United States Patent Office

3,436,303

Patented Apr. 1, 1969

3,436,303

WATER-LAID LEATHER SUBSTITUTE CONTAINING LEATHER FIBERS, STAPLE FIBERS AND POLYURETHANE AQUEOUS SLURRY AND METHOD FOR MAKING SAME

Albert E. Raymond, Roseville, and William J. Fraser, Forest Lake, Minn., and Frank Swedish, Jr., Hudson, Wis., assignors to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

No Drawing. Filed Sept. 16, 1965, Ser. No. 487,890
Int. Cl. D21h 3/40
U.S. Cl. 162—123 11 Claims

ABSTRACT OF THE DISCLOSURE

Leather substitutes formed from aqueous slurry containing a major portion of globular nonfibrous elastomeric polyurethane material and a minor portion of fibrous material, at least one-third of the fibrous material being leather fibers and the remainder being staple fibers such as nylon fibers, such slurry being formed into a sheet by deposition on a papermaking screen, said sheet then being dried and preferably heated to at least 120° C.

This invention relates to leather substitutes and compositions useful in the preparation thereof. More particularly the invention relates to leather substitutes based on water-laid sheet material formed of a major portion of globular, nonfibrous elastomeric material and a minor portion of fibrous material.

Previous efforts have been made to form leather substitutes using papermaking technology in order to take advantage of the economies inherent in such procedures, see for example, U.S. Patent 3,051,612, issued to Bennett, Aug. 28, 1962, and U.S. Patent 2,601,671, issued to Wilson et al., June 24, 1952. Efforts in the past have generally been limited to compositions containing a major portion of fibers and a minor portion of polymeric binding material. Such compositions, particularly those containing leather fibers, when formed into water-laid sheets form a stiff board-like product generally suitable only for limited uses, for example, leatherboard useful as sole leather or the like.

Known leather substitutes suitable for forming shoe uppers have been manufactured without utilizing papermaking technology by complex procedures designed to create microporosity in a substantially wholly synthetic polymeric coating, see for example, U.S. Patent 3,190,766, issued to Yuan, June 22, 1965. Such processes do not afford the economies made possible by the use of papermaking technology and have other disadvantages.

It is an object of the present invention to provide a leather substitute suitable for the manufacture of shoe uppers, having physical characteristics comparable to those of the finest quality natural leathers. The constructions of the present invention are permeable to air and moisture vapor, are strong, tough, porous and have good flex endurance. The materials further have the appearance and general performance characteristics of leather, preferably displaying a delayed elastic recovery as contrasted to either a snappy rubbery characteristic or a permanent set of the type displayed by some resinous materials. The polymeric components of the sheet materials are sufficiently resistant to flow at ambient temperatures to preclude loss of porosity and moisture permeability under the temperature and stress conditions normally encountered by footwear. The materials further have significantly higher moisture regain value than do leather substitutes based wholly on synthetic polymers.

These and other objects and advantages are achieved by forming a water slurry in which the solids are about 50 to 80 percent by weight globular elastomeric polyurethane particles and 20 to 50 percent fibrous material, at least ⅓ of the fibrous material being leather fiber and substantially the remainder being staple fiber such as nylon and preparing a water-laid sheet therefrom.

It has been found that elastomeric polyurethane compositions, of the type hereinafter described, particularly when coagulated from a latex, result in a dispersion containing globular (i.e. nonfibrous) polymer particles having properties such that the same can be formed into a useful sheet on a foraminous surface even when used in compositions containing a major proportion of the globular polymeric particles and a minor portion of fibrous material. In order to provide the desired leather-like qualities such as the moisture regain characteristic, the fibrous component of the composition should be at least one-third by weight tanned leather fibers, the remainder of the fibrous component being substantially composed of staple fibers, preferably of a high strength flexible type such as nylon, polyethylene terephthalate, polypropylene or acetal copolymers (such as those based on trioxane). The total composition should, in any event, contain a minimum of at least about 10 percent by weight leather fibers, 20 to 25 percent leather fibers being preferred. The staple fibers impart high tensile and tear strength and flex endurance to the sheet material, and serve to make the sheet more porous.

The elastomeric polyurethane materials useful in forming the sheet materials of the present invention are present in the form of discrete globular particles in the 1–100 micron average particle size range. Even though such particles may tend to agglomerate, the individual particles are readily identifiable as falling within the abovementioned size range. These polyurethane particles are preferably formed from latices based on polyetherurethane or polyurethane-urea elastomers. Other urethane elastomers, for example, polyesterurethanes having the hereinafter specified minimum physical properties are also useful. Examples of the suitable latices are those disclosed in U.S. Patent 2,968,575, issued Jan. 17, 1961 (Mallonee), and British Patent No. 880,665, issued Oct. 25, 1961. The preferred polyurethanes are those formed from the reaction product of an organic diisocyanate with a polyalkylene ether glycol or polyol chain extended with a compound having at least two active hydrogen atoms, especially a diamine such as piperazine, dimethyl piperazine, hydrazine, methylene bis-3-chloro-4-aniline, 2,4-tolylene diamine, ethylene diamine, ethanol amines, polyalkylene ether diamines or the like. Alternatively polyalkylene ether glycols or water may be used as chain extending agents. Leather substitutes having outstanding characteristics can be prepared by using chain-extended polymers formed by the reaction of isocyanate terminated prepolymers of polyalkylenether glycols and organic diisocyanates with the above-noted diamines to provide a polyurethane having a number average molecular weight of at least about 10,000.

The elastomeric polyurethane materials can be formed into globules suitable for sheet formation on a paper machine by coagulation from a latex under controlled conditions, hereinafter exemplified, or alternatively, without going through a latex stage, by a direct reaction in aqueous medium under suitable conditions of an isocyanate-terminated prepolymer with water or a diamine or by other techniques providing the desired globular particle.

Globular polymer particles may be prepared by adding one or more flocculating agents to a latex to cause coagulation. Examples of suitable flocculating agents are alum, sodium carbonate, sodium chloride, karaya gum, locust bean gum, and the like. These agents may be added to the aqueous latex either prior to or subsequent to admixture with the fibrous materials.

As stated above the fibrous constituent of the constructions must be at least one-third weight of leather fibers. The presence of at least about 10 percent by weight of the total construction of leather fibers imparts to the construction a leather-like feel and appearance and a high moisture regain value and assists in the formation of a breathable sheet which has a surface receptive to finishing by standard leather finishing techniques. The leather fibers are preferably derived from leather scrap comminuted to fibrous form, the degree of comminution of the fibers being varied in accordance with the properties desired in the final sheet material. Fibers ranging in length from about 0.25 to about 2 millimeters have been found preferable. Shorter fibers such as beater-treated leather fibers generally result in a smoother sheet surface. But unbeaten chrome-tanned fibers are preferred where higher strength is desired. Vegetable tanned fibers have also been found suitable.

The staple fibers significantly improve tensile strength, tear strength and flex durability as well as breathability of the leather substitutes of the invention, thereby enabling their use as shoe uppers materials and the like. Although polyamide, e.g., nylon fibers are preferred, high strength products can also be prepared using fibers of wholly synthetic polymers such as polypropylene, polyesters, e.g., polyethylene terephthalate and acetal copolymers (e.g., those based on trioxane). By "wholly synthetic polymer" as the term is used herein is meant polymeric material synthesized by man as distinguished from polymeric products of nature or derivatives thereof. High strength fibers generally have a tensile strength of at least 4 gm. per denier. In applications as in a base sheet for shoe uppers where high tensile and flex strength are necessary, the high strength flexible fibers should form at least 10 percent of the weight of the construction, 10 to 20 percent being preferred. Other fibers such as rayon, cellulosic fibers, glass, asbestos, and the like may be used to vary the physical properties of the sheet. The staple fibers preferably are in the size range of from 1 to 6 denier and range in length from 1/8 to 1/2 inch, 1/4 to 3/8 inch being preferred. Minor amounts (e.g., 1 percent by weight of the sheet) of fibrids may also be included as part of the fibrous constituents of the sheet.

Sheets having smoother surfaces may be formed by increasing the proportion of leather fibers in the fibrous component at least near the top surface of the sheet. Thus a typical leather substitute may be formed from a base sheet containing 50 percent to 80 percent polyurethane particles, the remainder being fibrous material preferably present in the approximate proportion of two parts leather fibers to one part nylon or other staple fibers upon which is superimposed another layer or ply having approximately the same or higher polymer content but in which substantially all (e.g., at least 85 percent) of the fibers are leather. Such constructions can be prepared by forming the individual layers separately on a papermaking machine and then laminating the same, generally using adhesives and/or heat and pressure, or more preferably by using paper making apparatus having two or more head boxes or cylinders to form a multiply composite sheet.

When a multiply construction is produced by assembling two or more layers of material formed in accordance with the invention, typically a substrate layer will contain 60 to 70 percent elastomeric polyurethane, 15 to 30 percent leather fibers and 10 to 20 percent staple fibers maintaining an approximate ratio of leather to staple fibers of 2 to 1. An intermediate ply may be formed comprising for example, 75 percent globular elastomeric polyurethane material and 25 percent nylon fibers and a top ply may comprise about 75 percent elastomeric polyurethane materials and 25 percent leather fibers. These plies typically have an approximate thickness of 50 to 55 mils, 12 to 15 mils, and 20 to 25 mils, respectively. When hot pressed the multiply sheet is typically 70 mils thick. The composite sheet may then be ground or buffed to smooth the surface and reduce the thickness to about 60 to 65 mils. A multiply construction of this type is then in a form suitable for finishing by conventional leather finishing techniques.

An alternative method of forming a leather substitute using the water-laid sheet materials of the present invention involves the application with or without an adhesive of a microporous polymeric layer, for example of the type disclosed in Holden U.S. Patent 3,100,721, issued Aug. 13, 1963 to a substrate layer described in the preceding paragraph.

In most instances it has been found that hot pressing or simple heating of the sheets for a period of time sufficient to cause deformation of the polyurethane and some flow around the fiber junctures increases both the tensile strength and the breathability of the sheet. However, protracted exposure to elevated temperatures combined with pressure, as in a press or between heated rollers, can cause the polyurethane to flow into a continuous phase and form a more dense, essentially impervious sheet.

The slurry from which the sheets are formed should have a consistency approximately that normally used in papermaking procedures. The degree of mixing and smoothness of the slurry can be improved by beater treatment. Slurries of the type described can be formed into a water-laid sheet using Fourdrinier machines, simple cylinder machines, or modified cylinder machines such as those which are vacuum assisted and have a head box rather than a vat. Laboratory size sheets may be formed by depositing the slurry on any suitable foraminous surface, such as a screen or felt, to form hand sheets.

In spite of the high polyurethane content of the sheet materials of the present invention they are surprisingly open and breathable. Gurley densometer (TAPPI T–460) readings of about 5 to 500 seconds for 400 cc. air per 60 mil sample thickness being typical for the single ply constructions prior to hot pressing. Sheets have readings of about 5 to 2,000 seconds generally are useful, while less than about 500 seconds is preferred for leather substitutes intended for use as shoe uppers in order to provide comfort to the wearer. It has been found that the tensile strength of the sheet material generally is at a maximum at about 60 percent to 75 percent polyurethane concentration when utilizing a mixture of leather and staple fibers. The percent stretch of the material generally increases progressively as the polyurethane content is increased. When the polyurethane is present in concentrations of less than about 50 weight percent the tensile and elongation properties of the resulting constructions are unacceptably low for leather substitutes intended for foot wear. The porosity and hence breathability of the sheet materials on the other hand decreases with increasing polyurethane concentration, concentrations above about 80 weight percent resulting in inadequate porosity for leather substitute materials.

The polyurethanes which result in useful leather substitutes must be elastomeric and resistant to creep or flow at ambient temperatures. They generally have been found to have a brittle temperature of about −10° C. or lower, and preferably −30° C. or lower. The heat distortion temperature as hereafter defined should be at least +40° C. or preferably at least +75° C. The polyurethane should have a tensile of at least 300 p.s.i., more preferably at least 1000 p.s.i., and should have an elongation at break of at least 100 percent, preferably at least 300 percent. The modulus (stress at 100 percent elongation) should be between 100 and 2,000 p.s.i. and preferably between 150 and 400 p.s.i. for shoe uppers. These properties can be measured on the polymer as isolated and formed in any suitable manner into a coherent shape, such as a film, and the resulting form, e.g., cast film, may be heated or hot pressed prior to testing to insure the effective removal of solvent, etc. However, it should be understood that the above properties are merely illustrative of those displayed by elastomeric polyurethanes useful in the practice of the invention, since the measurements obtained on any given test sample may vary with the technique used to prepare the sample for test purposes. For example, the properties may be altered by the presence of residual amounts of emulsifying agents, incomplete solvent removal, additional heat curing occurring during or after film formation, physical working of the film, or the presence of moisture. Therefore the above values are representative of the properties measured on samples of the preferred elastomeric polyurethanes. Test samples should be prepared by using conditions as similar as practically possible to those encountered in manufacturing the sheets of the invention.

As noted above, the chain extension of isocyanate-terminated prepolymers provides one method of forming polymers useful for the invention. For example, prepolymers bearing terminal isocyanate groups may be prepared by adding one or more polyalkylenether glycols, polyalkylenether diamines or hydroxy terminated polyesters to an excess of organic diisocyanate and by carrying out their reaction in a temperature range from about room temperature to about 100° C. Another procedure is to react the diisocyanate with an excess of polyalkylenether glycol, polyester glycol or polyalkylenether diamine so as to prepare the dimerized glycol or diamine, and then cap this material with isocyanate groups, i.e., add it to an excess of diisocyanate to form a prepolymer having terminal isocyanate groups. Reactive prepolymers such as these may subsequently be converted to the desired polyurethanes of this invention by reaction with compounds having at least two reactive hydrogen atoms. By "active hydrogens" as the term is used herein, is meant hydrogens which display activity according to the Zerewitinoff test described in J.A.C.S., 49, 3181 (1927). Typical groups are hydroxyl, carboxyl, primary or secondary amino, and mercapto groups.

Various organic diisocyanates may be used in the preparation of prepolymers for use in the invention. Because of their ready availability and the fact that they are liquid at room temperature, mixtures of the 2,4- and 2,6-toluene diisocyanate isomers are preferred. Other preferred diisocyanates are 4,4'-diphenylene methane diisocyanate, and 3,3'-dimethyl-4,4'-diphenyl diisocyanate. Further examples of useful aromatic diisocyanates include paraphenylene diisocyanate, meta-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenyl ether diisocyanate, 3,3'-dimethoxy-4,4'-diphenyl diisocyanate, and 4-chloro-1,3-phenylene diisocyanate. Suitable aliphatic or cycloaliphatic diisocyanates include the simple alkyl diisocyanates such as hexamethylene diisocyanate as well as more complex materials such as bis(2-isocyanatoethyl)fumarate, bis(2-isocyanatoethyl)carbonate, bis(2-isocyanatoethyl)-4-cyclohexene - 1,2-dicarboxylate, bis(2-isocyanatoethyl) - 1,4,5,6,7,7'-hexachloro-5-norbornene - 2,3-dicarboxylate.

Polyalkylenether glycols or polyols used in preparing such prepolymers have molecular weights generally ranging from about 300 to about 5,000 and preferably from about 400 to about 3,000, the more resilient polymers normally being obtainable from higher molecular weight glycols. Examples of such polyalkylenether glycols are polyethylenether glycol, polypropylene ether glycol, polytetramethylene ether glycol and higher polyalkylenether glycols. These polyether glycols are prepared by well known ring opening or condensation polymerizations. When these polyols contain recurring oxyethylene groups, the total weight fraction of such oxyethylene groups should be controlled since this structure tends to confer water sensitivity to the finished product. Other suitable polyols include castor oil, hydroxyl terminated polybutadiene and hydroxyl terminated vinyl polymers, preferably in the 500–5,000 molecular weight range.

Polyalkylenether diamines prepared from polyglycols, such as polypropylene glycol, may also be used to prepare useful polyurethane-ureas, as described in U.S. Patent 3,179,606. Such diamines usually have molecular weights from about 1,000 to about 10,000.

Polyester glycols or polyols may be used alone or together with polyether glycols or polyols in the preparation of the polymers for use in this invention. Polyester glycols or polyols may be prepared for example by reacting dicarboxylic acids, esters or acid halides with simple glycols or polyols. Suitable glycols are polymethylene glycols, such as ethylene, propylene, tetramethylene, decamethylene glycols, substituted polymethylene glycols, such as 2,2-dimethyl-1,3-propane diol, and cyclic glycols, such as cyclohexanediol. Polyols such as glycerine, pentaerythritol, trimethylol propane and trimethylol ethane, may be used in limited amounts to introduce chain branching into the polyester. These hydroxy compounds are reacted with aliphatic, cycloaliphatic or aromatic dicarboxylic acids or lower alkyl esters or ester forming derivatives thereof to produce polymers bearing terminal hydroxyl groups, having melting points less than about 70° C., and being characterized by molecular weights in the same approximate range as for the aforementioned polyalkylene ether glycols; preferably the molecular weights are from about 400 to about 4,000 and more preferably from about 1,000 to about 2,000. Examples of suitable acids are, for example, succinic, adipic, suberic, sebacic, phthalic, isophthalic, terephthalic and hexahydro terephthalic acids and the alkyl and halogen substituted derivatives of these acids.

The formation of a prepolymer can be carried out with or without solvents, although the presence of solvent may often facilitate mixing and handling. Common solvents which are inert to isocyanates may be used, such as toluene, xylene, etc. Chain extension of the prepolymer may be carried out in solution, using such highly polar solvents such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-methyl pyrrolidone, etc.

In many cases it is desirable to obtain the final polymer in the form of an emulsion. In this event the prepolymer may be chain extended with water or polyamine during the emulsification process, as in the procedure of Mallonee, U.S. Patent 2,968,575; or Wyandotte, British Patent 880,665. Alternatively an emulsion can be prepared by pouring a polymeric solution slowly into water containing suitable dispersing agents with vigorous agitation. The solvent contained in the polymer can be allowed to remain in the emulsion or removed by distillation if the emulsion is sufficiently stable.

Emulsions may be treated with alum, salt or other agents to produce the coagulated particles desired for this invention. Agents such as Na_2CO_3 are also preferably added to control the pH of the mixture to optimize coagulation conditions. It will be apparent to those skilled in the art that the pH, type and amount of precipitating agents, etc., should be selected according to the type of emulsifiers, stabilizers, etc., present in the latex. In such cases the individual coagulated particles usually have a number average particle size between about 1 and 5 microns. Another method of coagulation involves freezing the latex.

In some cases the globular particles desired for this invention may be prepared directly during the polymerization step, or they may be formed by taking a solution of the polymer and adding it to a nonsolvent with stirring. When thus formed, the globular particles are usually larger than those formed by the coagulation of latices, and may range from 2 to 100 microns in diameter, although they usually have a diameter of 5 to 30 microns. It will be apparent that, although the polyurethane particles can be formed in various ways, the particle size must be controlled within the earlier mentioned limits.

The prepolymers before chain extending, or the emulsions before coagulation, or the polymer solutions before precipitation, or the coagulated globular particles after they are formed, can be modified with other ingredients such as surfactants, plasticizers, dyes, pigments, minor amounts of other compatible polymers, or agents which provide light, heat, or oxidative stability, and the like, as long as the elastomeric character and particulate nature of the polyurethane is not lost.

As an alternate to the use of a di- or polyisocyanates, phosgene chemistry may be used directly to prepare the polyurethanes. For example, as is well known, phosgene may be reacted with a glycol to form a bis-chloroformate, and the latter material then may be reacted with a diamine to yield the desired polyurethane.

The following examples, in which all proportions are given in parts by weight unless otherwise indicated, will serve to illustrate but not limit the invention. They will also exemplify the surprising fact that most of the relatively small nonfibrous polyurethane particles are retained on the screen even though the slurry contains only a minor amount of fibrous material and the screen mesh openings are normally significantly greater than the diameter of the polyurethane particles.

EXAMPLE I

A slurry was formed by adding 770 gm. of chrome-tanned leather fibers having in their unbeaten form a freeness of 10 to 20 seconds when tested on a Williams freeness tester (Lorum Fiber Co. Y–020–015) to 22 liters water in a 1 pound Valley beater, in which the slurry was mixed for about 7 minutes at which time the consistency was checked and found to be approximately 2.7 percent solids. 370 ml. of this slurry (10 dry gm. leather fibers) were mixed with 1.5 liters tap water in a 3,000 ml. beaker equipped with an air-motor driven stirrer and mixed at 600 revolutions per minute while adding the following remaining ingredients in the indicated order and amount:

10 ml. 1% surfactant solution Na salt sulfonated naphthalene-formaldehyde condensation product (Rohm & Haas Tamol SN).

TABLE I

Ratio polymer: Fiber	Bas. wt., lb./3,000 ft.^{2}	Caliper, mils	Density, lb./3,000 ft.^{2} x caliper	Tensile, lbs./in. width	Percent stretch at rupture	Gurley porosity, sec. for 400 cc.'s	Taber stiffness gm.-cm.	Percent moisture regain
67:33 (Ex. I)	820	68	12.1	148	52	231	142	----------
80:20	789	52	15.2	94	70	1,880	65	3.2
70:30	826	61	13.5	150	59	156	131	4.1
60:40	837	73	11.5	154	54	53	169	4.9
50:50	837	85	9.8	136	42	20	224	5.7
40:60	861	100	8.6	70	30	12	281	6.5

60 gm. latex, 50% solids, emulsified reaction product of organic diisocyanate and polyalkylene ether glycol chain extended with piperazine (a film cured 10 min. at 121° C. had a tensile strength of 4,190 p.s.i., a 100% modulus of 240 p.s.i., elongation at rupture of 580 percent, and a Shore A hardness of 55).

30 ml. 5% alum.

20 ml. 5% Na_2CO_3 (five minutes mixing time was allowed after the addition of the alum before addition of the Na_2CO_3).

The contents of the beaker were transferred to an 8" x 8" Williams hand sheet mold with an 80 mesh screen. 5 gm. nylon fiber ¼" length, 1.5 denier (Du Pont 200–D) dispersed in 500 ml. water were added and mixed in uniformly. 15 gm. 0.25% karaya gum containing 0.08% NH_4OH were added to insure complete coagulation of the latex. The Na_2CO_3 served to raise the pH thereby improving the fiber dispersing properties of the karaya gum. The NH_4OH served to deacetylate and improve the solubility of the karaya gum. After thorough mixing, the mixture was deposited on the wire and allowed to drain. Excess water was blotted from the hand sheet which was then removed from the wire. The hand sheet was placed between two blotters and pressed in a Meade press at 35 lbs. per inch for 1 minute. The sheet was removed from the press and dried on a Williams sheet drier at surface temperatures of about 230° to 240° F. for about 30 minutes.

The 8" x 8" sheet was first weighed carefully. It was then cut to 7" x 7" and again weighed. The basis weight was calculated from this (TAPPI T–410) and the caliper determined with a hand gauge (TAPPI T–411). Three cuts (½" x 7") were then successively run on a Thwing-Albert electrohydraulic tensile tester to determine tensile and elongation using a 4" separation between the jaws and a rate of 10" per minute (TAPPI T–404 and T–457). Porosity was measured following the procedure of TAPPI T–460 and the time in seconds is that required to pass 400 cc. of air. The stiffness was determined at 70° F. on a 2¾" x 1½" piece using a Taber V–5 tester at a 15° deflection according to TAPPI T–489. The properties of the sheet are given in Table I.

EXAMPLE II

Example I was repeated employing the same latex, the same amounts of precipitating agents and maintaining a 2:1 leather to nylon ratio in the fiber composition to produce a series of hand sheets in which the ratio of polymer to total fiber was varied between 80:20 and 40:60. The hand sheets were formed and dried from each of the compositions following the procedure set forth in Example I. The properties of the resulting sheets are summarized in Table I.

The moisture regain values for the samples were obtained by drying the same to constant weight over P_2O_5, weighing, maintaining the samples at 24° C. over a saturated $Ca(NO_3)_2$ solution (51% relative humidity) until constant weight was again reached, reweighing, and calculating moisture regain as percent of the weight of the humidified sample.

The sample containing only 40% polymer was a loose fibrous porous material useful for only such applications as insoles, gaskets or the like. The 50:50, 60:40, and 70:30 samples all formed materials suitable as base sheets for the formation of shoe uppers, the density and rubberyness of the sheets increasing with increasing polymer content. The 80:20 sample was somewhat more dense than the preferred materials and represented the approximate upper limit of polymer content. The latter four samples were subjected to more than 500,000 flexes using a Newark Leather Finish Co. flex tester without any sign of failure. The specimens improved significantly in their resistance to piping, or wrinkle formation when doubled over, with increasing polyurethane concentration.

EXAMPLE III

The experiments of Example I were repeated maintaining the same weight proportion of polymer, leather fiber and staple fiber, namely 6–2–1, and substituting various other staple fibers for the nylon fibers. The results are tabulated in Table II.

TABLE II

Staple fiber	Basis weight, lb./3,000 ft.²	Caliper, mils	Density, lb./3,000 ft.² x caliper	Tensile, lb./in. width	Percent stretch at rupture	Gurley porosity, sec. for 400 cc.'s	Taber stiffness, gm.-cm.
Polyethylene terephthalate (Dacron) ½", 6 denier	696	71	9.8	91	37	48	210
Polyethylene terephthalate (Dacron) ¼", 3 denier	682	67	10.2	127	35	52	181
Polypropylene, ¼", 1.5 denier	738	72	10.3	98	39	43	144
Acetal copolymer based on trioxane (Celcon) ¼", 2 denier	787	73	10.8	100	45	157	157
Dull rayon, .1-1.5 mm	764	62	12.3	87	29	411	165
Bright rayon, ¼", 1.5 denier	793	67	11.8	93	33	187	152
Polyamide (Zytel 63) ¼"	812	70	11.6	66	58	131	106
No. 701 glass fiber	731	61	12	67	37	288	200

All of the hand sheets were remarkably similar in appearance and general feel to that of Example I, which contained the nylon staple fibers. The sheets containing the polyethylene terephthalate, polypropylene and acetal copolymer fibers most closely approximated the properties of the nylon containing sheet, these sheets being useful as a substrate sheet in the formation of shoe uppers, nylon fibers being preferred. In addition to the properties tabulated it was noted that all of the sheets made with fibers other than rayon were inferior to the sheet of Example I made with nylon in piping.

EXAMPLE IV

A urethane prepolymer was prepared by mixing 239 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate and 1,340 parts polyoxypropylene glycol of molecular weight about 2000 (Hydroxyl No. 57.5) in a dry nitrogen purged 3-liter reaction vessel. The mixture was heated to 90 to 95° C. for 2 hours during which time it was stirred slowly.

A polymer dispersion was formed by mixing 250 ml. H_2O, 1.3 gm. KOH, 1.3 gm. polyvinyl pyrrolidone and 1.2 gm. ethylene diamine in a 2-liter resin flask with an Eppenbach Homo-Mixer. 70 gm. of the prepolymer mixed with 4 gm. oleic acid was added and mixing was continued for 1 minute. The mixture was transferred to a 1 pint round bottle which was placed on a roller revolving at 2 revolutions per second for 15 minutes. A dispersion of globular particles ranging in size from about 8–15 microns was obtained.

370 gm. of the 2.7% leather slurry of Example I and 1,500 ml. of soft water were placed in a 3,000 ml. beaker. This was stirred at 600 r.p.m. with a 3-blade stainless steel agitator. 10 gm. of a 1% solution of the disodium salt of condensed naphthalene sulfonic acid (Tamol SN) as a dispersant, and 24 gm. of 5% sodium carbonate solution, were added. Enough of the dispersion of globular particles to give 30 gm. of solids was added and the mixture was stirred for 5 minutes, and then poured into an 8" x 8" Williams hand sheet mold with a 70 mesh wire, containing 1 inch of water at the bottom. A dispersion of 5 gm. of nylon fibers (¼" x 1½ denier) in 500 ml. of water and 15 gm. of 0.25% solution of karaya gum were added. The slurry was raked well in both directions several times and then allowed to drain. The resultant sheet was blotted with blotting paper, then pressed between blotting paper at 35 pounds per square inch for 1 minute, and subsequently placed on a hot drier at 230° F. until dry (about 30 minutes). The sheet was then placed in a constant temperature and humidity chamber (70° F. at 50% relative humidity) for 24 hours for water recovery before testing. Properties are reported in Table III. After 1,000,000 flexes on a Newark Leather Finish Co. flex tester the sheet showed no sign of failure.

EXAMPLE V

The prepolymer of Example IV was chain-extended with hydrazine rather than ethylene diamine, and emulsified with a compound formed of 10% polyoxyethylene and 90% polyoxypropylene (Wyandotte Pluronic L 61); the molecular weight of the propylene base of this emulsifier is 1,750 and of the total, therefore, 1,930.

250 cc. H_2O, 0.5 gm. of hydrazine hydrate and 2 gm. of Pluronic L 61 were stirred in a 2 liter resin flask and a mixture of 60 gm. of prepolymer and 2 gm. of Pluronic L 61 were added as in Example IV. An emulsion was obtained. For sheet preparation the procedure and the proportion of ingredients were the same as in Example IV except that 50 gm. of sodium chloride in 500 cc. of water were added after adding the latex to cause coagulation of the latex. Sheet properties are given in Table III.

EXAMPLE VI

Into a 2,000 gallon Dowtherm heated kettle equipped with a fractionating head and a decanter was charged 530 pounds of toluene, 11,655 pounds of #1 castor oil, and 945 pounds of diglycolic acid and an inert gas purge was passed through the batch. The jacket was heated and the batch brought to the toluene reflux temperature of 300 to 315° F. Water was removed azeotropically and the toluene returned to the batch. The reaction was continued until the acid number was reduced to below 5. The final batch temperature was 425° F. The toluene was removed by blowing with an inert gas. The batch was cooled and dropped into a 3,000 gallon tank containing 5,085 pounds of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate, maintained at a temperature below 170 to 180° F. The final viscosity was about 15,000 cps. at 25° C. and the isocyanate equivalent was 445.

250 ml. of water, 2 gm. of isooctylphenyl polyethoxy ethanol surfactant (Triton X–102) and 1.5 gm. of a 64% hydrazine solution in water were placed in a 2 liter flask equipped with an Eppenbach Homo-Mixer and after stirring briefly, 70 gm. of the above prepared prepolymer containing 2 gm. of isooctylphenyl polyethoxy ethanol were added slowly with stirring. Mixing was continued for 1 minute after the addition, and the resultant latex then placed in a 1 pint bottle and rolled at 2 revolutions per second for 15 minutes. A stable emulsion was obtained.

Coagulation of the emulsion and preparation of the sheet containing leather and nylon fibers was the same as for Example V. Sheet properties are given in Table III.

EXAMPLE VII

Into a 200 gallon reaction vessel equipped with a gas purge were placed 1,558 pounds of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate and 785 pounds of polypropylene glycol 400. The reaction temperature was kept below 145° F. by cooling. After reaction, the batch was cooled to 100° and 157 pounds of a triol prepared from trimethylol propane and propylene oxide and having a molecular weight of from 420 to 450 were added. The exotherm was again held to 145° F. After reaction the batch was heated to 150° F. for 2 hours, then cooled to 105° F. with full vacuum.

One part of the above resin was then heated at 200° F. for 2 hours with 2 parts of polypropylene glycol of molecular weight 2,000. The product had an isocyanate equivalent of 1,000.

An emulsified polymer was formed by mixing 250 ml. of water, 1.3 gm. of KOH, and 0.6 gm. of 64% hydrazine in water in a 2-liter resin flask equipped with an Eppenbach Homo-Mixer. 70 gm. of the above prepolymer mixed with 4 gm. of oleic acid was added and mixing was continued for 1 minute. The mixture was transferred to a 1 pint round bottle which was placed on a roller at 2 revolutions per second for 15 minutes. A stable latex was obtained.

A sheet was formed as in Example V. Properties of the sheet are given in Table III. The sheet showed no sign of failure after 500,000 flexes on a Newark Leather Finish Co. flex tester. The sheet was tested after air drying and after placing in an oven at 280° F. for 1 hour. The effect of heat to help unify the sheet, probably by improving the adhesion between the polyurethane and the fibers without harming the porosity, is shown by the data given in Table IV. When heating was tried in a press using zero ram pressure, the surface was fused sufficiently to reduce the porosity to a considerable extent.

EXAMPLE VIII

Two prepolymers were used, the first being that of Example IV. The second prepolymer was a triol prepared as follows: 458.2 parts of a 30:20 mixture of 2,4- and 2,6-toluene diisocyanate and 2597 parts of a 1,000 molecular weight triol prepared from glycerine and propylene oxide were stirred slowly at 73° C. for 2 hours under a nitrogen purge to form a product having an isocyanate equivalent of 1175. An emulsion was formed by mixing 35 gm. of each of the two prepolymers and processing the same as in Example VII. Sheet preparation was the same as in Example V and sheet properties are given in Table III. After 640,000 flexes on a Newark Leather Finish Co. flex tester the sheet showed no sign of failure. Another polyurethane latex was prepared from the same two prepolymers except using 60 gm. of the diol prepolymer of Example IV and 10 gm. of the triol prepolymer of Example VIII. A sheet was made as in Example V (designated VIII–B). This sheet was tested after drying at room temperature, and after heat treatment, with results similar to those obtained in Example VII as seen in Table IV.

EXAMPLE IX

1,000 parts of a blend of 0.8 mole of polytetramethylene ether glycol (mol. wt. 1,060) and 0.2 mole of polyproplyene glycol (mol. wt. 1,080) were added to a distilling flask together with 250 parts of isooctane. 135 parts of the isooctane were distilled off and the batch cooled to 70° C. 245 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate were added and the heat of reaction raised the temperature to 90° C. where it was held for 2½ hours.

60 gm. of the above prepolymer and 10 gm. of the triol prepolymer described in Example VIII were emulsified according to the procedure given in Example VII and a sheet prepared as in Example V. Sheet properties are reported in Table III. After 560,000 flexes on a Newark Leather Finish Co. flex tester the sheet showed no sign of failure.

EXAMPLE X

Into a 25 gallon hot oil heated kettle were added 45 pounds of adipic acid and 37.6 pounds of neopentyl glycol. Enough toluene was added to fill the decanting system which was purged with inert gas. The batch was heated and water was removed azeotropically until the acid number was reduced to zero. The batch was cooled to 300° F., and the entrainer removed by vacuum. The batch was then cooled to room temperature. 140 parts of the above polymer were added to 35 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate in a suitable reaction vessel, blanketed with an inert gas purge and then heated with slow stirring to 160° F. for 2 hours before cooling. Emulsification was the same as in Example VII and sheet preparation the same as in Example V. After 880,000 flexes on a Newark Leather Finish Co. flex tester, the sheet showed no sign of failure.

EXAMPLE XI

From a mixture of 400 parts by weight of polyethylene adipate (Multrathane R14) and 300 parts by volume of toluene was distilled 160 ml. of toluene to remove traces of water. 69.6 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate were added and the mixture heated to 107° C. for 3 hours and then cooled.

This prepolymer (60 parts) and the triol prepolymer of Example VIII (10 parts) were emulsified as in Example VII and a sheet was made as in Example V. After 1,215,000 flexes on a Newark Leather Finish Co. flex tester the sheet showed no signs of failure.

EXAMPLE XII

105 gm. of a hydroxy terminated polybutadiene containing 0.1 hydroxyl equivalents were mixed with 18 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate and placed in a bottle which was purged and sealed for 24 hours. Emulsification was carried out as in Example VII using a mixture of 60 gm. of the polybutadiene prepolymer and 10 gm. of the triol prepolymer of Example VIII. A sheet was formed as in Example V. After 1,215,000 flexes on a Newark Leather Finish Co. flex tester, the sheet showed no sign of failure.

EXAMPLE XIII

Into a suitable reaction vessel were placed 2,400 parts of polytetramethylene ether glycol (molecular weight 1,060), and 960 parts substantially water free toluene, 288 parts of toluene were distilled to render the charge substantially water free. The batch was cooled to 73° C. and 591.4 parts of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate were added. The temperature dropped to 68° C. and subsequently rose to 96° C. When the temperature dropped back to 90° C. it was held there for 155 minutes before cooling. Emulsification was carried out as in Example VII and a sheet formed as in Example V.

EXAMPLE XIV

Into the 2 liter resin flask were placed 250 ml. of water, 5 gm. sodium alkyl arylsulfonate and 0.9 gm. of hydrazine hydrate. 60 gm. of the prepolymer of Example XIII were added as in Example XIII. An unstable emulsion resulted which was useful for about 8 hours if shaken gently from time to time. Sheet preparation was the same as in Example V. Use of a sodium alkyl arylsulfonate dispersing agent instead of potassium oleate produced a sheet having better physical properties.

EXAMPLE XV

70 gm. of the diol prepolymer described in Example IX were mixed with 4 gm. of oleic acid. Chain extension and particle formation were carried out as in Example IV. A dispersion of moderately fine particles resulted which tended to form agglomerates which could be broken down again by placing on the Waring Blendor for 1 minute with enough water to fill half the cup. Sheet formulation was the same as in Example IV. Sheet properties are given in Table III. Sheet properties (Table IV) were also obtained after air drying and after heating in an oven at 230° F. and at 280° F.

EXAMPLE XVI

Into a 1 liter 3-neck round bottom flask were charged 500 gm. of dihydric polyoxyethylene-polyoxypropylene, of molecular weight 1148, and 320 gm. of toluene. 160 gm. of the toluene were distilled off to remove traces of water. The charge was cooled to 98° C. and 151.7 gm. of an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate were added. The charge was heated to 120° C. for 3 hours and then cooled to room temperature. 250 gm. of the above prepolymer solution (220 gm. of prepolymer) was placed in a Waring Blendor. To this were added 30.8 gm. of toluene and 12 gm. of an emulsifier consisting of a dihydric polyoxyethylene-polyoxypropylene of molecular weight 10,000, with a polyoxyethylene content of about 80%, and a molecular weight of 2,250 for the polyoxypropylene base, dissolved in 200 gm. of water. The blender was run for 1 minute at high speed. 11.0 gm. of piperazine dissolved in 50.0 gm. of water were added and blending continued for 2 additional minutes. A very stable emulsion resulted which was coagulated into fine particles by quick freezing. A film formed by casting the latex on a glass plate, air drying, and oven curing for about 2 hours at 105° C. had a tensile strength of 2,300 p.s.i., elongation at rupture of 580%, a modulus at 100% elongation of 195, a brittle temperature of —36° C. In heat distortion test run in accordance with ASTM D1637–61 the sample elongated 10% at 62° C. and 50% at 111° C. A sheet was formed using these particles following the procedure of Example IV.

TABLE III

Example	Caliper, mils	Basis weight, lb./3,000 ft.^{2}	Density	Tensile, lb./in. width	Elongation, percent	Porosity, sec.	Taber stiffness, gm.-cm.
IV	85	907	10.7	28	46	128	120
V	76	820	10.8	96	43	30	98
VI	62	760	12.3	182	37	280	460
VII	72	820	11.4	42	25	161	117
VIII	73	840	11.5	28	23	187	107
IX	65	766	11.8	58	35	523	124
X	67	750	11.2	40	26	117	102
XI	63	710	11.3	29	15	41	89
XII	77	792	10.3	36	24	114	109
XIII	78	790	10.1	28	29	12	41
XIV	78	860	11.0	134	54	110	102
XV	69	780	11.3	49	29	36	112
XVI	82	745	9.1	36	42	9	94
XVII:							
(A)	92	---	---	84	53	7	---
(B–1)	68	---	---	128	---	45	---
(B–2)	82	---	---	95	---	11	---

EXAMPLE XVII

To a 5 liter split resin flask equipped for distillation were charged 2,400 gm. of polytetramethylene ether glycol of molecular weight 1128 (2.128 moles) and 960 gm. of toluene. The charge was heated to boil off 288 gm. of toluene and traces of water. The remaining charge was cooled to 72° C. and 555.85 gm. (3.192 moles) of an 80:20 blend of the 2,4- and 2,6-isomers of tolylene diisocyanate was added. The temperature rose to 90° C. and was maintained at 90° C. for 3 hours. The resulting solution contained 81.5% prepolymer and 18.5% toluene.

(A) To a 1 gallon bottle were charged 490.8 gm. of the above described prepolymer solution, 309.2 gm. of toluene, 16.5 gm. of polyoxyethylene sorbitan monostearate and 13.5 gm. of sorbitan trioleate. While this solution was stirred at 1,600 r.p.m. with a 2 in. 3-blade propeller a solution of 7.928 gm. of hydrazine hydrate in 2,400 gm. of water was added over a period of 15 minutes. After all of the water phase had been added, stirring was continued for an additional 15 minutes. The product of this procedure is a dispersion of fine particles of the chain-extended prepolymer in water. A distribution of particle sizes was present with a mean size of 59 microns.

This material was substituted for the latex of Example I and a sheet was prepared.

(B) A similar run was carried out in which the same quantities of prepolymer, toluene, and emulsifiers were charged to a 1 gallon Waring Blendor. Using the high speed setting (free running speed of 14,500 r.p.m.), the hydrazine hydrate was added using the same period as above. Unlike the previous run, which remained fluid throughout the addition, the charge in the blender thickened until approximately ⅓ of the water phase had been added and then inverted to a dispersion of particles in water. The mean size of particles in this run was 233 microns. A sheet was prepared as in Example I.

The sheet was very thick and had a low tensile strength believed to be caused by the excessively large size of the polyurethane particles.

The sample was blended with an equal amount of the latex of Example I and used to prepare a leather sheet as in Example I. Sheet properties are given in Table III (Example XVII, (B–1)).

Another sheet was prepared as in Example I except that a blend of two parts of this material and one part of the latex of Example I was used. See Table III for properties (Example XVII, (B–2)).

TABLE IV

	Tensile, lbs. per in. width	Elongation, percent	Porosity, secs.
Example VII:			
(a) Standard drying procedure	42	25	161
(b) Dried at room temperature	27	15	150
(c) b heated for 1 hour at 280° F	98	41	102
(d) b heated for 1 hour at 220° F. under low pressure	66	26	>2,000
Example VIII(B):			
(a) Dried at room temperature	29	23	140
(b) a heated for 1 hour at 270° F	110	50	110
(c) a heated for 1 hour at 220° F. under low pressure	74	36	>2,000
Example XV:			
(a) Dried at room temperature	21	12	28
(b) Heated for 1 hour at 230° F	49	29	36
(c) Heated for 1 hour at 280° F	66	31	30

EXAMPLE XVIII

60 gm. of latex, 50.6% solids, a chain extended reaction product of an organic diisocyanate and polyalkylene ether glycol (Wyandotte E–204) (a film cast from the latex and cured 10 minutes at 121° C. having a tensile strength of 3,465 p.s.i., a 100% modulus of 225 p.s.i., an elongation at rupture of 700%, and a Shore A hardness of 50), was added to 2 liters H_2O containing 2 ml. of 30% colloidal silica dispersion (Monsanto Co. Syton C–30). 30 ml. of 5% alum solution and 20 ml. of 0.25% partially deacetylated karaya gum were added to coagulate the latex. 800 cc. of the coagulated latex, which contained 1.5% solids, were mixed with 6.5 gm. leather fibers (Lorum Y–024), and formed into an 8" x 8" hand sheet in a Williams hand sheet mold, adding enough water in the mold to provide a total of 4 liters of water. The hand sheet was dried at room temperature. The dried sample was then heated at 121° C. for 10 minutes in a forced draft oven. This sheet had a relatively low tensile strength and was suitable for use as a top ply in a multiply leather construction.

EXAMPLE XIX

30 lbs. of leather fibers (Lorum Y–020–015) and 116 gal. water were lightly beaten in a Valley beater and were pumped into a 1,500 gal. tank along with 604 gal. water. 136 gm. of Na salt of a sulfonated naphthalene formaldehyde condensation product (Rohm & Haas Tamol SN), and 175 lbs. of the latex of Example I (50% solids) were added. 2 lbs. alum (solids) were added as a 5% solution to coagulate the latex. The pH of the mixture was 5.1. 3 lbs. of Na_2CO_3 were added to raise the pH value to 8.2. 15 lbs. nylon (¼", 1.5 denier) were dispersed in 116 gal. water with 2 gal. of 1% deacetylated karaya gum in a Valley beater. The dispersion was blended into the mixture in the tank. This mixture was fed into the head box of a 27" wide Four-

drinier paper machine and formed into a sheet 60 mils thick and dried in the conventional manner over heated drums at temperatures of 95–125° C. The sheet had a basis weight of 623 lbs. per 3,000 ft.^{2}, a tensile strength of 120 lbs. per inch width in the machine direction and 58 lbs. per inch width in the cross direction, percent stretch at rupture of 30% in the machine direction and 60% cross direction, a Gurley densometer reading of 22 secs. for 400 cc.

EXAMPLE XX

A sheet made using the same proportions of ingredients and generally following the same procedures as set forth in Example XIX, had a caliper of .042″ when dry. The dry sheet had a Gurley porosity of 36 secs. for 400 cc., a tensile strength of 63 lbs. per inch width and an elongation at rupture of 34%. The sheet after soaking in water had a tensile strength of 19 lbs. per inch width and an elongation of 25%. A portion of the sheet was heated at 150° C. for 10 minutes. The heated sheet had a caliper of .041″, a Gurley porosity reading of 38 secs., a dry tensile strength of 75 lbs. per inch width and elongation at rupture of 44%. After soaking in water the sheet had a tensile strength of 38 lbs. per inch width and an elongation of 40%. Thus, the heat cure approximately doubled the wet tensile strength of the sample.

We claim:

1. An air permeable flexible water-laid sheet having at least one ply comprising between about 50 and 80 weight percent of elastomeric polyurethane in the form of globular floc particles having an average diameter between about 1 and 100 microns and between 20 to 50 weight percent of fibrous material, at least one-third of said fibrous material being leather fibers and the remainder being substantially staple fibers, at least 10 weight percent of said ply being leather fibers and at least 10 weight percent of said ply being staple fibers, said sheet having a dry porosity value as measured by a Gurley densometer of 5 to 2,000 seconds per 400 cc. air per 60 mil thickness.

2. A porous, breathable, flexible, water-laid sheet comprising betwen about 50 to 80 weight percent elastomeric polyurethane globules, at least some of which are present as agglomerates, and about 20 to 50 percent fibrous material, at least one-third of said fibrous material being tanned leather fibers and substantially the remainder being staple fibers, at least 10 percent of the dry weight of said sheet being leather fibers, said globules having an average diameter of about 1 to 100 microns.

3. The leather substitute of claim **2** wherein said elastomeric polyurethane globules comprise the reaction product of an organic diisocyanate and a polyalkylene ether polyol chain-extended with an organic polyamine to an average molecular weight of at least 10,000.

4. The leather substitute of claim **3** wherein said polyurethane globules comprise the reaction product of an aromatic diisocyanate and a polyoxyalkylene glycol chain extended with piperazine.

5. A flexible water-laid sheet comprising between about 50 to 80 weight percent elastomeric polyurethane in the form of globular floc particles having an average diameter between about 1 and 100 microns and about 20 to 50 weight percent of fibrous material, at least one-third of said fibrous material being leather fibers and the remainder being staple fiber, at least 10 percent by weight of the solid matter in said sheet being tanned leather fibers.

6. An aqueous slurry suitable for preparing a leather-like water-laid sheet comprising water and slurried solids having a papermaking consistency, said slurried solids comprising between 50 and 80 percent globular particles of elastomeric polyurethane having an average particle size between 1 and 100 microns and between 20 and 50 weight percent of fibrous material, at least one-third of said fibrous material being tanned leather fibers and essentially the remainder being high strength, flexible staple fibers, at least 10 percent of said solids being tanned leather fibers, so that when a sheet is formed by depositing said aqueous slurry on a foraminous surface said sheet when dried without pressure will have a porostiy value as determined on a Gurley densometer of 5 to 2000 seconds per 400 cc. of air per 60 mil sample thickness.

7. A method for forming a porous breathable leather-like sheet which comprises (a) depositing the slurry of claim **6** onto a foraminous surface to form a water-laid sheet (b) drying said sheet (c) heating said sheet at an elevated temperature of at least 120° C. for a time sufficient to cause flow of said polyurethane particles without degrading said fibers, to form a tough, flexible, leather-like sheet having improved tensile strength over that resulting after step (b).

8. A method for forming a porous breathable leather-like sheet comprising (a) providing a slurry defined by claim **6**, (b) depositing said slurry on a foraminous surface to form a water-laid sheet, (c) drying said sheet, and (d) heating said sheet without pressure at an elevated temperature of at least about 120° C. for a time sufficient to cause flow of said polyurethane particles, (e) discontinuing said heating prior to flowing together of said polyurethane particles into a continuous phase, whereby a sheet having increased tensile strength over that resulting after step (c) is produced.

9. A sheet according to claim **1** formed from at least two plies laminated to each other.

10. A sheet according to claim **9** wherein one of said plies is smoother and the proportion of staple fibers contained therein is less than in the other plies.

11. The sheet of claim **1** wherein said staple fibers are wholly synthetic high tensile strength, flexible fibers selected from the group consisting of nylon, polyethylene terephthalate, and polypropylene.

References Cited

UNITED STATES PATENTS

2,999,788	9/1961	Morgan	162—146
3,100,733	8/1963	Bundy	162—129 X
3,102,835	9/1963	White	161—170 X

S. LEON BASHORE, *Primary Examiner.*

U.S. Cl. X.R

162—144, 146, 168, 183; 161—156, 157, 158; 117—140, 142; 260—41