agents, on the removable filler so as to make it removable.

As an example the removable filler may be an insoluble salt of a weak acid, for example calcium carbonate, and at least one of the leaching agents may include an acid, for example hydrochloric acid, which forms a soluble salt with the cation in the removable filler. Alternatively the removable filler may be an amphoteric metal salt, for example aluminium oxide, and the leaching agent may include an alkali, for example sodium hydroxide, in sufficient concentration to dissolve the amphoteric metal salt.

The proportion of removable filler to working material may be in the range in parts by weight of 0.5 parts to 6 parts of removable filler to 1 part of working material.

The solvent leaching agent may comprise water or methanol and the removable filler leaching agent may also comprise water.

The formation of the porous body by exposure to leaching agents may be effected by at least four different methods.

The choice of method may depend on a variety of factors such as simplicity of the process, economic factors such as ease of solvent and/or removable filler material recovery, solubility relationships between the materials in the mixture and/or the physical properties of the materials in the mixture.

Thus in the simplest method the exposure of the mixture to leaching agents is effected in one stage and a single leaching agent, the solvent and filler leaching agent, is used to remove the solvent and the removable filler, to form a porous body. As an example of this method the mixture may include a thermoplastic elastomeric polyurethane, which has a predominantly linear structure and which is derived from a polyester by reaction with a diol and a di-isocyanate, dimethyl formamide and sodium chloride, and the solvent and filler leaching agent may comprise water and this

removes the removable filler.

Alternatively the solvent leaching agent may be used in two stages, the first stage to remove the solvent and the second stage to remove the removable filler.

As an example the solvent leaching agent may be used in one stage to remove the solvent and the removable filler.

In the case of a removable filler which is a salt of a weak acid, the leaching agent may include an acid, for example hydrochloric acid, which forms a soluble salt with the cation in the removable filler.

Alternatively the removable filler may be an amphoteric metal salt, for example aluminium oxide, and the leaching agent may include an alkali, for example sodium hydroxide, in sufficient concentration to dissolve the amphoteric metal salt.

The proportion of removable filler to working material may be in the range in parts by weight of 0.5 parts to 6 parts of removable filler to 1 part of working material.

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removes the solvent, dimethyl formamide, and the removable particulate filler, sodium chloride.

Alternatively, for example in order to aid solvent recovery, the exposure of the same mixture to leaching agents may be effected in two stages, a first stage consisting of the solvent being substantially removed by the solvent leaching agent, for example methanol and a second stage consisting of the removable filler being removed by the removable filler leaching agent, for example water.

As a further alternative, for example when the solubility relationships of the solvent and the removable filler require that two different leaching agents be used, the exposure of the mixture to leaching agents may also be effected in one stage, the mixed leaching agent one-stage method, or in two stages in at least one of which the leaching agent is a mixture of solvent and filler leaching agents.

In the case of the mixed leaching agent one-stage method a mixture of a solvent leaching agent and a removable filler leaching agent may be used. As an example, the mixture may include a vinyl chloride vinylidene chloride copolymer, cyclohexanone and sodium chloride, and the leaching agent may be a mixture of a solvent leaching agent, methanol and a removable filler leaching agent, water.

It will be appreciated that in the mixed leaching agent one-stage method the solvent leaching agent and the removable filler leaching agent should be miscible.

The exposure to leaching agents may be effected by immersing the shaped mixture including solvent, working material and removable filler in the respective leaching agent.

The mixture of working material, solvent and removable filler may also include a surface active agent. The surface active agent is preferably insoluble in the leaching agents used and is preferably capable of withstanding the working conditions and the working temperatures and pressures involved without undergoing any substantial chemical degradation, so as to remain in an active state in substantial proportions in the finished porous body.

Where the agent is relied on to modify wettability it will, of course, be necessary that a sufficient amount of the agent should remain in the finished material.

The invention is applicable to the production of hydrophilic microporous sheet material for various purposes, for example artificial leather for the lining of shoes.

For such purposes the wetting agent must be inert and insoluble with regard to the substances with which it will be in contact and in particular should be capable of making the material hydrophilic at pHs of about 6 to 9.

Thus when the material is for use as or in the production of shoe linings there may be

incorporated with the working material as a wetting agent a sodium salt of a bis (alkyl) sulphosuccinate, the wetting agent rendering the finished material hydrophilic or wettable.

Examples of such suitable agents for use in particular in connection with shoe linings are the proprietary materials sold under the Trade Mark Manoxol, for example Manoxol IB, MA, OT, N or TR.

Preferably the alkyl groups are the nonyl or tridecyl groups.

The invention is also applicable to the production of hydrophobic microporous sheet material for various purposes, for example artificial leather for the outers of shoes and for general upholstery purposes.

Once more the surface active agent must be inert and insoluble with regard to the substances with which it will be in contact while at the same time imparting hydrophobic or water repellancy properties to the material. Thus when the material is to be used as or in the production of shoe outers there may be incorporated with the working material a proofing agent comprising a long chain polymer of dialkyl or aryl alkyl siloxane units which renders the finished material hydrophobic or water repellent. A particular example of a suitable proofing agent comprises a solution of a silicone resin in white spirit (approximately 50% by weight of solids), for example a proprietary material sold by I.C.I. Ltd. under the trade name Silicone M492. Another suitable proofing agent is one having the same composition as the proprietary material sold by I.C.I. Ltd. under the trade name of Silicone R 205.

Conveniently the surface active agent is mixed with the solvent for the working material so as to be distributed throughout the mixture.

The word shaping is to be understood in its broadest sense and includes all the following processes. Thus the shaping of the mixture includes impregnating a permanent support (i.e. one from which the mixture is not subsequently removed) with the said mixture, or moulding the mixture, onto a temporary support (i.e. one from which the mixture is subsequently removed) or a permanent support, or passing the mixture through calender rolls in the presence of a temporary or permanent support, or extruding the mixture through a suitable die onto a temporary or permanent support, or spreading, casting or spraying the mixture onto a temporary support or permanent support.

It will be appreciated that the various shaping processes given above require mixtures of suitable viscosities, and the viscosity of the mixture may be adjusted by varying the amount of solvent in the mixture. Thus if the mixture is to be shaped by moulding, calendering or extruding the amount of solvent may be adjusted to give the mixture a dough-

like consistency. If the mixture is to be shaped by impregnating a permanent support, or spreading, casting or spraying on a temporary or permanent support the amount of solvent may be adjusted to give the mixture a consistency similar to that of ordinary paint.

The temporary support may be a stainless steel conveyor or a sheet of solvent resistant synthetic plastics material.

The temporary support or permanent support may be previously shaped to a desired configuration, for example a glove shape.

It will be appreciated that the present invention can be used to form a microporous layer of working material on any suitable permanent support.

Thus the support may be a permanent support comprising a plastics materials, for example a porous synthetic plastics material. Alternatively the support may be a permanent support comprising a material derived from fibres, and will be called the permanent fibrous filler.

The fibres of the permanent fibrous filler may be natural or synthetic or a mixture of natural and synthetic fibres. Thus the permanent fibrous filler may be a paper, or a woven knitted or non-woven textile material, for example a felt.

Preferably the felt is made by mechanically entangling staple fibres.

The fibres of the permanent fibrous filler may comprise nylon or polyethylene terephthalate fibres or polypropylene fibres or mixtures thereof.

Felts impregnated by the method according to the present invention may find uses in the production of artificial leather materials.

Published microscopic studies have indicated that natural leather can be considered as essentially consisting of two zones, an inner zone which has been called the main fibre structure, and a surface zone which has been called the grain layer.

An artificial leather may also conveniently comprise a zone at least partially simulating the grain layer of natural leather to a greater or lesser degree, which zone for the purposes of this specification will be called the surface zone, and a zone at least partially simulating the main fibre structure of natural leather to a greater or lesser degree, which zone for the purposes of this specification will be called the fibrous base zone.

It will be appreciated that the present invention may conveniently be used to prepare a fibrous base zone by impregnating a felt as described above. It will also be appreciated that the present invention may conveniently be used to form a surface zone on any suitable fibrous base zone by a suitable method such as coating a suitably prepared surface of a suitable fibrous base zone, such as one prepared by the present invention.

Thus the method according to the present invention may be applied to the production of an artificial leather by using the method of the present invention to form a surface layer in adherence with a permanent support, which may comprise a porous synthetic plastics material.

Alternatively the permanent support may comprise a porous fibrous base zone made from a non-woven textile material by impregnation with a polymeric plastics material for example it may comprise a felt, made by mechanically entangling staple nylon, poly(ethylene glycol terephthalate) or polypropylene fibres, impregnated with a substantially linear thermoplastic elastomeric polyurethane, the density of the felt before impregnation being in the range 0.07 gm. per cc to 0.18 gm. per cc, and the ratio of polyurethane to felt in the fibrous base zone being in the range of ratios by weight of 0.3 to 1 to 1.5 to 1.

The following solvents, tetrahydrofuran, N methyl pyrrolidone, dimethyl sulphoxide, or dimethyl formamide may be used as solvents for one or more of the proprietary polyurethane materials sold under the trade names Estane, Elastollan and Texin. Water may be used as the leaching agent.

The surface of the fibrous base zone is preferably prepared so as to be substantially smooth before a surface zone is formed on it. This preparation may involve slitting the fibrous base zone parallel to its major plane, for example with a band knife.

It will be appreciated that a fibrous base zone or an artificial leather comprising a surface zone and a permanent support made in accordance with the present invention may be treated by any of the known techniques, such as grinding to produce a suede like finish or lacquering to produce a gloss finish.

It will also be appreciated that the nature of the artificial leather will be affected by which type of surface active agent is selected.

Thus in connection with the preparation of a material suitable for use as rainwear or as a water repellant artificial suede a proofing agent is selected.

A material according to this aspect of the invention incorporating a wetting agent is also of great use as a fibrous base zone in the manufacture of an artificial leather. Thus an artificial leather, according to this aspect, may comprise a water absorbent fibrous base zone and a water vapour permeable water repellant surface zone.

Such a material has the advantage that moisture liberated by the foot is absorbed by the surface in contact with the foot and can readily escape to the atmosphere through the surface zone as vapour, whereas liquid water outside the shoe is repelled.

The invention also extends to a method of

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making a laminated microporous polymeric plastics sheet material which comprises:

- (a) forming a mixture comprising a solution of synthetic organic polymeric plastic working material comprising thermoplastic elastomeric polyurethane having a predominantly linear structure in N,N' - dimethyl formamide, the said solution having evenly distributed through it particles of water soluble powdered removable filler preferably graded to a narrow range of particle sizes,
- (b) forming a layer of the mixture in adherence with a porous synthetic plastics material support, and
- (c) treating the layer with water so as to coagulate the working material, and leach out the removable filler to leave the working material in a microporous solid form as a surface layer having the said porous support as a permanent support. The synthetic organic polymeric plastics working material may comprise a blend of the thermoplastic elastomeric polyurethane having a predominantly linear structure and a vinyl chloride polymer.

The invention may be put into practice in various ways but certain specific embodiments will be described by way of example, some of which are as applied to the manufacture of an artificial leather.

In the examples all parts are given in parts by weight.

In all the examples, the removable particulate filler is sodium chloride ground to a particle size range of 7—25 microns.

Felts

- The felts are made from nylon fibres by mechanical entangling. Felt A weighs 350 grams per sq. metre and has an average thickness of 5 millimetres and thus a density of 0.07 grm. per cc. Felt B weighs 450 grams per sq. metre and has an average thickness of 2.5 millimetres and thus a density of 0.18 grm. per cc. Either of these felts may be used in the examples as desired.

It will be appreciated that there are four different leaching methods which can be used as follows:

Method 1. involves one stage and a single leaching agent which removes both the solvent and the removable filler.

- Method 2. involves 2 stages and two different leaching agents (which need not be miscible) one for each stage.

If the leaching agents are not miscible it may be desirable to dry the material between the two stages.

Method 3 involves one stage and a mixture of leaching agents.

Method 4 involves two stages in at least one of which the leaching agent is a mixture.

EXAMPLE 1

This example relates to the production of a microporous film and is an example of Method 1.

Mixture 1

This contains the following ingredients:

Working material

Polyurethane rubber (Estane X7 trade name) 80

Polyvinyl chloride—polyvinylidene copolymer (Breon 202 Trade Mark) 20

Solvent

Dimethyl formamide 300

Removable particulate filler

Sodium chloride 300 80

The working material is dissolved in the solvent. The removable particulate filler is then added and the mixture evenly mixed using a three roll mill or similar means to give a smooth cream of spreadable consistency which is degassed under vacuum with stirring. The mixture so formed is spread on to a temporary support such as a stainless steel conveyor and immersed in the *one stage leaching agent water*, for sufficient time to remove substantially all of the solvent and the removable particulate filler, for example 1 to 3 hours.

The water may be cold or hot, but hot water speeds removal of the solvent and the removable particulate filler and may have some effect on the final pore size. The temperature of the water should not be such as to cause softening of the working material sufficient to result in collapse of the porous structure or reduction in porosity.

In this example the temperature of the water may be as high as 100°C.

The porous working material is then stripped from the support and washed to remove all traces of filler and dried at a temperature which should not be such as to cause softening of the working material sufficient to result in collapse of the porous structure or reduction in porosity. The drying temperature in this example is conveniently 60°C.

EXAMPLE 2

This relates to the production of a flexible microporous film or coating and is another example of Method 1.

Mixture 2

Working material—a polyurethane granulate (a thermoplastic polyurethane supplied by

Elastollan Limited under the trade name Elastollan TN61

EH98AHK 100

Solvent—dimethyl formamide 300

Examples 8 to 12 are concerned with the production of fibrous base zones suitable for use in combination with surface layers according to the invention in the production of arti-

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ficial leathers. Such surface layers may be made in accordance with Examples 1, 2, 4, 5, 6 or 7. Examples 8 to 11 are in accordance with the invention.

5 EXAMPLES 8, 9, 10 and 11

These relate to the production of a fibrous base zone for use in the manufacture of an artificial leather and are also further examples of Method 1.

10 EXAMPLES 8 and 9

Mixtures 8 and 9

Working material and solvent—a polyurethane (a thermoplastic polyurethane supplied by B. F. Goodrich Company under the Trade Mark Estane X7) as a 20% by weight solution in dimethyl formamide

20 —Vinylchloride / Vinylidene chloride copolymer (a material supplied by British Geon Limited under the Trade Mark Breon 202) as a 12% by weight solution in dimethyl formamide

Removable Particulate filler—sodium chloride

Additional Solvent for the working material—dimethyl formamide

The mixtures are prepared as in Example 1.

35 The felt is mangled when immersed in the mixture 8 or 9 until it has become thoroughly impregnated and all the air in its interstices has been displaced. The impregnated felt is then passed through calender rolls to remove a proportion of the impregnant, two samples being produced resulting in ratios of working material to felt of 0.8 to 1 and 0.5 to 1 respectively.

40 The impregnated felt is then immediately immersed in water at 25°C for some hours then leached at 85°C for 1 to 3 hours and dried at 85°C to produce a porous fibrous base zone.

EXAMPLE 10

Mixture 10

Working material and solvent—a polyurethane granulate (a thermoplastic polyurethane supplied by Elastollan Limited under the trade name Elastollan TN61 EH75AHK as a 20% by weight solution in dimethyl formamide

Removable Particulate filler—sodium chloride

60 The felt is treated exactly as in Examples 8 and 9 the ratio of working material to felt being 0.5 to 1.

EXAMPLE 11

Mixture 11

Working material and solvent—a polyurethane (a polyurethane elastomer supplied by Monsanto Chemicals Limited under the trade name Texin 480A) as a 10% solution by weight in dimethyl formamide.

Removable Particulate filler—sodium chloride

The felt is treated exactly as in Examples 8 and 9 except that the ratio of working material to felt is 0.3 to 1.

EXAMPLE 12

This relates to the production of a fibrous base zone for use in the manufacture of a synthetic leather and is an example of Method 5.

Mixture 12

Working material and solvent—a polyurethane granulate (a thermoplastic polyurethane supplied by Elastollan Limited under the trade name Elastollan TN 61 EH 75 AHK as a 20% by weight solution in dimethyl formamide

Removable Particulate filler none.

The felt is impregnated by immersing it in Mixture 12 and then exposing the mixture containing the felt to a vacuum for a time sufficient to ensure that all the air is removed from the interstices of the felt.

The impregnated felt is then passed through calender rolls to remove a proportion of the impregnant a sample being produced having a working material to felt ratio of 0.5 to 1.

The impregnated felt is then immediately immersed in water, the solvent leaching agent, at 20°C for some hours and then dried at 90°C to produce a porous fibrous base zone.

It will be appreciated that a surface zone in the form of a film or coating as described in any one of Examples 1 to 7 could be formed on a suitably prepared surface of any suitable fibrous base zone to form a synthetic leather. Examples 8 to 12 provide suitable examples of fibrous base zones and a suitably prepared smooth surface is prepared by slitting the fibrous base zone parallel to its major plane, for example, with a band knife.

The microporous films produced by examples 1' to 7 have a thickness of the order of 10—20 thousandths of an inch, the materials produced by examples 8 to 12 have a thickness of the order of 40 thousandths of an inch.

The water vapour permeabilities (W.V.P.) of certain of the examples was measured and are given below. This property was measured at 38°C with a calcium chloride

dried atmosphere on one side of the film and a relative humidity of 100% on the other side of the film and is expressed as grams/sq. metre/24 hours.

- 5 Example 1 product W.V.P. 4460
 Example 2 product W.V.P. 6640
 Example 3 product W.V.P. 5600
 Example 5 product W.V.P. 7500
 Example 6 product W.V.P. 6760
 10 Example 7 product W.V.P. 6480

The addition of at least 5 parts by weight of Manoxol N or TR or Silicone M 492 to any of the initial mixtures given in the examples results in the product having a useful degree of modification in its wettability or water repellancy properties.

WHAT WE CLAIM IS:—

1. A method of making a microporous polymeric plastic material which comprises:
 20 (a) forming a mixture comprising a solution of at least one synthetic polymeric plastics working material in an organic solvent, the said solution having evenly distributed through it solid particles of a powdered removable filler,
 25 (b) shaping the mixture, and
 (c) coagulating the working material by treating the shaped mixture with at least one leaching agent, which is at least partially miscible with the organic solvent, and either at the same time or afterwards leaching out substantially all the removable filler to leave the working material in a microporous solid form.
 2. A method as claimed in Claim 1 in which the removable particulate filler is a material in which substantially all the particles have diameters less than 100 microns.
 40 3. A method as claimed in Claim 1 in which the removable particulate filler is a material in which substantially all the particles have diameters falling within the range 7—25 microns.
 45 4. A method as claimed in Claim 2 or Claim 3 in which the microporous material is in sheet form and when dried has a thickness in the range 0.010" to 0.020".
 50 5. A method as claimed in any one of the preceding claims in which the proportion of removable filler to working material is in the range, in parts by weight of 0.5 parts to 6 parts of removable filler to 1 part of working material.
 55 6. A method as claimed in any one of Claims 1 to 5 in which the proportion of working material to solvent is in the range of 10 to 70% of working material by weight.
 60 7. A method as claimed in any one of the preceding claims in which the proportion of working material to organic solvent is in the range 1 to 2 to 1 to 4 in parts by weight and the proportion of filler to working material

is in the range 3 to 1 to 5 to 1 in parts by weight.

8. A method as claimed in any one of the preceding claims in which the working material comprises at least one of the following materials: plasticized polyvinyl chloride, a copolymer of vinyl chloride and vinylidene chloride, a copolymer of vinyl chloride and vinylacetate, a butadiene-styrenecopolymer, a polyester, a polyamide, a polyesteramide, a polyvinyl formal, a polyacrylate, a polystyrene or a polyurethane.

9. A method as claimed in Claim 8 in which the working material is a polyurethane which has a predominantly linear structure.

10. A method as claimed in Claim 9 in which the polyurethane is derived from a polyester by reaction with a diol and a diisocyanate.

11. A method as claimed in any one of the preceding claims in which the exposure of the mixture to leaching agents is effected in one stage and a single leaching agent, the solvent and filler leaching agent, is used to remove the solvent and the removable filler, to form a micro-porous body.

12. A method as claimed in Claim 11 in which the shaped mixture includes a thermoplastic elastomeric polyurethane, which has a predominantly linear structure and is derived from a polyester by reaction with a diol and a diisocyanate, dimethyl formamide and sodium chloride, and the mixture is treated with a solvent and filler leaching agent comprising water which removes the solvent, dimethyl formamide, and the removable particulate filler, sodium chloride.

13. A method as claimed in any one of Claims 1 to 7 in which the shaped mixture includes a thermoplastic elastomeric polyurethane which has a predominantly linear structure and is derived from a polyester by reaction with a diol and a diisocyanate, dimethyl formamide and sodium chloride, and the mixture is treated with a solvent leaching agent comprising methanol which removes the solvent dimethyl formamide, and with a removable filler leaching agent comprising water which removes the sodium chloride.

14. A method as claimed in any one of Claims 1 to 10 in which at least one of the leaching agents is a mixture of a solvent leaching agent and a removable filler leaching agent.

15. A method as claimed in Claim 14 in which the shaped mixture includes a vinyl chloride vinylidene chloride copolymer, cyclohexanone and sodium chloride, and the leaching agent is a mixture of a solvent leaching agent, methanol, and a removable filler leaching agent, water.

16. A method as claimed in any one of the preceding claims in which the shaping of the mixture of working material, solvent, and removable filler includes impregnating a per-

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dried atmosphere on one side of the film and a relative humidity of 100% on the other side of the film and is expressed as grams/sq. metre/24 hours.

- 5 Example 1 product W.V.P. 4460
- Example 2 product W.V.P. 6640
- Example 3 product W.V.P. 5600
- Example 5 product W.V.P. 7500
- Example 6 product W.V.P. 6760
- 10 Example 7 product W.V.P. 6480

- The addition of at least 5 parts by weight of Manoxol N or TR or Silicone M 492 to any of the initial mixtures given in the examples results in the product having a useful
- 15 degree of modification in its wettability or water repellancy properties.

WHAT WE CLAIM IS:—

- 1. A method of making a microporous polymeric plastic material which comprises:
 - 20 (a) forming a mixture comprising a solution of at least one synthetic polymeric plastics working material in an organic solvent, the said solution having evenly distributed through it solid particles of a powdered removable filler,
 - 25 (b) shaping the mixture, and
 - (c) coagulating the working material by treating the shaped mixture with at least one leaching agent, which is at least partially miscible with the organic solvent, and either at the same time or afterwards leaching out substantially all the removable filler to leave the working material in a microporous solid form.
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 - 35
- 2. A method as claimed in Claim 1 in which the removable particulate filler is a material in which substantially all the particles have diameters less than 100 microns.
- 40 3. A method as claimed in Claim 1 in which the removable particulate filler is a material in which substantially all the particles have diameters falling within the range 7—25 microns.
- 45 4. A method as claimed in Claim 2 or Claim 3 in which the microporous material is in sheet form and when dried has a thickness in the range 0.010" to 0.020".
- 50 5. A method as claimed in any one of the preceding claims in which the proportion of removable filler to working material is in the range in parts by weight of 0.5 parts to 6 parts of removable filler to 1 part of working material.
- 55 6. A method as claimed in any one of Claims 1 to 5 in which the proportion of working material to solvent is in the range of 10 to 70% of working material by weight.
- 60 7. A method as claimed in any one of the preceding claims in which the proportion of working material to organic solvent is in the range 1 to 2 to 1 to 4 in parts by weight and the proportion of filler to working material

is in the range 3 to 1 to 5 to 1 in parts by weight.

8. A method as claimed in any one of the preceding claims in which the working material comprises at least one of the following materials: plasticized polyvinyl chloride, a copolymer of vinyl chloride and vinylidene chloride, a copolymer of vinyl chloride and vinylacetate, a butadiene-styrenecopolymer, a polyester, a polyamide, a polyesteramide, a polyvinyl formal, a polyacrylate, a polystyrene or a polyurethane.

9. A method as claimed in Claim 8 in which the working material is a polyurethane which has a predominantly linear structure.

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

11. A method as claimed in any one of the preceding claims in which the exposure of the mixture to leaching agents is effected in one stage and a single leaching agent, the solvent and filler leaching agent, is used to remove the solvent and the removable filler, to form a micro-porous body.

12. A method as claimed in Claim 11 in which the shaped mixture includes a thermoplastic elastomeric polyurethane, which has a predominantly linear structure and is derived from a polyester by reaction with a diol and a di-isocyanate, dimethyl formamide and sodium chloride, and the mixture is treated with a solvent and filler leaching agent comprising water which removes the solvent, dimethyl formamide, and the removable particulate filler, sodium chloride.

13. A method as claimed in any one of Claims 1 to 7 in which the shaped mixture includes a thermoplastic elastomeric polyurethane which has a predominantly linear structure and is derived from a polyester by reaction with a diol and a di-isocyanate, dimethyl formamide and sodium chloride, and the mixture is treated with a solvent leaching agent comprising methanol which removes the solvent dimethyl formamide, and with a removable filler leaching agent comprising water which removes the sodium chloride.

14. A method as claimed in any one of Claims 1 to 10 in which at least one of the leaching agents is a mixture of a solvent leaching agent and a removable filler leaching agent.

15. A method as claimed in Claim 14 in which the shaped mixture includes a vinyl chloride vinylidene chloride copolymer, cyclohexanone and sodium chloride, and the leaching agent is a mixture of a solvent leaching agent, methanol, and a removable filler leaching agent, water.

16. A method as claimed in any one of the preceding claims in which the shaping of the mixture of working material, solvent, and removable filler includes impregnating a per-

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manent support with the said mixture, or moulding the mixture on to a temporary or permanent support, or passing the mixture through calender rolls in the presence of a temporary or permanent support, or extruding the mixture through a suitable die onto a temporary or permanent support, or spreading, casting or spraying the mixture onto a temporary or permanent support.

10 17. A method as claimed in Claim 16 in which the support is a temporary support and is a stainless steel conveyor or a sheet of solvent resistant synthetic plastics material.

15 18. A method as claimed in Claim 16 in which the temporary or permanent support is previously shaped to a desired configuration.

20 19. A method of making an artificial leather which comprises forming a surface layer by the method claimed in any one of claims 1 to 15 in adherence with a permanent support.

25 20. A method as claimed in Claim 19 in which the permanent support comprises a porous synthetic plastics material.

25 21. A method as claimed in Claim 16 or Claim 18 in which the support is a permanent support comprising a woven, knitted or non-woven textile material.

30 22. A method as claimed in Claim 19 in which the permanent support comprises a porous fibrous base zone made from a non-woven textile material by impregnation with a polymeric plastics material.

35 23. A method of making an artificial leather as claimed in Claim 22, in which the fibrous base zone comprises a felt made by mechanically entangling staple nylon, poly (ethylene glycol terephthalate) or polypropylene fibres, impregnated with a substantially linear thermoplastic elastomeric polyurethane, the density of the felt before impregnation being in the range of 0.07 gm. per cc to 0.18 gm. per cc, and the ratio of polyurethane to felt in the fibrous base zone being in the range of ratios by weight of 0.3 to 1 to 1.5 to 1.

45 24. A method of making a laminated microporous polymeric plastics sheet material which comprises:

50 (a) Forming a mixture comprising a solution of synthetic organic polymeric plastics material comprising thermoplastic elastomeric polyurethane having a predominantly linear structure in N,N'-dimethyl formamide, the said solution having evenly distributed through it particles of water soluble powdered removable filler,

55 (b) forming a layer of the mixture in adherence with a porous synthetic plastics material support, and

60 (c) treating the layer with water so as to coagulate the working material, and leach out the removable filler to leave

the working material in a microporous solid form as a surface layer having the said porous support as a permanent support. 65

25. A method as claimed in Claim 24 in which the synthetic organic polymeric plastics working material comprises a blend of thermoplastic elastomeric polyurethane having a predominantly linear structure and a vinyl chloride polymer. 70

26. A method as claimed in any one of the preceding claims in which there is incorporated with the working material as a wetting agent a sodium salt of a bis (alkyl) sulphosuccinate. 75

27. A method as claimed in Claim 26 in which the alkyl groups are the nonyl or tri-decyl groups. 80

28. A method as claimed in any one of Claims 1 to 25 in which there is incorporated with the working material as a proofing agent a long chain polymer of dialkyl or aryl alkyl siloxane units. 85

29. A laminated microporous polymeric plastics sheets material when made by a method as claimed in Claim 24 or Claim 25.

30. An unsupported microporous polymeric plastics material made by a method as claimed in any one of Claims 1 to 18 and Claims 26 or 27 or any one of Claims 1 to 18 and Claim 28. 90

31. An artificial leather made by a method as claimed in Claim 19, 20, 22, or 23, and Claims 26 or 27, or Claim 19, 20, 22, or 23, and Claim 28. 95

32. An unsupported microporous polymeric plastics material made by a method as specifically described herein with reference to any one of Examples 1 to 7. 100

33. A supported microporous polymeric plastics material made by a method as specifically described herein with reference to any one of Examples 8 to 11 suitable for use as a fibrous base zone in the manufacture of an artificial leather. 105

24. An artificial leather comprising a fibrous base zone made by a method as specifically described herein with reference to any one of Examples 8 to 12 and a surface zone made by a method as claimed in any one of claims 1 to 16 and 26 or 27, or in any one of Claims 1 to 16 and 28. 110

35. An artificial leather comprising a fibrous base zone made by a method as specifically described herein with reference to any one of Examples 8 to 12 and a surface zone made by a method as specifically described herein with reference to any one of Examples 1, 2, 4, 5, 6 or 7. 115

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