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Day

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[54] **PROCESS FOR FORMING BACKED MICROPOROUS SHEET**

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[73] Assignee: **USM Corporation,** Boston, Mass.

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[21] Appl. No.: **288,563**

[52] **U.S. Cl.** .... **156/78,** 156/242, 156/247, 156/289, 260/2.5 A, 260/2.5 AT, 264/41
[51] **Int. Cl.** **B32b 5/18**
[58] **Field of Search** 156/78, 79, 242, 247, 289; 264/41

[56] **References Cited**

UNITED STATES PATENTS

3,551,364	12/1970	McGarr	117/63 X
3,679,783	7/1972	McGarr	264/41 X

Primary Examiner—Edward G. Whitby
Attorney, Agent, or Firm—Benjamin C. Pollard

[57] **ABSTRACT**

Process for forming a microporous polyurethane body backed with fibrous sheet material in which process a body of an emulsion is prepared of which the discontinuous phase is a volatile non-solvent liquid and the continuous phase is a liquid polymeric material which sets through reaction to solid condition, the liquid emulsion is formed as a layer and reacted under conditions preserving the uniformity of the emulsion to pressure flowable stage having a pre-gel structure which will prevent sinking in of a fibrous sheet material and fibrous sheet material is laid on the layer and pressed into engagement with it to cause the emulsion to adhere to the fibrous sheet and to conform to irregularities. The reaction is continued to solidify the emulsion in firmly adherent relation to the fibrous sheet and the volatile liquid is removed from the solidified emulsion.

10 Claims, 3 Drawing Figures

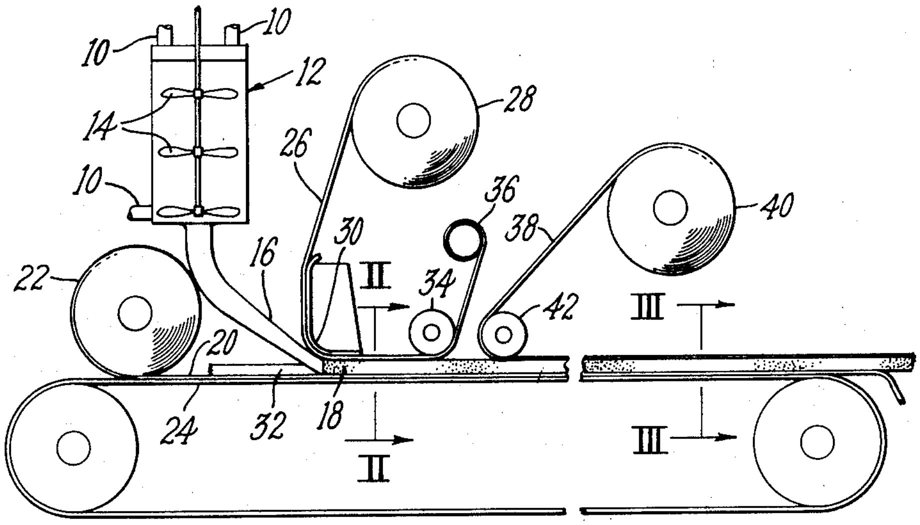


Fig. 1

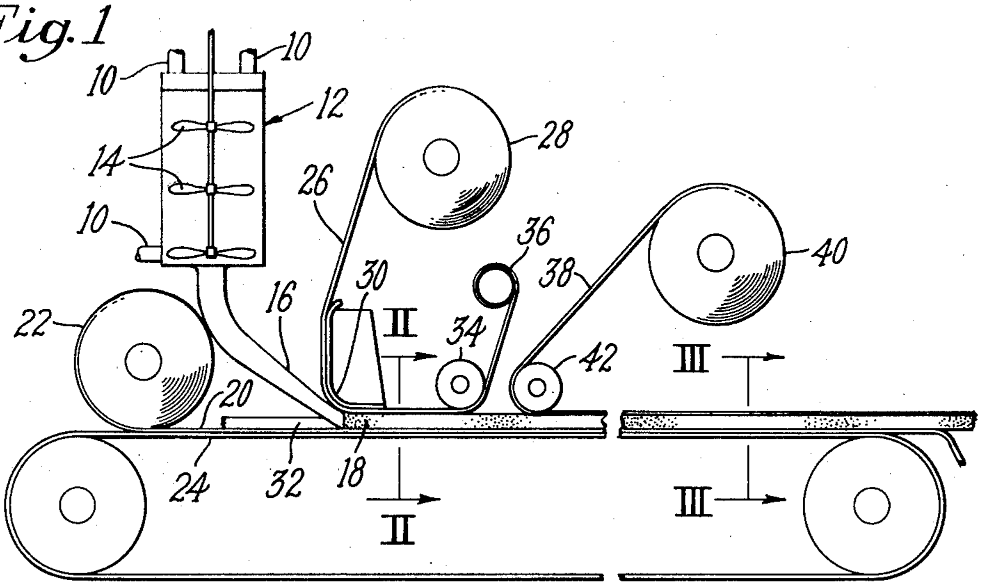


Fig. 2

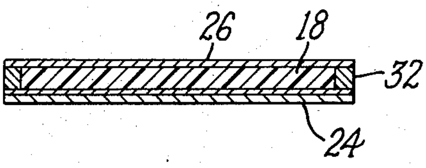
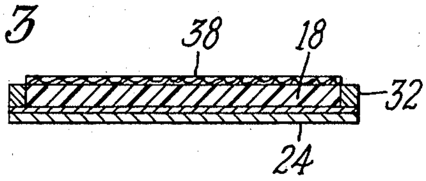


Fig. 3



PROCESS FOR FORMING BACKED MICROPOROUS SHEET

FIELD OF USE, BACKGROUND AND PRIOR ART RELATIVE TO THE INVENTION

This invention relates to an improved process for making a microporous polyurethane body backed with fibrous sheet material.

In the U.S. Pat. of John J. McGarr, No. 3,551,364, dated Dec. 29, 1970, entitled "Processes for Making Microporous Polyurethane Bodies Employing Non-Boiling Liquid Alkyl Ethers or Liquid Aliphatic Hydrocarbons," there is disclosed a process in which an emulsion formed in which the discontinuous phase is droplets of a non-solvent liquid and the continuous phase is a reactive polymeric material convertible through reaction to a tough, solid, resilient film-forming condition. The emulsion is formed into a body of desired shape and reacted to solidify the reacted material with the droplets of non-solvent liquid held in the solidified body. The non-solvent liquid of the droplets is removed from the solidified body leaving spaces constituting openings or pores.

The patent also discloses procedure in which a layer of reactive emulsion is formed on a casting surface and a porous fibrous sheet is laid on the free surface of the layer while the layer is still in liquid condition before solidification through reaction. As noted in that patent, conditions adjacent the surface of the layer may cause the surface to be less porous than other portions of the layer.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for forming a microporous polyurethane body integrally united to a fibrous backing in which process improved uniform porosity is secured in the polyurethane material.

To this end and in accordance with a feature of the present invention liquid reactive urethane emulsion is cast as a layer on a casting surface with the surface opposite the casting surface stabilized until development of limited gel structure and thereafter a fibrous sheet is laid on the surface of the still pressure flowable emulsion and pressed into intimate engagement with the emulsion.

I have discovered a process for forming a microporous sheet with a fibrous backing in which overall uniform porosity of the microporous sheet is secured by casting a layer of an emulsion of which the liquid continuous phase is based on a polymeric material reactive to solid resilient condition and the dispersion phase is non-solvent liquid droplets and maintaining the layer of emulsion undisturbed with its surfaces covered during an initial period for development of a preliminary gel structure in which the layer has sufficient integrity to allow separation of a cover from the cast surface without distortion of the surface but the emulsion is flowable under pressure. At this point, a cover is removed from a surface of the layer and a fibrous sheet is pressed into intimate engagement with the layer. The reaction is continued to solidify the emulsion in firmly adherent relation to the fibrous sheet and the volatile liquid is removed from the solidified emulsion.

BRIEF DESCRIPTION OF THE DRAWING

Reference is made to the attached drawings forming part of the disclosure of the present case in which:

FIG. 1 is a diagrammatic elevational view of an arrangement of apparatus suitable for practicing the invention;

FIG. 2 is a fragmentary sectional elevational view taken on the line II—II of FIG. 1 of a cast layer with casting surfaces and cover sheet as may be formed on the apparatus of FIG. 1;

FIG. 3 is a fragmentary sectional elevational view of a cast layer with casting surface and fibrous backing layer taken on the line III—III of FIG. 1;

DESCRIPTION OF THE PREFERRED EMBODIMENT

Pores or passageways in a body of resilient polymeric material in the present process are secured by solidifying a reactive emulsion in which the dispersed phase is droplets of non-solvent liquid and the liquid continuous phase comprises reactive polymeric material, and removing the non-solvent liquid from the solidified continuous phase leaving the spaces previously occupied by the non-solvent liquid as pores and passageways. Reactive emulsions for use in the present process may be similar to the formulae used in the earlier filed patent of McGarr, referred to above.

Forming the combined microporous layer and fibrous backing according to the present invention involves providing a layer of the emulsion on a casting surface, directly disposing a cover sheet on the layer, maintaining the layer under conditions which do not disrupt the layer of emulsion during an initial period in which the emulsion thickens through reaction to develop a preliminary gel structure and through cooling of the emulsion and, at this point, removing the cover sheet and pressing a fibrous sheet into intimate engagement with the layer. Thereafter, the reaction to solidify the emulsion in firmly adherent relation to the fiber sheet is carried out and the volatile liquid is removed from the solidified emulsion leaving a uniform microporous layer integrally united with the fibrous sheet backing.

The process will be described in connection with an apparatus suitable for the manufacture of the backed microporous sheet; but it is to be understood that the procedures may be carried out by hand or with other suitable apparatus.

Referring to FIG. 1, polymeric reactants and non-solvent organic liquid to be mixed and emulsified are introduced through inlets **10** into the mixer-emulsifier **12** where they are acted on by the agitating blades **14**. The resulting emulsion is discharged through nozzle **16** and deposited as a layer **18** on the casting surface **20**.

In the form shown, the casting surface **20** is a release sheet supplied from a roll **22**. The release sheet casting surface **20** is moved, suitably on conveyor **24** or on a slip plate (not shown) beneath the nozzle **16** which deposits the emulsion on successive portions of the surface. Where the deposited emulsion is to be cooled, suitable cooling means may be provided such as a chilled plate (not shown) beneath the sheet casting surface **20** carrying the layer **18** of emulsion.

A flexible cover sheet **26** from the roll **28** is laid down on the emulsion carried by the casting surface. Preferably, this is done by feeding the cover sheet **26** around the curved member **30** which brings the cover sheet in contact with the edge of the nozzle **16** so that in effect, the release sheet **20** and cover sheet **26** with edge strips **32** at the edges of the relesase sheet **20** constitute a continuation of the nozzle to provide back pressure across the nozzle proper and effectively to eliminate shear movement in the emulsion layer **18.** As shown in FIG. **2,** the nozzle **16** may be so designed that all portions of the emulsion have similar time and temperature histories at the time the emulsion leaves the nozzle proper and enters between spaced moving webs. The contacting surface of the cover sheet **26** preferably carries or provides a material giving a low adhesion interface between cover sheet **26** and emulsion layer **18** to minimize separational stress when the cover sheet is later removed and to insure that the adhesion of the layer **18** to cover sheet **26** is less than its adhesion to casting surface **20.** Thus, the cover sheet may be wet with an inert liquid, non-solvent for the continuous phase of the emulsion. This may be one of the liquids useful as the discontinuous phase. Alternatively, the cover sheet may be dusted with a powder not readily wet by the continuous phase or a gas or liquid interface may be interposed between the cover sheet **26** and the emulsion layer **18** as by using a permeable cover sheet and forcing the gas or liquid through the cover sheet. The cover sheet need not move with the emulsion in this case. The deposited emulsion is carried along undisturbed after leaving the nozzle with the surfaces of the emulsion layer **18** protected by the cover sheet **26,** release sheet **20** and edge strips **32.**

The cover strip **26** is then drawn up from the surface of the emulsion layer **18** around the roller **34** and is wound up on the roll **36.** The location of the roller **34** which draws the cover sheet **26** away from the layer **18** is determined by the requirement of maintaining back pressure to give proper flow characteristic to the nozzle and by the rate at which the emulsion thickens and reaches the preliminary gel stage allowing the cover sheet to be withdrawn without disruption of the layer **18.**

After the cover sheet is withdrawn and after any further time dwell, if needed, for additional thickening of the emulsion to prevent undesired sinking in of the backing, fibrous backing material **38** is pressed down onto the emulsion layer **18.** The backer materials may be practically any fabric which does not have chemical activity which would interfere with the ongoing action and which does not carry a surface active material which would influence the surface active balance of the emulsion. These materials include woven and nonwoven fabrics. The nonwoven fabrics may be needle punched, knit stitched, impregnated or resin bonded. The fabrics may be napped or unnapped. A very useful material includes napped and sheared sateen but plain sateen, cotton drill and other weave knits may be used. Backers have been made of rayon, polyester, polypropylene, nylon, cotton filaments and other fibers and combinations. It has been found desirable to pre-wet the backing material **38** with an inert liquid non-solvent for the continuous phase, e.g., liquids suitable for the disperse phase of the emulsion, before associating the backing material with the emulsion layer. This is done conventionally by dipping the fabric in the liquid and passing it through a wringer prior to winding it into the roll **40.** As shown in the drawing, the fibrous backing **38** from the roll **40** is fed around the roller **42** which presses it against the surface of the emulsion layer **18** to form the assembly shown in FIG. **3.**

After the fibrous backing has been pressed onto the surface of the emulsion layer, the composite is carried along to allow the reaction to proceed to a point at which the structure of the emulsion layer **18** is stable and resistant to harm by handling. At this point, the composite of solidified emulsion layer **18** and fibrous backing **38** may be stripped from the release sheet **20** for further treatment such as curing and removal of the non-solvent liquid of the droplets.

Reactive materials for use in the solidifiable continuous phase are those for forming elastomeric polyurethane or polyurea reaction products, both of which are hereafter referred to as polyurethanes, and are selected on the basis of their ability to provide toughness, flexibility, hardness and other physical properties required in the final product. The reactive material may be a "one shot" mixture of an organic compound having at least two active hydrogens such as a polymeric polyol, e.g., polyalkylene ether polyol and/or polyester polyol with a reactive compound having at least two reactive -NCO groups, e.g., a polyisocyanate. Alternatively, there may be used a prepolymer system in which an -NCO terminated reaction product of a polyol with excess polyisocyanate is combined with chain extenders which may be polyhydroxy or polyamine or amino alcohol compounds having at least two hydroxyl or amine groups providing active hydrogens for reaction with -NCO groups.

It has been found desirable to use polyol material or prepolymers which at room temperature are solid or pasty. The term "pasty" refers to consistency which may be very high viscosity or may be partially solid which is capable of permanent deformation or even flow under substantial pressure, but which does not allow rapid, effective intimate mixing with other reagents and with the non-solvent liquid component to form a free flowing liquid emulsion with ordinary mixing and emulsifying equipment such as a high shear propeller type mixer. These materials offer the special advantage that cooling of the emulsion after formation into a layer helps to thicken the emulsion layer to aid in resisting distortion when the cover sheet **26** is removed.

Polyols useful in the "one shot" mixture or for forming the reactive prepolymer include substantially linear or only moderately branched polyether polyols, and substantially linear or moderately branched polyester polyols from the condensation of polybasic acids, e.g., adipic acid, sebacic acid, azelaic acid, dimerized linoleic acid and other aliphatic and aromatic dibasic acids with polyols such as butane diol, ethylene glycol, propylene glycol and the like. Castol oil is also a suitable polyol for making a prepolymer. Controlled portions of polyols or polybasic acids having more than two reactive -OH or -COOH groups may be included in the compositions reactive to form polyester polyols to introduce moderate branching or cross linking.

The action of the non-solvent pore-forming liquid is primarily physical, that is, the non-solvent liquid is a readily removable space filler which is present as dispersed droplets until the coating at least partially solidifies around the droplets and is removed thereafter leaving open spaces and pores. Removal is effected without expansion of the solidified body. Suitable liquids may readily be selected by a chemist on the basis of the known physical properties of liquids. Any liquid having substantially non-solvency and non-reactivity with the polymeric material together with suitable volatility characteristics may be used. Normally liquid aliphatic hydrocarbons including petroleum hydrocarbon fractions, particularly those commercially available as mineral spirits, petroleum naphtha and kerosene which are largely or completely aliphatic in composition are generally preferred because of their low cost and satisfactory behavior in the composition; but other substantially inert organic liquids such as liquid alkyl ethers, e.g., amyl ether and dibutyl ether and liquid halogenated hydrocarbons, preferably halogenated aliphatic hydrocarbons such as chlorodecane, tetrachloroethylene and tetrachlorodifluoroethane may be used. To avoid premature evaporation from the body of emulsion so that it can serve its space filling function until it has solidified, the pore-forming liquid is chosen to have a boiling point above the selected mixing and reaction temperatures and should preferably have a boiling point of at least about 100°C. and preferably at least 130°C. to allow use of temperatures giving a desirable fluidity and rate of reaction of the polymeric material. On the other hand, the liquid will be chosen with low enough boiling point for removal without heat injury to the solidified body or to a base with which it may be associated. Thus, the liquid should ordinarily not contain substantial quantities of high boiling or low volatility components, and preferably at least 90 percent of the components should boil at temperatures below 232°C. It is to be understood that other means than evaporation, e.g., extraction may be used to remove high boiling or low volatility liquid and in such cases the upper limit of boiling point does not apply.

The extent of heating of the reactive polymeric material needed to bring the material to a suitably low viscosity, which may be of the order of 6,000 centipoises, for emulsion forming, depends on the properties of the material. Higher melting point and higher molecular weight reactive polymeric materials require higher temperatures. Polymeric materials giving the desired improvements in retention of uniform droplet distribution of the emulsion in layer form call for heating to a temperature of at least about 50°C.

Dispersion of droplets of the pore-forming liquid in the heated liquid body of reactive polymeric material to form an emulsion in which the reactive polymeric material is the continuous phase, is effected by vigorous agitation during the course of addition of the pore-forming liquid to the body of polymeric material. Surface active agents are useful to aid in dispersing the liquid in the polymeric material and to control the stability of the resulting emulsion. Preferred emulsifying agents have included anionic and non-ionic surface active agents such as commercially available silicone emulsifiers, polyoxyalkylene ethers such as a commercial polypropoxy/polyethoxy ether, partial long chain fatty acid esters and the polyoxyalkylene derivatives of such esters, also sulfuric acid esters of long chain fatty alcohols, etc.

The amount of pore-forming liquid dispersed will vary with the desired porosity of the final product and may vary from as low as, based on parts by weight, **25** parts of the liquid to 100 parts of the polymer up to as high as 300 parts of the liquid to 100 parts of the polymer material. It is preferred to use from about 60 parts to about 200 parts of liquid to 100 parts of the polymeric material. It is desirable that the mechanical conditions of dispersion of the liquid and the polymer be controlled to form very small droplet sizes of which the majority will be in the range of from 0.001 mm. to about 0.03 mm. in diameter.

Reaction of the polymeric material to higher molecular weight solid condition is brought about and controlled by the time and temperature conditions of bringing together of the reactive components and/or by the introduction of catalyst. In the one step process in which a polymeric polyol such as the polyester polyol or polyether polyol is reacted with a polyisocyanate, mixing and emulsification involves bringing together these materials together with the liquid to be dispersed and a catalyst effective to control the reaction rate.

In the two step process, an -NCO terminated prepolymer prepared from a polymeric polyol such as an hydroxyl terminated polyether or polyester and a polyisocyanate, the pore forming liquid, and chain extenders reactive with the prepolymer to give higher molecular weight materials are combined and emulsified, with the prepolymer material forming the continuous phase. Chain extenders effective to increase the molecular weight of the prepolymer are compounds having two or more active hydrogen atoms such as p,p'-methylenedianiline, 4,4'-methylene-bis-(2,-chloroaniline), trimethylolpropane, m-phenylediamine, 1,4 butanediol and triethanolamine.

Cover sheet **26** (see FIG. **1**), which may be wet with an inert non-solvent liquid is laid down on the surface of the deposited emulsion layer **18** opposite the casting surface **20** as the layer is formed, or promptly after it is formed. The cover may be a release sheet such as a paper sheet carrying a non-adhesive deposit for example, of silicone, polytetrafluoroethylene, polychlorotrifluoroethylene, wax, polyethylene or polypropylene or may be a non-adhesive supported or unsupported resin or elastomer sheet. The cover cover sheet **26** is preferably flexible for convenience in handling and may be laid down on the emulsion layer **18** by hand or by any of the known devices for laying a sheet down smoothly on a surface.

With the cover sheet **26** in place, the reaction of the polymeric material rapidly produces a preliminary gel structure in which the emulsion has sufficient stability that the stripping of the cover sheet does not disrupt of distort the surfaces of the emulsion from which it is stripped.

Control of the reaction to insure reaching the desired partial gellation by the time the cover sheet is stripped off may be controlled by such factors as temperature, catalyst and rate of speed of the conveyor. The known catalysts for urethane reactions may be used. It has been found particularly desirable to use a catalyst having an induction period during which no important physical changes occur in the reaction mixture so that in the present process mixing and deposition as a layer **18** between the casting sheet **20** and the cover sheet **26** occurs before preliminary gellation has begun, while at the same time, once the induction period has passed, the catalyst is effective to complete the cure of the urethane in a minimum time. As the catalyst having an induction period there may be used mercuric salts of aliphatic and/or aromatic carboxylic acids. Among such materials are phenyl mercuric acetate, phenyl mercuric propionate, mercuric formate, mercuric acetate, mercuric isobutyrate, mercuric propionate, mercuric octoate, mercuric oleate, mercuric stearate, mercuric oxalate, mercuric adipate, mercuric benzoate, mercuric anthranilate, phenyl mercuric chloride, phenyl mercuric nitrate, mercuric naphthenate and phenyl mercuric oleate. This catalyst may be used in amount of from about 0.01 percent to about 0.4 percent, preferably about 0.10 percent by weight based on the weight of the resin.

With this catalyst there may be used a catalyst effective to cause rapid but limited initial build up in viscosity or precursor gellation. Such catalysts may include triethylene diamine, N,N,N'N' tetramethylene butane diamine, dibutyl tin dilaurate, stannous octoate and lead naphthenate. These materials will ordinarily be used in proportion of from about 0.002 percent to about 0.7 percent by weight based on the weight of the resin.

The use of a rapid catalyst such as a tin compound is believed to reduce the desparity between the rate of reaction of the isocyanate and the polyester or polyether polyol on the one hand and the rate of reaction between the isocyanate and the short chain diol modifier on the other hand and to give best product quality. Rapid catalysts are also effective to speed up the reaction between the isocyanate with hydroxyl terminated compounds so that the tendencies for the isocyanate to be extruded into the inert liquid of the discontinuous phase is reduced. The rapid reaction also enables the cover sheet **26** to be removed in a very brief space and the combination of rapid catalyst and catalyst having an induction period operates so that the composite of fibrous backing sheet **38** and solidified emulsion layer **18** will reach a condition in which it can be handled in a minimum time. It is to observed that the tin catalyst tends to give immediate action and that there is evidence that the mercury catalyst slows the action of the tin catalyst so that time is available for forming the emulsion layer.

The following examples are given to aid in understanding the invention but it is to be understood that the invention is not restricted to the materials, proportions or procedures of the examples.

EXAMPLE 1

130 grams (0.0844 mols) of -NCO terminated prepolymer prepared by reaction of p,p'-diphenyl methane diisocyanate and hydroxyl terminated polybutylene adipate in a mol ratio of 2:1, resulting prepolymer having molecular weight of 1,540, and being solid at room temperature was liquefied and degassed at 100°C. and mixed with 3.9 grams of an emulsifier defined as blended polypropoxy/polyethoxy ether having an hydroxyl number of **20** which is a solid at 25°C. and the mixture was brought to a temperature of 100°C. 148 cc. of a liquid, paraffinic hydrocarbon mixture (boiling range 346°F. to 405°F.) was added slowly to the heated mixture of polybutylene adipate and the emulsifier with vigorous agitation to form an emulsion with the hydrocarbon as the internal phase. 7.75 grams (0.0860 mols) of 1,4 butane diol, about 7 grams of methyl isobutyl ketone and about 0.26 grams of an organosilicone block copolymer surfactant were added and mixed in. The resulting reactive emulsion was at a temperature of 100° C. and was supplied through a nozzle to the space between a casting sheet of release paper and an upper cover sheet of release paper, the surface of the cover sheet having been wet with the liquid paraffinic hydrocarbon mixture forming the internal phase of the emulsion, the layer of emulsion being 0.08 inch in thickness. The layer was carried by the cover sheet between cooled aluminum plate maintained at a temperature of 75°C. After 7 minutes, the cover sheet was stripped from the layer of emulsion and the temperature of the emulsion layer was increased 100°C. After 30 minutes at this temperature a napped and sheared cotten sateen backer which had been wet with naphtha and squeezed to remove excess naphtha was laid on the surface of the emulsion. The assembly was held in a closed condition which inhibited naphtha evaporation and was stripped from the casting sheet and held in an oven at 100°C. for 24 hours to complete curing of the layer and evaporation of the hydrocarbon layer of the composite sheet. An excellent backed microporous polyurethane sheet material was obtained.

EXAMPLE 2

An emulsion of the prepolymer, emulsifier and liquid paraffinic hydrocarbon mixture, butane diol and surfactant was prepared as in Example 1 with the addition of a commercial tin catalyst for the reaction of isocyanate and hydroxyl in amount of 20 parts of catalyst per million parts of polyurethane and the emulsion was supplied at a temperature of 60°C. between a casting sheet and a cover sheet as a layer about 0.02 inch in thickness. The emulsion layer, with the casting and cover sheets in place, was passed in contact with cooled aluminum plates maintain at a temperature of 45°C. The cover sheet was stripped off after 15 seconds and the layer of emulsion was brought to 50°C. for 1 minute. At this point, a nonwoven polyester fiber sheet was laid on the exposed phase of the emulsion layer and the assembly was brought to 100°C. After 8 minutes at 100°C., the backer and solidified emulsion layer were stripped from the casting sheet and air dried at 100°C. for 30 minutes. The resulting sheet was a fine microporous polyurethane backed sheet material.

EXAMPLE 3

The procedure of Example 2 was repeated; but there was also included 1,500 parts per million of a mercury salt of a carboxylic acid as well as the tin catalyst. The emulsion was supplied between the casting sheet and the cover sheet at a temperature of 55°C. and the composite of casting sheet emulsion layer and cover sheet were passed between cooled aluminum plates maintained at 35°C. After 25 seconds the cover sheet was peeled off and the emulsion layer was brought to a temperature of 60°C. After 4 minutes at this temperature a stitch bonded continuous filament polyester nonwoven fibric was laid on the emulsion layer. This assembly was held at 115°C. for 5 minutes in a closed chamber which inhibited evaporation and was then stripped from the carrier sheet and pressed in an oven at 100°C. for 25 minutes to evaporate the liquid hydrocarbon and complete the cure of the polyurethane of the emulsion layer.

Having thus described my invention what I claim as new and desire to secure as Letters Patent of the United States is:

1. The process of forming a microporous sheet of solid polyurethane comprising the steps of casting an emulsion of fine droplets of a volatile organic liquid as the internal phase in a continuous phase comprising reactive material convertible through reaction to solidified, resilient, film-forming condition, said reactive material comprising a mixture of an organic compound providing at least two reactive -NCO groups per molecule and an organic compound having at least two active hydrogens per molecule for reaction with said -NCO groups, said organic liquid being substantially non-solvent for and non-reactive with said reactive material, being immiscible in said continuous phase and being present in amount from about 60 percent to about 300 percent by weight based on the weight of the reactive material, reacting said material at a temperature below the boiling point of said liquid so that the liquid never boils to cause the emulsion to gel and solidify with said droplets held in the solidified material and removing said liquid without expanding the solidified material leaving pores and discontinuities in the solidified material to constitute passageways for air and vapor, the improvement which comprises forming a layer of the liquid emulsion, reacting the materials of the continuous phase of the emulsion under conditions preserving the uniformity of the emulsion to a thickened pressure flowable stage having a pre-gel structure which will prevent sinking in of a fibrous sheet material, bringing fibrous sheet material into intimate engagement with said layer to cause the emulsion to adhere to the fibrous sheet, completing said reaction to form a stable solid body and removing said volatile organic liquid from the solidified material.

2. The process of forming a microporous sheet of solid polyurethane as defined in claim **1** in which said layer of emulsion is formed between spaced release surfaces promptly after formation while said emulsion is liquid and in which one of said release surfaces is stripped from said layer of emulsion when said emulsion has thickened to a stage where the emulsion is no longer freely liquid and maintains undeformed the surface from which the release surface is stripped.

3. The process of forming a microporous sheet of solid polyurethane as defined in claim **2** in which said layer of emulsion is formed between said release surfaces and is cooled to aid in thickening the emulsion prior to stripping one of said release surfaces from the layer of emulsion.

4. The process of forming a microporous sheet of solid polyurethane as defined in claim **3** in which at least one of said reactive materials is polymeric and is solid or pasty at room temperature, said solid or pasty reactive material is heated to bring it to free fluid state for mixing with other reactive materials, said immiscible liquid is emulsified with said reactive materials while said solid or pasty reactive material is in heated state, and in which said layer of emulsion is formed between said release surfaces while in heated condition.

5. The process of forming a microporous sheet of solid polyurethane as defined in claim **2** in which said reactive material comprises a member of the group consisting of mixtures of at least one polymeric polyether polyol or one polyester polyol, an organic compound having at least **2** reactive -NCO groups per molecule and a diol chain extender having from **2** to **10** carbon atoms and a mixture of at least one prepolymer from reacting stoichiometric excess of an organic compound having at least **2** reactive -NCO groups per molecule with a polymeric polyether polyol, polyester polyol and a diol chain extender having from two to 10 carbon atoms, and a catalyst favoring reaction of isocyanate radicals with the active hydrogens of polyester polyols or polyether polyols over reaction between said polyisocyanate and the active hydrogens of said chain extender.

6. The process of forming a microporous sheet of solid polyurethane as defined in claim **5** in which at least one of said reactive materials is polymeric and is solid or pasty at room temperature, said solid or pasty reactive material is heated to bring it to freely fluid state for mixing with other reactive materials, said immiscible liquid is emulsified with said reactive materials while said solid or pasty reactive material is in heated state and in which said layer of emulsion is formed between said release surfaces while in heated condition and is cooled to aid in thickening the emulsion prior to stripping one of said release surfaces from the layer of emulsion.

7. The process of forming a microporous sheet of solid polyurethane as defined in claim **2** in which said emulsion is deposited promptly after formation while in freely fluid condition between spaced sheets of release material moving at the same rate and maintained in spaced relation a distance corresponding to the desired thickness of said microporous sheet material, progressively stripping one of said release surfaces from said layer of emulsion when said emulsion has thickened to a stage where the emulsion is no longer freely liquid and maintains undeformed the surface of the emulsion from which the release surface was stripped, progressively laying down a fibrous sheet material on said layer of emulsion when said emulsion has gelled to a stage at which the fibrous sheet material will not sink into said layer of its own weight, completing the reaction of the reactive materials of said emulsion to convert said layer to resilient film-forming condition combined in firmly adherent relation to said fibrous sheet and thereafter progressively stripping the combined fibrous sheet material and reacted emulsion layer from the remaining release sheet.

8. The process of forming a microporous sheet of solid polyurethane as defined in claim **6** in which said emulsion is deposited promptly after formation while in freely fluid condition between spaced sheets of release material moving at the same rate and maintained in spaced relation a distance corresponding to the desired thickness of said microporous sheet material, progressively stripping one of said release surfaces from said layer of emulsion when said emulsion has thickened to a stage where the emulsion is no longer freely liquid and maintains undeformed the surface of the emulsion from which the release surface was stripped, progressively laying down a fibrous sheet material on said layer of emulsion when said emulsion has gelled to a stage at which the fibrous sheet material will not sink into said layer of its own weight, completing the reaction of the reactive materials of said emulsion to convert said layer to resilient film-forming condition combined in firmly adherent relation to said fibrous sheet and thereafter progressively stripping the combined fibrous sheet material and reacted emulsion layer from the remaining release sheet.

9. The process of forming a microporous sheet of solid polyurethane as defined in claim **8** in which material is supplied at the surface of one of said release sheets providing a low adhesion interface between said release sheet and said emulsion.

10. The process of forming a microporous sheet of solid polyurethane as defined in claim **9** in which said release sheet is a flexible cover sheet of release material which is wet with inert non-solvent liquid at the surface which will contact said layer of emulsion.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,793,102 Dated February 19, 1974

Inventor(s) John T. Day

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 1, first line, delete The and insert

--In the--

Signed and sealed this 30th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents