HYDROPHILIC NONWOVEN WEB AND METHOD OF MAKING IT

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14 Claims

ABSTRACT OF THE DISCLOSURE

The disclosed hydrophilic webs are obtained by impregnating nonwoven webs with an isocyanate-terminated prepolymer and foaming the prepolymer in situ with water or steam. The prepolymer is preferably derived from an aromatic diisocyanate and a polyoxyethylene diol having an OH equivalent weight of about 300—2,200. The resulting webs have good strength (adequate for use in leather substitutes), and low stiffness (temper) properties. When the web is moist, the strength properties are substantially retained, and the stiffness is even lower.

FIELD OF THE INVENTION

This invention relates to a hydrophilic nonwoven web and a method of making it from available nonwoven materials and an isocyanate-terminated oxyethylene-containing prepolymer impregnant. The method involves foaming the prepolymer impregnant in situ with water or steam. The resulting polymer-containing nonwoven product has particular useful temper and strength characteristics, wet or dry. The fibers of this product are bound together by filmy deposits of a cured, hydrophilic polyurethane-polyurea or polyurea. Despite the previously described foaming step, a cellular polymeric structure within the interstices of the web is not readily discernible upon microscopic examination.

DESCRIPTION OF THE PRIOR ART

It has been found that useful fabrics can be obtained by impregnating woven or nonwoven materials with an aqueous emulsion, comprising (1) a partially or fully blocked prepolymer of a polyoxyethylene diol and a diisocyanate, and (2) a polyol curing agent. A subsequent heat treatment unblocks the prepolymer, liberating free isocyanate which reacts with the curing agent. See U.S. Patent 3,384,506 (Elkin), issued May 21, 1968. The resulting fabric has hydrophilic properties, due to the presence of chains of oxyethylene (—CH₂—O—) units in the cured polyurethane impregnant. Impregnants lacking oxyethylene units (see, for example, U.S. Patent 3,340,335) provide far less hydrophilicity. However, a drawback frequently encountered with the nonwoven material is that low or high temperatures have been impregnated with hydrophilic oxyethylene-containing materials is their undue stiffness (high temper, etc.) and/or low mechanical strength, i.e., low tensile strength, low stretch and tongue tear resistance, etc., particularly when wet or damp. Indeed, a foam derived from the water curing of a polyoxyethylene diol—tolylenediisocyanate system usually tends to dissociate in water. See U.S. Patent 2,977,330 (Brower), issued Mar. 28, 1961. Generally speaking, the strength of these impregnated nonwoven materials cannot be increased without increasing stiffness; conversely, increasing flexibility often involves sacrificing strength.

Accordingly, this invention contemplates providing an air-laid nonwoven web with hydrophilic properties, good strength, and low temper, which retains a substantial portion of its strength when wet. This invention further contemplates a nonwoven web bound together with a hydrophilic, elastomeric, oxyethylene-containing binder, wherein the web has greater flexibility and conformability or drape when wet. This invention further contemplates a flexible nonwoven web which is permeable to and absorbs water vapor and is strong enough to be used as a base web for a shoe upper material.

SUMMARY OF THE INVENTION

Briefly, this invention involves (1) impregnating an air-laid, nonwoven web with an impregnant comprising an isocyanate-terminated prepolymer containing at least one oxyethylene-containing oxyalkylene chain, said chain having a molecular weight of 600—4400, preferably 1000—4000 (optionally, the prepolymer can be chain extended with compounds having two active hydrogen-bearing groups, provided the NCO equivalent weight is kept below 100,000); (2) exposing the impregnated, air-laid, nonwoven web or batting to water or steam such that the NCO-terminated prepolymer is reacted in situ, i.e., is cured (chemically) reacted with water, resulting in the evolution of carbon dioxide. After completion of the water cure, the resulting web or batting has a lower temper, particularly when the aforementioned molecular weight of the oxyalkylene chain is less than about 4,000.

DETAILED DESCRIPTION

By "temper" is meant the test described in The Chemistry of Leather Manufacture, 2nd ed., vol. 2, by John A. Wilson, American Chemical Society Monograph Series, 1929, pages 1111—1116, which involves cutting an inch-wide strip of sheet material, winding it into a substantially circular coil, and measuring the force (in grams) required to flatten the coil to three-fourths of its original diameter. This test can be suitably modified to permit measurement of the force with a modern constant rate tensile tester machine such as an "Instron" (trade designation of the Instron Corporation, Canton, Mass., U.S.A.). This type of machine is described generally in The Science and Technology of Polymer Films, volume I, O. J. Sweeting, Ed., Interscience Pub., N.Y., 1968, pages 553—554. The temper is dependent upon the thickness of the sheet material to be tested. Webs up to 250 mils thickness (6.4 mm) can easily be made and split to any useful thickness, e.g., 15—100 mils (0.2—2.5 mm). A convenient thickness for typical industrial uses of impregnated webs of this invention is 45 mils (1.143 mm). The temper of a sample t millimeters thick can be corrected to 1.143 mm thickness by multiplying the force in grams by the correction factor: (1.143)/t (or 45/T, where T is the thickness in mils). Impregnated, water or steam-cured webs of this invention can have a temper (corrected to 45 mils thickness) of less than about 100 grams, though impregnants containing high molecular weight oxyalkylene chains (e.g. greater than 3,000) may raise the temper to as high as 220 grams. For base webs to be used in synthetic shoe upper material, the impregnated, cured webs of this invention are designed to have a temper when dry of about 15 to about 90 g., preferably 25—50 g. The range of temper values of materials of this invention is always below 90 g. and generally in the range of about 5—30 grams. 20% sample webs have been made to contain 20—25% of percent of water based on the dry weight of the samples, i.e. the weight of fiber and binder. Surprisingly, even relatively stiff webs (200—220 grams temper) of this invention are lowered to the 5—30 gram range by such moistening. The lowered temper provides high flexibility. As a part of a composite shoe upper material, the webs of this invention help to provide ease of lasting during shoe manufacture and ease of fitting for the uppers of finished shoes. This ease of lasting and fitting is a property hitherto absent in virtually all known synthetic shoe upper materials.
This highly desirable property of low temper in the moist hydrophilic webs of this invention would be no more than a laboratory curiosity if the mechanical strength properties of the webs were largely sacrificed. It is a feature of this invention that the tenacity tear resistance (American Leather Chemists Association [ALCA] Provisional Test Method E–10 [April 1953]), stitch tear resistance (ALCA Provisional Test Method E–13 [April 1953]), and tensile strength properties of the moist webs (those containing 20–25 wt. percent water, based on dry weight of fiber + binder) compare favorably used in the same sample with the stitch and tongue tear values for the wet webs generally exceed 40%, and can be as high as 90%, of the dry values. The tensile strength of the wet webs may drop to 10 or 20% of the dry value, but typically is greater than 40% or even 50% of the dry value.

The strength of impregnated, cured base webs of this invention equals or exceeds many synthetic materials now being used in commercial products. For example, in shoe manufacture, synthetic sheet materials with a stitch tear resistance (when dry) of 250–300 lb. per linear inch have been used; see, for example, Kirk-Othmer, Encyclopedia of Chem. Technology, vol. 12, p. 341. Materials can be made according to this invention which exceed this performance, even when wet. When dry, materials of this invention typically have a tensile strength of at least 900 p.s.i. (64 kg./cm.²) and a tongue tear resistance of at least 150 lb. per linear inch. Although this invention is not bound by any theory, it is believed that the in situ water or steam cure of a suitable hydrophilic (i.e. oxyethylene-containing polyisocyanate) prepolymer impregnant is somehow responsible for a strong but flexible bond between the resulting cured polymeric binder and the fibers of the air-laid nonwoven web providing a unique combination of binder and fiber. The uniqueness of the combination may be due to the compatibility of the prepolymer and the water used to cure it and/or the low viscosity and good fiber-wetting characteristics of the impregnants and/or the evolution of carbon dioxide in somewhat confined areas, and/or the formation of particular chemical linkages such as urea linkages or the like. In any event, contrary to the teachings of the aforementioned Patent No. 3,848,506, column 4, the in situ water or steam cure and the consequent formation of urea

\[ \text{NH} - \text{CO} - \text{NH} \]

linkages and carbon dioxide is indeed useful.

Thus, a large increase in flexibility (decrease in temper) can be obtained when the webs of this invention absorb moisture, and the resulting sacrifice in mechanical strength is disproportionally small, particularly in view of the teachings of the prior art, particularly the weakness of foams made according to the aforementioned 2,977,350 patent.

The cured, impregnated webs of this invention have a peculiar structure. Microscopic examination reveals that they do not resemble the mere combination of a foam and a fibrous web, but appear instead to be webs containing filmy deposits of polymer forming along the long axes of the fibers, with some polymer accumulation at fiber junctures and at random locations along the length of fibers or fiber bundles. Some of these filmy deposits contain micropores or macropores, but, generally speaking, the usual “foam” structure, i.e., 3D-structured sponginess or cellular matrix, is not readily apparent. It may be that the cells of the “foam” are masked in some way by the fibers, but it is not possible to confirm this masking effect by microscopic examination.

Impregnated and cured nonwoven sheet materials or webs of this invention have good leather permability values, i.e., good moisture vapor transmission (MVT) characteristics. The MVT measurements are taken in a conventional manner (see, for example, U.S. Patent 2,723,935, issued November 1955) at 23° C. and a relative humidity difference (from one side of the sample to the other) of 100%/50%, the units of measurement being grams per hour per 100 square meters (g./hr./100 m²). An MVT of 2000 g./hr./100 m² is considered adequate for many types of leather replacements, and the materials of this invention exceed this standard by a considerable margin; MVT’s up to 5,000 g./hr./100 m² or more can be obtained in practice. Furthermore, the hydrophilic binder absorbs and desorbs water much as the hydrophilic constituents of natural leather do. A web of this invention, in contrast to those containing a water vapor impermeable shoe construction, can absorb moisture from a human foot over an eight-hour period in an amount greater than 20 wt. percent or even greater than 30 wt. percent, based on the dry (fiber + binder) weight of the web. The three-hour moisture pickup rate (after conditioning in a 32% R.H. atmosphere at 24° C.) is more than 10% of the weight of the conditioned samples.

The impregnated, cured webs of this invention are useful in a wide variety of applications where a flexible, strong, nonwoven sheet material is needed. Examples of such applications include the fabrication of leather substitutes and poromeric articles, such as shoe uppers. More specifically, control of breathability and comfort are a major concern. Other areas of potential application, in addition to dress shoes of the Oxford type, include footwear which requires exceptionally high abrasion resistance and/or the ability to protect against water damage and/or to mitigate either problem. That is, by following the teachings disclosed herein, the properties of high strength (even greater than 1000 p.s.i. (69 kg./cm.²)), high breathability, and a moisture and water absorptive nature of the impregnated web can aid in the maintenance of foot comfort.

The term “hydrophilic” normally denotes an affinity for water. In the context of this invention, it has a somewhat more specific meaning; namely, the ability of a material, at equilibrium in a 100% relative humidity atmosphere, to absorb at least 10, preferably at least 25, percent by weight of water. For many specific uses contemplated for the webs of this invention, the loading of hydrophilic polymer and the proportion of oxyethylene groups should be sufficient to provide an equilibrium 100% R.H. absorption of at least 40 percent by weight of water.

The hydrophilic webs of this invention are particularly useful in the manufacture of multi-layered synthetic shoe upper materials or similar multi-layered constructions or composite materials having a base web, a topcoat at least about 0.2 mm. thick, and, optionally, at least one porous, back-up interlayer between the topcoat and the base web. The interlayer can be surface bonded to, or otherwise made integral with, the topcoat. A particularly suitable construction for a composite material is described in a U.S. patent application of Robert L. Elton, Ser. No. 867, 538, filed Oct. 20, 1969 now Pat. 3,560,290. Other useful constructions are disclosed in U.S. Pat. 3,564,098 (Pat- sin), issued January 1968; 3,591,049 (Manwaring), issued July 1968; 3,524,757 (Sharp), issued August 1970; and 3,520,767 (Manwaring), issued July 1970. In many of these materials, the fibrous or cellular polymeric interlayer improves the overall properties of the material, making the material more suitable for use in inter alia, sports, boxing, and military shoes. Problems associated with the incorporation of fibrous, woven (i.e. cloth) interlayers are the noticeable loss of flexibility (increase in temper) of the total composite and a decrease in the ability to conform to a shape. A problem with using only polymeric cellular interlayers is the relatively lower strength properties of the composite and the lack of uniformity of the cloth. The materials of this invention, when used as base webs in these composite materials, can help to mitigate either problem. That is, by following the teachings disclosed herein, the properties of high strength (even
when moist) and high flexibility and conformability (particularly when moist) can be designed into the base webs, thus providing overall benefits for the composite without sacrificing the overall porosity, MVT, or the like. The cured, impregnated nonwoven materials of this invention are reasonably light in weight. Apparent densities well below 1.0 g./cc. or, preferably, below 0.5 g./cc. are possible, depending on the apparent density of the impregnated web and the amount of impregnant (i.e., binder) take-up or add-on. The apparent density of the impregnated web, though well below 0.5 g./cc. should be at least 0.05 g./cc., preferably at least 0.1 g./cc. The nature of the web will be described in greater detail subsequently. (*Apparent density* is determined by the weight per unit of "apparent volume"; "apparent volume" includes voids as well as solid material.) The amount of binder add-on can be much greater with impregnant systems of this invention, as compared to aqueous emulsion or suspension systems. Surprisingly, however, there appears to be no measurable improvement in the hydrophilic properties of these impregnated webs as the amount of binder added on is increased beyond about 290% by weight of the impregnated web, i.e., when the binder: fiber ratio exceeds 2.9:1 by weight. A striking improvement in hydrophilicity is obtained over an impregnated web when as little as 30 wt. percent binder is added on and temper is still satisfactory at 280% add-on; therefore, the preferred binder: fiber ratio (by weight) of this invention is in the range of 0.3:1-2.8:1. It has also been found that, although solventless impregnants can be used (100% solids), solutions of prepolymer impregnate the web in an especially efficient and uniform manner and provide a convenient means for controlling the percent polymer add-on in the final product. Although, theoretically, any concentration of prepolymer from 1-99% can be used, particularly suitable prepolymer concentrations range from about 10 to about 75 wt. percent.

The polymers used in this invention contain recurring oxyethylene units and ordinarily have an isocyanate functionality of two, tri- and tetra-isocyanate prepolymers being less preferred due to the risk of increasing temper in the cured web. Accordingly, the isocyanate-terminated prepolymers are ordinarily derived from linear polyoxyethylene diols. It should be understood, however, that the use of a polyoxyethylene diol having an oxyalkylene side chain capped with a group (such as allyloxy) inert to isocyanates is permissible. Similarly, other types of introducing capped side chains into the prepolymer may be permissible. After curing, the webs may be air or oven dried; in either case, the drying step need not involve heat shrinking or further heat shrinking of the fibers in the web. Alternatively, heat shrinking can be carried out at this point. The resulting impregnated and dried webs can, if desired, be finished, e.g., sanded and split, in the conventional manner. After the conventional finishing steps, the webs are ready for use in the various fabricated products described previously.

The OH equivalent weight of a polyoxyethylene polyl used in this invention should range from about 300 to about 2,200, preferably at least 500, to provide good hydrophilicity. Particularly good results are obtained with an OH equivalent weight which is slightly greater than 500, e.g., 770. Mixtures of 500 and 770 equivalent weight polyols also provide good results. For optimum temper properties, the lower end of this range is most suitable, i.e., below 1500, when linear polyoxyethylene diols are used. A particularly suitable commercially available series of glycols is available from Union Carbide Corporation under the tradename "Carbowax." Although triols, tetrols, and similar polyls and diols are available, they are not provided, impregnated, cured webs with the optimum temper properties, polymers derived from reaction mixtures substantially free of crosslinking agents are preferred. Polyoxyethylene diamines with an equivalent weight as low as 1,000 are known and can also be used in this invention, as can polystyrene dimercaptans and the like. The polyoxyalkylene chains of prepolymers of this invention preferably contain mostly or entirely oxyethylene units (e.g., >30 mole percent), but copolymers, terpolymers, etc., containing a minor amount of oxypropylene, oxy-1,2-butylene, or oxy-1,4-butylene units are not detrimental and may increase the flexibility of the cured polymer. These copolymers can be random or block copolymers, as is known in the art. It is thus permissible to use random or block copolymer oxyalkylene chains in which a majority (>50 mole percent) of the repeating units are oxyethylene. It is also permissible to use simple mixtures of polyoxyethylene polyls with other polyls to make the prepolymers of this invention, and to use mixtures of oxyethylene-containing prepolymers with other prepolymers, provided, that the total oxyalkylene units in the cured polymer will always be at least 50 mole percent oxyethylene. These various mixtures and copolymers can be selected with a view toward varying the amount of hydrophilicity, flexibility, and stretchability or conformability of the cured web. In accordance with equivalent weight guidelines previously discussed, the molecular weight of each oxyethylene-containing oxyalkylene chain will be in the range of 600-4,400, preferably at least 1000 for good hydrophilicity, and preferably less than 5,000 for linear oxyalkylene chains. The —NCO equivalent weight of these prepolymers is determined by the —OH equivalent weight of the glycol used to make the prepolymer and the amount of chain extension, if any, of prepolymer molecules. Ordinarily there is only one oxyethylene chain per prepolymer molecule. Under these circumstances, the NCO equivalent weight should be at least 300, to provide a significant amount of hydrophilicity. In addition, however, but less than 2,500, preferably less than 2,200, to avoid causing unduly high temper in the impregnated web after curing. If chain extension of the prepolymer is carried out, prior to water cure, with minor amounts of compounds having two active hydrogen bearing groups, the NCO equivalent weight is preferably kept below 100,000, more preferably below 20,000, to avoid the necessity of using large amounts of solvent. The term "active hydrogen" is to be understood as defined according to the Zerweinski Test, JACS 49, 3181 (1927), and suitable di-functional active-hydrogen containing materials, besides water, are the lower aliphatic diols and diamines, arylenediamines, dimercaptans, and the like. As pointed out previously, the isocyanate compound of the polymers of this invention is derived from an aliphatic, aromatic, or aralkyl polycyanate, preferably a diisocyanate such as tolylene diisocyanate (TDI), xylylene diisocyanate (XDI), naphtalene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), phenylene diisocyanate, etc. Any suitable isomers of these diisocyanates can be used, or mixtures thereof, e.g., 2,4-TDI, 2,6-TDI, 1,5-napththalene diisocyanate, m-phenylene diisocyanate, etc.

Prepolymers of this general type are well known in the art, and the polystyrene-polylethers or the like obtained from water curing these prepolymers are also well known. Typically, the prepolymers will contain at least one oxyalkylene chain (as described previously) preferably of the formula

\[
\text{CH}_2-\text{CH}_2-\text{O}_n
\]

wherein \( n \) is selected to provide the molecular weights described previously, i.e. \( n \) is about 13 to about 100; the prepolymers will also have no more than two terminal groups of the formula

\[
\text{OCN}-\text{Ar}-\text{NH}-\text{Co}
\]

wherein Ar is an aromatic nucleus derived from tolylene diisocyanate, xylylene diisocyanate, 4,4'-diphenyl-methyl methylene diisocyanate, or one of the other arylene diisocyanates described previously. The presence of only two isocyanate functions will help to insure low temper in the cured web,
particularly if the web has been densified for strength. Optionally, units of the formula

\[ \text{CO-NH-Ar-NH-CO} \]

can also occur in the prepolymer if chain extenders (such as the previously described difunctional active-hydrogen bearing materials) are used to increase the molecular weight of the prepolymer. Although some chain branching in the prepolymer chain is permitted, linear prepolymer is preferred. If chain branching is present, it is preferred that all but the two isocyanate-terminated branches be capped with groups inert to isocyanates.

The prepolymer systems used in this invention are soluble in a variety of organic liquid carriers or solvents, but water miscible solvents such as acetone, tetrahydrofuran, and dioxane, or less preferably, dimethylformamide and dimethylacetamide provide significant advantages. Solvents with little or no water miscibility are much less preferred, e.g., chloroform, methylene chloride, ethyl acetate, methyl ethyl ketone, xylene, toluene, benzene, and other common solvents inert, or substantially inert, to isocyanate groups. Acetone is particularly suitable because its miscibility with water provides excellent impregnation of the web. Its water solubility further obviates the necessity for complete solvent removal before the initiation of the web or steam cure, and its high volatility permits easy solvent removal during or subsequent to curing. It is also possible to use water as a solvent; however, in such cases impregnation of the web must be accomplished before the prepolymer cures. The hiatus between dissolving the hydrophilic prepolymer and the insolubilization and cure of the prepolymer by the water can be controlled by the temperature of the water: the colder the temperature of the aqueous solution, the greater the working time before cure. It is possible to impregnate the web with prepolymer without using a solvent, provided suitable prepolymer and impregnating temperatures are selected to keep the viscosity of the impregnant as low as is practical. The unimpregnated fibrous web or batt should be of the nonwoven (preferably air-laid) type and can be produced on a "Rando-Webber" or "Garnett" machine in the conventional manner. Suitable discontinuous fibers, 0.5-10 denier x 5-15 mm. in length, can be used, e.g., polypropylene (including polyalkylene or polypropylene), polyesters, aromatic polyamides, polyurethanes (i.e., polymers of dicarboxylic acids and glycols such as polyethylene terephthalate, polyethylene isophthalate, copolymers of these, etc.), vinyl polymers (polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, and copolymers of these), polyacrylates, natural cellulose or wool fibers, mixtures of these or any of the commonly used fibers from nonwoven webs or batts are made. See, for example, U.S. Patent 2,908,064 (Lauterbach et al.) issued October 1959. The fibers can be substantially thermostable or easily heat-shrinkable. Heat-shrinkable fibers are preferred for their ability to make a stronger, more compact web upon being heat-shrunk at least 10% of their length after web formation. Needle punching or the like can be used to further compact and densify the web. For the high strength needed in shoe upper materials, the web should be densified to an apparent density of at least 0.1 g./cc. For less demanding uses, this apparent density should still be at least 0.05 g./cc. This invention permits these higher density webs to be used without unduly increasing the temper.

The usual procedure of this invention is as follows: A suitable fibrous web is impregnated with the prepolymer or, preferably, a solution of the prepolymer. If a prepolymer solution is used, the concentration of prepolymer is preferably less than 75 weight percent to keep the room temperature viscosity within suitable bounds. The impregnated web is then drained, e.g., by squeezing between rollers to remove excess prepolymer, thereby controlling prepolymer add-on and web properties. Alternatively, a particular solvent concentration can be selected to control prepolymer add-on. If the solvent is not water miscible, it can be removed prior to curing of the prepolymer with heat and/or subatmospheric pressure. The impregnated web is then brought into contact with water (the term “water” being used herein to mean liquid water, water vapor, or steam). One of the preferred water cure methods involves the simple immersion of the impregnated web in a liquid water bath. The temperature of the bath is preferably room temperature or greater, e.g., 50–70 °C. Water at 60–65 °C. (hot tap water) can cause the prepolymer to cure in one to five minutes. Higher or lower bath temperatures can be used to cause faster or slower cures, and to produce coarser or finer macro pores in the cured impregnant.

Another preferred water cure method involves the use of a steam chest. The impregnated and squeezed or drained web can be continuously passed through the steam chest in any suitable manner, preferably while in a vertical position so that gravity ensures uniform curing throughout the web. The steam can be maintained at 100 °C. (1 atm. pressure, disregarding reaction exotherm) or superheated, but, if superheated, it is preferably cooler than about 150 °C., disregarding the effect of the reaction exotherm. There are many advantages to a steam cure, including highly efficient and uniform curing, good control over impregnant losses, and the like. This water curing step converts free isocyanate to urea linkages, with the liberation of carbon dioxide. The carbon dioxide does not create any serious difficulties of processing, nor does it result in a significant loss of impregnant material, particularly in the case of the steam cure. It appears to be essential to this invention to limit at least some gas generation, with the concomitant formation of —NH—CO—NH— linkages. Thus, the resulting cured polymers are hydrophilic polyetherureas or polyetherurethane-ureas which contain oxycyclene units.

The following non-limiting examples illustrate the preferred practice of this invention. All parts and percentages are by weight, unless otherwise specified.

Example 1

(A) Polyurethane prepolymer preparation: 1000 parts of polyoxytetraphenylene diol of average molecular weight 1000, i.e., Union Carbide's "Carbowax 1000" (trademark) was stirred and reacted, under substantially anhydrous conditions, with 351 parts of an 80:20 mixture of 2,4- and 2,6-tolylene diisocyanate (TDI). The resulting viscous liquid contained an oxycyclene chain of 1000 molecular weight (average) which was terminated with two OCN—Ar—NH—CO— groups (where Ar was the 2,4- or 2,6-substituted tolylene nucleus).

(B) Web impregnation and cure: A light, fluffy nonwoven web made on a Rando-Webber from 3.0 denier (diameter) x 1.5 inches (length) polypropylene staple fibers was passed through a conventional needle puncher four times to increase the apparent density of the web. After needle punching, conventional heat shrinking was used to increase the density still further until it reached an average of 0.19 gram/cc. Nine samples of the heat shrunk, needle-punched web were cut to convenient 2 x 3 inch size (5.08 x 7.62 cm.) and weighed. Samples Nos. 2–8 were soaked for one minute in acetone solutions containing varying concentrations of the prepolymer, prepared in Part A. The thus impregnated webs were then drained, placed between absorbent paper towels, and finally placed in a 100 °C. oven for five minutes. They were then completely immersed in water (60 °C.) for three minutes, drained, and dried to constant weight in a desiccator over P2O5. The increase in weight divided by the original weight of the web is defined as polymer add-on.

Sample No. 1 was given no impregnation treatment whatever.

Sample No. 9 was soaked in a 20 wt. percent sulfonated polyurethane aqueous latex, drained of excess latex, processed, and dried in the desiccator. (The sulfonated
latex was prepared by (1) forming an isocyanate-terminated prepolymer from polyoxypropylene diol of 1000 molecular weight and 80/20 2.4,-2.6 TDI, (2) sultanizing the prepolymer with less than 2.0% by weight of sulfuric acid, (3) neutralizing the sultanized prepolymer with triethylamine, and (4) adding the prepolymer, with agitation, to water, thus forming an emulsion, chain extended, polyetherurethane-polyurea, i.e. a stable aqueous latex, in accordance with the teachings of U.S. application Ser. No. 841,570, filed July 14, 1969.

All of the dry samples (Nos. 1–9) were then placed in a 100% relative humidity atmosphere at 23°C, and allowed to equilibrate to constant weight (312 hours). The increase in weight divided by the dry weight is defined as the water pick-up. The data is presented in the following table:

<table>
<thead>
<tr>
<th>TABLE I—POLYMER ADD-ON AND WATER PICKUP OF IMPREGNATED POLYPROPYLENE WEB</th>
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<tbody>
<tr>
<td>Sample number</td>
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</table>

*Latex (20% solids) processed as follows: coagulated, coalesced at 275°F for 15 minutes, washed, and dried.

Example 2

A larger sample, 9 x 7 inches (22.9 x 17.8 cm), of the web of Example 1 was impregnated with a solution (30 wt. percent solids) in acetone of the prepolymer of Example 1(A) by the technique used in Example 1(B). The dry, cured web was machine sanded (150 grit paper) on both sides of 103 mils thickness and split into 45 mil (a split) and 56 mil (b split) sections. Splits a and b were also prepared from a web impregnated with latex according to Example 1(B). A sample of the cured, the two b splits, and a sample of barded calf leather were tested for water sorption capacity over an 8 hour period and then for water desorption capacity over a 15.5 hour period. The initial sample weights were taken at 32% relative humidity (R.H.) and 75°F. (24°C). The water absorption tests were run at 100% R.H. and 75°F. (24°C) with weighings made at 3, 6, and 8 hours. The samples after 8 hours at 100% R.H. were allowed to dry for 15.5 hours at room conditions after which they were weighed again (32% R.H. and 75°F.) to measure moisture desorption. All the samples tested returned to their original moisture content. Moisture pickup is defined as increase in weight at 100% R.H. and 75°F. (24°C) divided by initial weight at 32% R.H. and 75°F. The moisture absorption-desorption data, as well as other properties of samples, are presented in Tables II and III. All physical properties not relating to moisture absorption or transmission were determined on dry samples.

### Physical properties of:

1. Cured, hydrophilic, and
2. Latex-impregnated webs (dry samples)

<table>
<thead>
<tr>
<th>Table II: Physical properties of cured and impregnated webs</th>
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<tbody>
<tr>
<td>Sample</td>
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<td>Split</td>
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</tbody>
</table>

The caliper, temper, density, and mechanical strength properties of the latex-impregnated samples are quite typical of base webs used in making leather substitutes. The properties of the cured hydrophilic webs were thus found to be quite typical for this use also; in fact, the mechanical strength of the hydrophilic samples was somewhat superior to the latex-impregnated samples.

### TABLE III—ABSORPTION AND TRANSMISSION OF MOISTURE OF SAMPLE WEBS AND LEATHER

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<thead>
<tr>
<th>Water pickup, <strong>after</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>Cured, hydrophilic, b split</td>
</tr>
<tr>
<td>Latex-impregnated, b split</td>
</tr>
<tr>
<td>Leather (barded calf)</td>
</tr>
</tbody>
</table>

* Moisture vapor transmission, determined by the procedure outlined previously in the detailed description of this invention. All MVT values were subjected to 1.5% experimental error.

**Relative to constant at 23.5% R.H., 75°F. (24°C). All samples described the moisture and returned to this moisture content after conditioning at room conditions for 15.5 hr.

### Example 3

The purpose of this example was to evaluate prepolymer based on three different molecular weight linear polyoxyethylene diols (end-capped with tolylene disocyanate), i.e. polyether diols of 1000, 1540, and 4000 molecular weights (MW) obtained from Union Carbide as "Carbowax" (trademark) 1000, 1540, and 4000. The prepolymer was made in Example 1(A) and were applied to four 9 x 7 in. densified polypropylene webs (see Example 1(B)) from 30% solids acetone solutions, as in Example 1(B). The four impregnated webs were placed in a steam chamber for three minutes, and then in 60°C water until gas bubble evolution ceased (approximately two minutes). The impregnated, cured webs were then dried and sanded to 100 mil thickness; then split into two 50 mil thicknesses for testing, as in Example 2. Each of the four samples (numbered I to IV) was thus divided into an a and b split to make Samples I-a, I-b, II-a, II-b, etc. Properties of the cured, impregnated hydrophilic webs were as follows:

### TABLE IV—SAMPLES CONTAINING LINEAR OXYETHYLENE CHAIN OF VARIOUS MOLECULAR WEIGHTS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>MW of diol used to make prepolymer</th>
<th>Percent binder to form in web</th>
<th>R/H in 100% R.H.</th>
<th>MVT pickup*</th>
<th>MVT** (g./hr/100 m²)</th>
<th>Apparent density (g./cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,000</td>
<td>54</td>
<td>23.1</td>
<td>3,000</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>2</td>
<td>1,000</td>
<td>54</td>
<td>23.1</td>
<td>3,000</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>3</td>
<td>1,540</td>
<td>54</td>
<td>28.2</td>
<td>3,500</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>4</td>
<td>1,540</td>
<td>54</td>
<td>28.2</td>
<td>3,500</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>5</td>
<td>4,000</td>
<td>57</td>
<td>31.5</td>
<td>2,500</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>6</td>
<td>4,000</td>
<td>57</td>
<td>31.5</td>
<td>2,500</td>
<td>0.50</td>
<td>0.352</td>
</tr>
<tr>
<td>7</td>
<td>(I)</td>
<td>55</td>
<td>28.4</td>
<td>3,500</td>
<td>0.50</td>
<td>0.352</td>
</tr>
</tbody>
</table>

* MVT as defined previously. All values accurate to ±10%.

The web impregnated with prepolymer containing 4000 MW oxyethylene chains performed better on water pickup, but had lower MVT and other serious disadvantages, as will be apparent from Table V, wherein both the wet and dry mechanical strength properties of the a splits are
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tabulated. The "wet" samples contained 20–25% water, based on the dry weight.

TABLE V—STRENGTH OF WET AND DRY SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temper, g. corr. to 45 mil</th>
<th>Tensile, lbs./in.</th>
<th>Stitch tear, lbs./lin.</th>
<th>Tongue tear, lbs./lin.</th>
<th>Stress at 25% elongation, lbs./in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-a, dry</td>
<td>29</td>
<td>1,800</td>
<td>640</td>
<td>230</td>
<td>285</td>
</tr>
<tr>
<td>I-a, &quot;wet&quot;</td>
<td>19</td>
<td>620</td>
<td>400</td>
<td>100</td>
<td>105</td>
</tr>
<tr>
<td>II-a, dry</td>
<td>16</td>
<td>1,010</td>
<td>400</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>III-a, dry</td>
<td>13</td>
<td>250</td>
<td>410</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>III-a, &quot;wet&quot;</td>
<td>17</td>
<td>1,220</td>
<td>800</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>IV-a, dry</td>
<td>12</td>
<td>340</td>
<td>250</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>IV-a, &quot;wet&quot;</td>
<td>730</td>
<td>730</td>
<td>600</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

From these data, it can be seen that the most suitable samples for use in shoe upper material appear to be those containing linear oxyethylene chains of 1000 or 1540 MW.

Example 4
Preparation of a shoe upper material: A 12 x 18 inch (30.5 x 45.7 cm.) impregnated, cured hydrophilic web was made according to Example 1 from the polypropylene web of Example 1(B) and the prepolymer of Example 1(A). The prepolymer concentration in acetone was 30 wt. percent, as in the case of Sample No. 4 of Example 1(B), and the resulting polymer add-on and hydrophilic properties were substantially the same as for Sample No. 4. Thus, the polymer add-on was about 150 wt. percent (a binder-fiber ratio of 60:40 or 1.5:1). To provide a suitable color, the 30 wt. percent prepolymer solution also contained a conventional black pigment dispersed in nitrocellulose paste ("Lampblack 6228" of Interchernical Corp.). Instead of the paper towels of Example 1, squeeze rolls were used after draining of the impregnant. The water cure was with wet steam instead of hot water, and was carried out as follows: The wet web, after passing through the squeeze rolls, was placed horizontally in a steam chamber for one minute. The partially cured web was then turned over to more fully expose the other major surface and steamed an additional 3 minutes, for a total of 4 minutes of cure time. During this 4-minute period the temperature in the steam chamber dropped from 98° to 90° C. The fully cured web was then air dried, sanded to 100 mils thickness, and split into two 50 mil layers, as in Examples 2 and 3.

A leather-like film suitable as a top coat for synthetic leather was extruded, according to the teachings of U.S. application Ser. No. 867,538, filed Oct. 20, 1969 now Patent 3,640,829, from

(1) 300 grams of pellets of polyurethane (the reaction product of 1.0 mole poly(1,4-butylene adipate) glycol, 1.85 moles 1,4-butanediol, and 2.85 moles 4,4'-diphenyl-methylene disiocyanate, available from B. F. Goodrich under the trademark "Estane 5707-F1");

(2) 480 grams 5-micron sodium chloride particles;

(3) 15 grams epoxidized soybean oil (MW 1040, iodine No. 0.81, epoxy equiv. wt. 237); and

(4) calcium stearate.

The extruded film was trimmed to 30.5 cm. in width and had a thickness of 375 microns (15 mils). The film was simultaneously laminated and embossed to a woven cotton cloth backup layer. The embossing provided a "grain"-like appearance on the surface of the extruded film. The extruded film was leached free of sodium chloride, with hot water, thus providing a microporous, embossed film, free of visible pores.

A polyurethane adhesive dissolved in dimethylformamide (DMF) was used to bond the extruded film to a 50 mil split of the impregnated, cured hydrophilic web described previously. The film/cloth/web laminate was square feet of shoe upper material, which was found to have the following properties:

Temper: 95–110 g. (corr. to 63 mils) MVT: 2000±200 g./hr./100 m² Tensile strength: 1400 psi

Tongue tear: 190 lb./linear inch

Flex life ("Bally" Flexometer): More than 350,000 flexes

Water pickup: 12.5% (7.5 hr. at 100% R.H. and 72° F. [22° C.] based on initial weight at 72° F. and 32% R.H.)

In the preceding examples it was found that the cured hydrophilic binder polymers, though capable of absorbing water, were water-insoluble.

What is claimed is:

1. A hydrophilic impregnated web comprising:

   (1) a sheet-like nonwoven fibrous web having an apparent density, prior to impregnation, of at least 0.05 g./cc., and

   (2) a water-insoluble organic hydrophilic binder polymerized in the interstices and along the longitudinal axes of the fibers of said sheet-like nonwoven fibrous web, said organic polymeric hydrophilic binder comprising a disiocyanate prepolymer chain extended in situ with water, said disiocyanate prepolymer containing at least one oxyalkylene chain having a molecular weight in the range of 600–4,400, the major number of the oxyalkylene units in said oxyalkylene chain having the formula

   $$-\text{CH}_2\text{CH}_2\text{O}$$

   wherein n is about 13 to about 100, and two terminal groups of the formula

   $$\text{CH}_2\text{CH}_2\text{OH}_n$$

   wherein Ar is an aromatic nucleus.

2. A hydrophilic impregnated web according to claim 1 wherein said prepolymer contains at least one oxyalkylene chain of the formula

   $$\text{CH}_2\text{CH}_2\text{O}_n\text{ArNH-CO}$$

   wherein Ar is an aromatic nucleus.

3. A hydrophilic impregnated web according to claim 1 wherein said web, prior to impregnation, has an apparent density of at least 0.1 g./cc.

4. A hydrophilic impregnated web according to claim 3 wherein the fibers of said web are heat shrinkable and have been heat shrunk at least 10% of their length.

5. A hydrophilic impregnated web according to claim 3 wherein said molecular weight of said oxyalkylene chain is less than 3000.

6. A hydrophilic impregnated web according to claim 5 wherein said hydrophilic impregnated web has a temper, corrected to 45 mils thickness, of 25–50 grams.

7. A hydrophilic impregnated web according to claim 1 wherein said hydrophilic impregnated web has a temper, corrected to 45 mils thickness, of 25–50 grams.
8. A hydrophilic impregnated web according to claim 1 wherein said hydrophilic, impregnated web has the following physical properties when dry:
ultimate tensile strength—at least 900 p.s.i.,
tongue tear resistance—at least 150 lb./lineal inch,
stitch tear resistance—at least 250 lb./lineal inch.
9. A hydrophilic impregnated web according to claim 1 wherein the ratio of the weight of said organic hydrophilic binder to the weight of said fiber is in the range of 0.3:1-2.8:1.
10. A hydrophilic impregnated web according to claim 1 wherein said web, at equilibrium in a 100% relative humidity atmosphere, absorbs at least 40% by weight of water, based on the dry weight.
11. A laminate comprising:
a microporous topcoat at least 1 mil thick, said topcoat being in superposed adherence to:
an impregnated, cured hydrophilic base web, said base web comprising:
(1) a sheet-like nonwoven fibrous web having an 20 apparent density, prior to impregnation, of at least 0.05 g./cc., and
(2) a water-insoluble organic hydrophilic binder polymerized in the interstices and along the longitudinal axes of the fibers of said sheet-like nonwoven fibrous web, said organic polymeric hydrophilic binder comprising a diisocyanate prepolymer containing at least one oxyalkylene chain having a molecular weight in the range of 600-4,400, the major number of the oxyalkylene units in said oxyalkylene chain having the formula —CH₂CH₂O—
12. A laminate according to claim 11 wherein a porous interlayer is interposed between said microporous topcoat and said base web.
13. A laminate according to claim 11 wherein said base web, tested independently of said laminate, has the following properties when dry:
ultimate tensile strength—at least 900 p.s.i.,
tongue tear resistance—at least 150 lb./lineal inch,
stitch tear resistance—at least 250 lb./lineal inch,
apparent density—at least 0.1 g./cc., and
temper—25 to 50 grams, corrected to a thickness of 45 mils.
14. A method of making a hydrophilic web comprising the steps of:
(1) impregnating a sheet-like nonwoven fibrous web having an apparent density of at least 0.05 g./cc. with a diisocyanate prepolymer containing at least one oxyalkylene chain having a molecular weight in the range of 600-4,400, the major number of oxyalkylene units in said oxyalkylene chain having the formula —CH₂CH₂O—; and
(2) curing the said prepolymer with water.

References Cited

UNITED STATES PATENTS
3,264,134 8/1966 Vill et al. 117—63
3,595,732 7/1971 Tingerthal 161—159

WILLIAM A. POWELL, Primary Examiner

U.S. Cl. X.R.
117—62.2, 140; 156—77, 84, 148; 161—151, 170, 190
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,694,301 Dated September 26, 1972

Inventor(s) Larry E. Gruenewald and John F. Kistner

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

Column 4, line 28, (after "protect") "again" should be -- against --.
Column 6, line 43, "Zerewitinoff" should be -- Zerewitinoff --;
    line 68 (in the formula), "Co" should be -- CO --,
    so that the formula reads
    -- OCN-Ar-NH-CO--.
Column 7, line 43, "0.5-10 denier" should be
    -- 0.5 - 10 denier --.
Column 9, line 39, "of 103 mils" should be -- to 103 mils --.

Signed and sealed this 13th day of March 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. ROBERT GOTTSCALK
Attesting Officer Commissioner of Patents