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PROCESS OF FORMING NON-WOVEN POROUS FIBROUS SYNTHETIC LEATHER SHEET

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This invention relates to synthetic leather and, more particularly, to the process of treating a non-woven polymeric fibrous sheet to form a synthetic leather.

Patents relating to methods and techniques of preparing synthetic leather compositions have been granted to inventors as far back as 1850; and even before that time, a great number of attempts have been made to devise a simple and rapid technique of producing synthetic leather compositions. In most of the early art, pyroxylin was used to coat or impregnate various types of fibrous base materials to prepare leather substitutes. As time went on, pyroxylin/oil/pigment compositions were widely used as coating or impregnating compositions for various woven or non-woven fibrous base materials. In the early stages of the synthetic leather industry, the main objective was to simulate the general appearance of leather.

In today's markets, coated fabrics, particularly the vinyl-coated fabrics, are outstanding as leather substitutes in such applications as handbags, bookbindings, brief cases, card table covers, luggage, etc. In such applications, the coated fabrics are satisfactory because the general appearance of leather is simulated; and the coated fabrics possess some of the desirable properties of leather. However, as compared to leather, the coated fabrics lack good tear strength, softness and the ability to "breathe" or transpire water vapor and air; and although the coated fabrics are used in such applications as chair coverings, much is left to be desired, especially with respect to water vapor and air permeability. Up to the present time, synthetic leather compositions have made little or no inroads into the boots, shoes, and gloves markets, mainly because of their inability to breathe in addition to lack of good tear strength and softness. As used hereinafter, the term "breathe" means transpire water vapor and air.

In general, the use of a synthetic leather composition in boots, shoes, gloves, etc., is mainly dependent upon its ability to breathe, usually expressed in terms of water vapor permeability or "leather permeability." Physical tests on the water vapor permeability of leather indicate that leather transpires water vapor about $\frac{2}{3}$ as readily as free air. In general terms, shoe upper leather samples having a thickness of 0.016"—0.104" have a leather permeability within the range of 2,000–18,000 gms./100 sq. meters/hr. when tested according to Kanagy & Vickers Journal of American Leather Chemical Association 45, 211–242 (April 1950), in an atmosphere of 23° C. and 90% relative humidity. Hereinafter, the ability of synthetic leather compositions to transpire water vapor will be expressed in terms of leather permeability in gms./100 sq. meters/hr. Based upon comfort tests, the minimum tolerable leather permeability for shoe upper leather is about 2,000 gms./100 sq. meters/hr. Preferably, for shoe upper leather, the permeability value should be 4,000–20,000 when tested at 23° C., and not greater than 90% relative humidity.

An object of the present invention is to provide a syn-

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thetic leather having outstanding breathing qualities. A further object of the present invention is to provide a process of preparing a synthetic leather having the requisite properties for fabricating boots, shoes, gloves, garments, chair coverings, and other articles wherein a composition capable of breathing is required. A still further object is to provide a process of preparing a synthetic leather having a tenacity, flex life, elongation, tear strength, modulus and leather permeability equal or superior to the various types of genuine leather. Other objects will be apparent from the description given hereinafter.

The above objects are accomplished according to the present invention by forming a compact, essentially impermeable, and continuous composite sheet by hot pressing a composition comprising a structural fiber component, an extractable pore-forming fiber component and a binder material, the proportion of pore-forming fiber, based upon the total volume of the sheet, being from 40–70%, the weight ratio of structural fiber to binder material being from 1:2 to 2:1, and thereafter forming interconnecting pores having essentially the shape of the pore-forming fibers in the sheet by extracting the pore-forming fiber.

The preferred structural fiber is an oriented synthetic linear polyamide, for example, polyhexamethylene adipamide, polyhexamethylene sebacamide, polycapromamide, or an interpolyamide of the type disclosed in U. S. P. 2,285,009. The pore-forming fiber is one which is readily extractable with a solvent, e. g., water, acetone, etc., that is substantially inert, i. e., has no solvent action, toward the structural fiber and the binder material. The preferred pore-forming fibers are cellulose acetate and polyvinyl alcohol. The binder material may be selected from the large class of soft, elastic, at least initially thermoplastic, synthetic polymers, the preferred polymers being N-methoxymethyl polyhexamethylene adipamide, polyethylene and its derivatives, copolyesters made from ethylene glycol and 60 mol per cent of terephthalic acid and 40 mol per cent of sebacic acid, synthetic rubbers such as neoprene (polymeric 2-chloro-1,3-butadiene) and compositions containing vinyl chloride polymers or copolymers.

The pore-forming fiber and the structural fiber components must have softening temperatures above the flow temperature of the binder material. Furthermore, the structural fiber component and the binder material must be insoluble in the solvent used to extract the pore-forming fiber component.

The following examples will serve to illustrate the principles and practice of the present invention and demonstrate the criticalness of the specified relative proportions of ingredients employed. Parts are by weights unless otherwise indicated.

Example 1

A mixture of 1.688 parts of 0.01" average length, 3 denier/filament, polyhexamethylene adipamide staple and 4.125 parts of 0.01" average length, 3 denier/filament, cellulose acetate staple was dispersed in 600 parts of water by stirring. To the dispersion was added 12.05 parts of a 14% latex of N-methoxymethyl polyhexamethylene adipamide having a DV (DV="dilution value," as defined in U. S. P. 2,430,923) of 55, together with 0.01 part of octyl phenyl polyglycol ether (to maintain the fiber dispersion) and 0.02 part of acetic acid (to flocculate the polyamide dispersion). After stirring briefly, a mat was formed by filtration through coarse filter paper, the area of the filter being such as to provide a retained weight of fibers plus binder of 3.0 oz./sq. ft. The mat was dried and pressed for five minutes at 140° C. under a pressure of 1930 lbs./sq. in., and the cellulose

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acetate component was then removed by extracting the mat for 18 hours with warm running acetone. The extracted product weighed 1.34 oz./sq. ft. and was leather-like in appearance and feel. It had a tongue-tear strength (average resistance to propagation in the Instron tester) of 1.6 pounds. (Tongue-tear strength is measured by cutting a 1" slit in the sheet to be tested and thereafter measuring the average force in pounds required to propagate the tear. The test is carried out in a manner similar to ASTM test method D39-39.) The product exhibited a leather permeability of 2369 gms./100 sq. meters/hr. when tested at 23° C. and 90% relative humidity. (In similar tests of water vapor permeability, various samples of representative shoe upper leathers exhibited the following leather permeabilities, all expressed in gms./100 sq. meters/hr.:

Suede calf	13,932
Glazed kid	3,718
Scotch grain cow	6,161
Cretan butt	7,863
English calf	9,430

A considerable series of actual wearing comfort tests has indicated that membranes exhibiting a permeability in this test of 2,000 to 10,000 will provide wearing comfort equivalent to that obtained with glazed leathers and heavy shoe upper leathers, while permeabilities of 10,000 to 22,000 were found to provide wearing comfort equivalent to that obtained with the lightest shoe upper leathers.)

The leather permeability test devised by Kanagy & Vickers, as described in the aforesaid article, was found to correlate with wearing comfort tests. In this test, a 3-inch diameter crystallizing dish was filled with 12-mesh calcium chloride, covered with a membrane of the substance under test, suspended inverted in an atmosphere of high humidity, and weighed at intervals. All values of leather permeability were measured at 23° C. and 90% relative humidity.

Example 2

A non-woven, fibrous, composite sheet was prepared by pressing the following plies of carded fibers into a composite sheet:

Ply	Pore-Former (Cellulose Acetate, 3 denier/fila- ment, 1.5")	Binder (Copoly- ester of ethylene glycol and 60 mol percent tere- acid and 40 mol percent sebacic acid, 3 denier/ filament, 1.5" staple fiber)	Structural Fibers	
			Polyethyl- ene tere- phthalate, 3 denier/ filament, 1.5"	Polyhexa- methylene adipamide, 3 denier/ filament, 1.5"
	Parts	Parts	Parts	Parts
Top	20	20		
Sub	30	10	10	
Center	90	30		30
Backing	160	40		40

Each ply was prepared by carding the fibers into a bat, and the plies were pressed together in cross-grain fashion at 170° C. and 500 p. s. i. to form a composite sheet. The weight ratio of structural fiber/binder/pore-former was 17/21/62. After extraction of the cellulose acetate pore-former, the sheet had a thickness of 0.038" and a weight of 1.30 oz./sq. ft. The leather permeability was 17,597 gms./100 sq. meters/hr. Furthermore, the product had a Schiltknecht flex life of 128,250, a tongue-tear strength of 5.5 pounds, (The Schiltknecht flex machine is described in Bulletin #105 of Alfred Suter, 200 Fifth Avenue, New York, New York), and a cold crack temperature of below -70° C. After application of saddle

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soap and shoe polish, the material had a leather permeability of 7151 and a resistance to penetration by liquid water of 36 flexes, when tested according to the procedure described in Federal Leather Specification KK-L-311, Method #271.1 (3/28/45). Representative shoe upper leathers have given the following values in this test:

Suede calf	405
Glazed kid	745,000
Scotch grain cowhide	2,206
Patent calf	745,000
Cretan butt	114
English calf	8,012

Example 3

A non-woven fibrous sheet was prepared in a manner similar to that of Example 2. The top ply was composed of 40 parts of the copolyester staple binder of Example 2 and 30 parts of cellulose acetate fiber pore-former, 3 denier/filament, 1.5" in length. The middle ply was composed of 60 parts of 3 denier/filament, 2.5" polyhexamethylene adipamide structural fiber, 60 parts of the copolyester binder fiber, and 180 parts of cellulose acetate pore-former. The base layer was composed of 60 parts of the polyamide structural fiber, 60 parts of the copolyester binder fiber, and 240 parts of the cellulose acetate pore-former. The composite structure contained an overall ratio of structural fiber/binder/pore-former of 16.5/21.9/61.6. The product was 0.034" thick and weighed 1.3 oz./sq. ft. It had a leather permeability of 14,284, a tensile strength of 1,739 lbs./sq. in., an elongation of 105%, a modulus of 3,101 lbs./sq. in., a tongue-tear strength of 10.6 pounds, and a Schiltknecht flex life of 826,000-4,645,000 flexes. After application of saddle soap and shoe polish, the product had a leather permeability of 7,555 and a Schiltknecht flex life of 1,677,000-28,000,000.

Example 4

This example illustrates the pertinent physical properties of the initial non-woven, fibrous, impermeable structure of the present invention prior to extraction of the pore-forming fiber.

A product was prepared as described in Example 1 except that the step of extracting the pore-forming cellulose acetate staple was omitted. The product weighed 3.0 oz./sq. ft., and it was very stiff and not leather-like in appearance or handle. It had a leather permeability of only 84 gms./100 sq. meters/hr., a tongue-tear strength of only 1.0 lb./oz./sq. ft., and a Schiltknecht flex life of only 11,875 flexes. As a matter of comparison, the product described in Example 1 had a tongue-tear strength of 1.20 lbs./oz./sq. ft.; and a product similar to that described in Example 1 had a Schiltknecht flex life of 25,000-66,000. Thus, the step of extracting the pore-forming fibrous component improved not only permeability to water vapor, but also tear strength and flex life.

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Example 5

A mat similar to that described in Example 1 was prepared except that the ratio of components was varied to provide a polyhexamethylene adipamide fiber/N-methoxymethyl polyhexamethylene adipamide binder fiber/cellulose acetate pore-former fiber ratio of 15/30/55 (structural fiber/binder ratio of 1/2). The product was permeable and had a tongue-tear strength of 1.1 pounds.

Example 6

A mat was prepared similar to that of Example 5 except that the structural fiber/binder/pore-former ratio was 30/15/55, thus giving a structural fiber/binder ratio or 2/1. The extracted product exhibited a leather permeability of 5,240 and a tongue-tear strength of 1.0 pound.

Summarizing the results of Examples 1, 5 and 6, it is seen that, while leather permeability increased as the ratio of structural fiber to binder was raised, tongue-tear strength passed through a maximum at a fiber-binder ratio at about 1/1 and became so low (1 pound or less) as to be substantially useless for shoe upper applications when the fiber/binder ratio was less than 1/2 or greater than 2/1. As will be illustrated hereinafter, the tear strength of the synthetic leather compositions of the present invention will vary with the length of the structural fiber. In Examples 1, 5 and 6, the length of the structural fiber was 0.01", a minimum value insofar as fabricating structures of substantial tear strength is concerned. In general, experience has shown that little additional strength is obtained by employing a structural fiber longer than about 1.5". However, it may be more convenient, from the standpoint of the type of textile machinery to be employed, to use structural fibers from 0.5" to 8" in length. Hence, employing a fiber/binder ratio of from 1/2 to 2/1 produces a composition having an optimum tear strength. This is a surprising discovery on the basis of what was known heretofore about fiber-reinforced compositions.

The following examples (7-15 inclusive) illustrate the effect of varying the content of pore-forming fiber in the initial composition upon the leather permeability and tear strength of the extracted product.

Example 7

A mat was prepared as described in Example 1 except that the ratio of structural fiber/binder/pore-former was in the ratio of 37.5/37.5/25. The product had a leather permeability of 496 and a tongue-tear strength of 3.6 pounds.

Example 8

A mat similar to that of Example 7 was prepared except that the structural fiber/binder/pore-former was in the ratio of 30/30/40. The resulting product had a leather permeability of 588.

Example 9

A mat similar to that of Example 7 was prepared except that the ratio of structural fiber/binder/pore-former was in the ratio of 27.5/27.5/45. The extracted product had a leather permeability of 3,680.

Example 10

A mat similar to that of Example 7 was prepared except that the ratio of structural fiber/binder/pore-former was in the ratio of 25/25/50. The product had a leather permeability of 8,853 and a tongue-tear strength of 2.7 pounds.

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Example 11

A mat similar to that of Example 7 was prepared except that the ratio of structural fiber/binder/pore-former was 20/20/60. The extracted product had a leather permeability of 15,701 and a tongue-tear strength of 1.4 pounds.

Example 12

A mat similar to Example 7 was prepared except that the ratio of structural fiber/binder/pore-former was 15/15/70. The extracted product had a leather permeability of 17,895 and a tongue-tear strength of 1.4 pounds.

Example 13

A mat similar to that of Example 7 was prepared except that the ratio of structural fiber/binder/pore-former was 10/10/80. The extracted product had a leather permeability of 23,721 and a tongue-tear strength of 0.4 pounds.

Example 14

To 16,000 parts of water containing 0.2 part of alkyl aryl polyglycol ether were added, with stirring, 4.00 parts of 0.5", 3 denier/filament polyhexamethylene adipamide structural staple and 5.34 parts of 0.5", 2.5 denier/filament polyvinyl alcohol pore-former fiber. The fiber dispersion was formed into a mat by filtration through an 8-mesh wire screen. The mat was impregnated with 40 parts of a solution of polyvinyl chloride/di-(2-ethyl hexyl) phthalate 100/60 dispersed at 10% concentration in tetrahydrofurane/dimethyl formamide 97.5/2.5. After drying, the impregnated mat was pressed for 10 minutes at 160 C. and 1,245 lbs./sq. in.; and the polyvinyl alcohol pore-former was finally extracted with 90° C. running water. Complete extraction required 96 hours. The product had a leather permeability of 3,805. The ratio of structural fiber/binder/pore-former was 30/30/40.

Example 15

A product similar to that of Example 14 was prepared except that the ratio of structural fiber/binder/pore-forming fiber was 15/15/70. The product was very pliable and highly permeable to air. The product had a leather permeability of 12,614 and a tongue-tear strength of 6.6 pounds.

Summarizing the foregoing Examples 7-15 inclusive, the effect of varying the weight of pore-forming fibers in the initial unextracted structures of the present invention appears in tabular form in Table I.

TABLE I

Example	Percent Pore-Former by Volume	Percent Pore-Former by Weight	Leather Permeability and Length of Pore-Forming Fiber	
			0.01" Flock	0.5" Staple
7	22.4	25	496	
8	36.7	40	588	
9	41.6	45	3,680	
10	46.6	50	8,853	
11	56.6	60	15,701	
12	67.2	70	17,895	
13	77.8	80	23,721	
14	39.7	40		3,805
15	69.8	70		12,614

In observing the above tabulation, it appears that at least about 40% by volume of the total structure, of pore-former fiber must be employed to provide adequate leather permeability.

Example 16

To 16,000 parts of water containing 0.2 part of octyl phenyl polyglycol ether were added, with stirring, 1.688 parts of 0.5", 3 denier/filament polyhexamethylene adipamide staple and 4.125 parts of 0.01", 3 denier/filament cellulose acetate staple. The fiber dispersion was formed into a mat by filtration through an 8-mesh wire screen of area such as to provide a fiber weight of 2.3 oz./sq. ft. The mat was impregnated with 12.05 parts of a 14% latex of N-methoxymethyl polyhexamethylene adipamide (DV=55), dried, pressed for five minutes at 140° C. and 1,930 lbs./sq. in. (structural fiber/binder/pore-former ratio of 22.5/22.5/55); and the cellulose acetate was finally extracted with warm running acetone.

The product had a leather permeability of 5,530 and a tongue-tear strength of 2.3 pounds. By comparison with the product described in Example 1, it will be seen that this increase in length of the structural fiber resulted in a corresponding increase in the tear resistance of the product. This product likewise resisted 301 flexes before allowing penetration of liquid water. When tested in the Schiltknecht flexing machine, the product of this example exhibited surface cracking after 49,875 flexes.

The following examples, 17 and 18 inclusive, in combination with Example 16, illustrate the effect of variations in length of the pore-forming fiber upon the value of leather permeability.

Example 17

A product was prepared as in Example 16 except that 0.5" polyhexamethylene adipamide staple was replaced with a corresponding amount of 0.01", 3 denier/filament polyhexamethylene adipamide staple; and the 0.01" cellulose acetate staple was replaced with a corresponding amount of 0.25", 1 denier/filament cellulose acetate staple. The product exhibited a leather permeability of 13,452 and a resistance to water liquid penetration of 172 flexes.

Example 18

The product was prepared in a manner similar to that of Example 16. In this example, 1.5 parts of 0.5" 3 denier/filament polyhexamethylene adipamide staple; 4.5 parts of 0.5", 3 denier/filament cellulose acetate staple; and 10.7 parts of a 14% latex of N-methoxymethyl polyhexamethylene adipamide were combined to give a structural fiber/binder/pore-former ratio of 20/20/60. The product had a leather permeability of 13,706 and a tongue-tear strength of 3.5 pounds.

A comparison of the permeabilities exhibited by the products of Examples 16-18 inclusive indicates that the permeability increased as the pore-forming fiber length was increased up to about 0.25", beyond which no further increase in permeability was obtained by increasing the pore-forming fiber length, even when the pore-forming content was raised from 55 to 60%.

Although little additional strength can be gained by increasing the length of the structural fiber beyond 1.5" and little additional ability to breathe can be gained by increasing the pore-former fiber length beyond 0.25", it may be convenient to use longer fibers. Various standard types of textile machinery which may be used in the production of these synthetic leather compositions are designed to handle staple fibers in limited length ranges which may lie anywhere in the neighborhood of 0.5" to as long as 8". It is also possible to make usable mats for these compositions using even longer fibers.

The following examples illustrate the effect of fiber denier, i. e., both structural and power-forming fiber, upon leather permeability.

Example 19

A product was prepared as in Example 16 except that 0.375", 1 denier/filament polyhexamethylene adipamide

staple and 0.01", 1 denier/filament cellulose acetate pore-former were used. After extraction of the cellulose acetate pore-former, the product had a leather permeability of 3,992 and a water liquid penetration resistance of 1,227 flexes.

Example 20

A product was prepared as in Example 19 except that 0.01", 1.5 denier/filament cellulose acetate staple was employed. After extraction of the pore-former, the product had a leather permeability of 3,940 and a water liquid penetration resistance of 171 flexes.

Example 21

A product was prepared as in Example 19 except that 0.01", 3 denier/filament cellulose acetate staple was employed as the pore-former. After extraction of the pore-former, the product had a leather permeability of 4,888 and a water liquid penetration resistance of 80 flexes.

Example 22

A product was prepared as in Example 19 except that 0.5", 3 denier/filament polyhexamethylene adipamide staple and 0.01", 1 denier/filament cellulose acetate staple were employed as structural fiber and pore-former, respectively. After extraction of the pore-former, the product had a leather permeability of 4,126 and a water liquid penetration resistance of 238 flexes.

Example 23

A product was prepared as in Example 19 except that 0.5", 1 denier/filament polyhexamethylene adipamide staple and 0.01", 1 denier/filament cellulose acetate were employed as structural fiber and pore-former, respectively. The extracted product had a leather permeability of 3,836.

Example 24

A product was prepared as in Example 19 except that 0.5", 3 denier/filament polyhexamethylene adipamide staple and 0.01", 1.5 denier/filament cellulose acetate were employed as structural fiber and pore-former, respectively. The extracted product had a leather permeability of 4,649 and a water liquid penetration resistance of 75 flexes.

The results of Examples 19-24, inclusive, indicate that variations in structural fiber and pore-forming fiber thickness result in little variation in the leather permeability of the synthetic leather compositions. Generally, increasing the thickness of the pore-forming fiber decreases the resistance to liquid water penetration.

Fibers which are finer than 1 denier are difficult to process on standard textile machinery; and when used as structural fibers in the present compositions, the fibers are too rigidly immobilized by the binder to give optimum strength, e. g., tear and tensile. In other words, the fibers of greater denier tend to shift within the binder under flexing or tearing, this action making the product more durable. Finer fibers, however, are rigidly held by the binder. Furthermore, fibers having a denier less than 1/2 have so much exposed surface, i. e., ratio of surface area to core volume is high, and are so soft that they no longer behave as normal textile staples. On the other hand, fibers coarser than 16 denier are extremely harsh and more closely resemble bristles.

The following Examples 25-26 illustrate the effects of thickness of the extracted sheets upon the value of leather permeability.

Example 25

A product was prepared in a manner similar to that described in Example 1 except that the thickness of the

extracted product was 0.019", and its weight was 0.67 oz./sq. ft. The product had a leather permeability of 8,442.

Example 26

A product was prepared in a manner similar to that of Example 25 except that the thickness of the resulting extracted product was 0.071". The leather permeability was 4,281.

The above examples indicate that permeability via internal surface diffusion is only halved by an approximate 4-fold increase in the thickness. This is in contrast to the fact that with homogeneous films, the relationship between thickness and permeability is essentially linear for relatively hydrophobic compositions, but varies from linearity with hydrophilic films wherein an increase in film thickness does not give the calculated decrease in permeability.

The following examples illustrate the use of various types of synthetic polymers as binders and the incorporation of such binder polymers into the compositions in various forms, e. g., as homogeneous films, from solvent solutions, from aqueous dispersions, etc.

Example 27

A mat consisting of 1.688 parts of 0.01", 3 denier/filament polyhexamethylene adipamide staple and 4.125 parts of 0.01", 3 denier/filament cellulose acetate staple was prepared from dispersion in 600 parts of water by filtration through a filter with an area such as to provide a fiber weight of 2.3 oz./sq. ft. The mat was dried, preheated for 15 minutes at 180° C. in an atmosphere of nitrogen, and then impregnated with 1.688 parts of a film of N-methoxymethyl polyhexamethylene adipamide (DV=86) by pressing for 10 minutes at 160° C. and 1450 lbs./sq. in. The product had a structural fiber/binder/pore-former ratio of 22.5/22.5/55. After extraction of the cellulose acetate, the leather permeability was 7,294; the product resisted 48 flexes before permitting water liquid penetration; and it resisted 213,000 flexes in the Schiltknecht machine before surface cracking developed.

Example 28

A mat was prepared in a manner similar to Example 16 using 0.5" cellulose acetate staple and replacing the latex with 29.6 parts of a dispersion of N-methoxymethyl polyhexamethylene adipamide (DV=86) at 5.7% concentration in ethanol/water 80/20. After drying, the impregnated mat was pressed for 15 minutes at 165° C. and 1245 lbs./sq. in.; and the cellulose acetate pore-former was finally extracted with acetone. The tough, permeable, pliable, leather-like product was 0.028" thick and weighed 1.48 oz./sq. ft. It had a leather permeability of 13,778, a tensile strength of 3490 lbs./sq. in., an elongation of 38%, a modulus of 13,652 lbs./sq. in., and a tongue-tear strength of 16.0 pounds.

Example 29

Applied non-woven fibrous mat was prepared in a manner similar to Example 3. This composition was composed of a top layer of 1 part of a copolyester of ethylene glycol, 60 mol percent of terephthalic acid, and 40 mol percent of sebacic acid as the binder; and 1 part of cellulose acetate fiber, 3 denier per filament, 1.5" in length. An intermediate layer was composed of 3 parts of the copolyester binder, 3 parts of polyethylene terephthalate structural fiber, and 9 parts of cellulose acetate pore-forming fiber. A base layer was composed of 5 parts of the copolyester binder, 5 parts of polyhexamethylene adipamide structural fiber, and 15 parts of cellulose acetate fiber pore-former. The layers were composited under heat and pressure, and the cellulose acetate was extracted. The resulting product

weighed 1.3 oz./sq. ft., had a leather permeability of 13,680 and a Schiltknecht flex life of 553,000 flexes.

Example 30

A product was prepared as in Example 27 except that the polyamide film was replaced with an equal amount of polyethylene film, and the pressing was conducted for 5 minutes at 175° C. and 3390 lbs./sq. in., after preheating the mat 15 minutes at 180° C. in a nitrogen atmosphere. After extraction of the cellulose acetate, the product had a leather permeability of 8,987, a water liquid penetration resistance of 11,000 flexes, and a Schiltknecht flex life of 6,000. It will be noted that this composition was superior to natural shoe leather such as Scotch Grain Cowhide and Cretan Butt in the incompatible properties of high leather permeability and low water liquid permeability.

Example 31

A mat comprising 1.688 parts of .001", 3 denier/filament polyhexamethylene adipamide staple and 4.125 parts of 0.01", 2.5 denier/filament polyvinyl alcohol staple was prepared by the procedure described in Example 27. The mat was preheated 15 minutes at 180° C. in an atmosphere of nitrogen and then impregnated with 1.688 grams of a film comprising a polyvinyl butyral resin/dibutyl sebacate composition 70/30 by pressing for 5 minutes at 155° C. at 1,450 lbs./sq. in. The polyvinyl alcohol pore-former was then extracted with hot running water. The extracted product had a leather permeability of 3,719, a water liquid resistance of 748 flexes, and a Schiltknecht flex life of 47,500.

Example 32

A product was prepared as in Example 31 except that the polyvinyl acetal film was replaced with an equal amount of a film comprising N-methoxymethyl polyhexamethylene adipamide (DV=55)/methyl 10-phenol stearate 50/50. This film was impregnated into the polyhexamethylene adipamide/polyvinyl alcohol fiber mat by preheating the mat for 15 minutes at 180° C. in an atmosphere of nitrogen, followed by pressing for 5 minutes at 160° C. and 1,450 lbs./sq. in. pressure. The product, after extraction of the polyvinyl alcohol, had a leather permeability of 12,428 and exhibited surface cracking after 78,000 Schiltknecht flexes.

Example 33

A mat was prepared at a weight of 3.3 oz./sq. ft. as described in Example 16, using 4.68 parts of 0.5", 3 denier/filament polyhexamethylene adipamide structural fiber and 11.46 parts of 0.5", 2.5 denier/filament polyvinyl alcohol pore-forming fiber dispersed in 16,000 parts of water containing 0.2 part of octyl phenyl polyglycol ether. After drying, the mat was impregnated with 65 parts of a dispersion at 7.2% concentration in methyl ethyl ketone of vinyl chloride/vinyl acetate 95/5 copolymer/di-(2-ethyl-hexyl) phthalate 100/60. The freshly impregnated mat was submerged in water, dried, and pressed for 10 minutes at 160° C. and 1245 lbs./sq. in.; and the polyvinyl alcohol pore-former was finally extracted with running water at 90° C. The extracted mat was split down the middle to give a very leather-like product with a fiber-rich "flesh" side and a binder-rich "grain" side. The split product was 0.027" thick and weighed 1.00 oz./sq. ft. It had a leather permeability of 12,058, a tensile strength of 2,025 lbs./sq. in., an elongation of 48%, a modulus of 14,983 lbs./sq. in., a tongue-tear strength of 6.3 lbs., and a Schiltknecht flex life of 285,000.

Example 34

A mat was prepared in a manner similar to that of Example 33 replacing the plasticized vinyl chloride/vinyl

acetate copolymer with an equivalent amount of polyvinyl chloride/di-(2-ethyl hexyl) phthalate 100/60, applied from dispersion at 6.2% concentration in tetrahydrofuran/dimethyl formamide 98/2. The impregnated mat was submerged in water, dried, pressed for 10 minutes at 160° C. and 1245 lbs./sq. in. using 0.030" shims; and the pore-former was extracted with running water at 90° C. The leather-like product was 0.031" thick and weighed 1.51 oz./sq. ft. It had a leather permeability of 7,908 and a tongue-tear strength of 4.1–7.1 pounds.

Example 35

A product was prepared as described in Example 16 except that the binder was composed of chlorosulfonated polyethylene/wood rosin/tribasic lead maleate/titanium dioxide/aluminum stearate/"Captex" (2-mercaptobenzothiazole)/diphenyl guanidine 100/10/20/20/2/3/0.5, dispersed at 7.6% concentration in toluene. The freshly impregnated mat was submerged in methanol, dried, pressed for 10 minutes at 170° C. and 1,245 lbs./sq. in. using 0.030" shims; and the cellulose acetate pore-former was finally extracted with acetone. The leather-like product was 0.028" thick and weighed 1.43 oz./sq. ft. It had a leather permeability of 16,551 and a tongue-tear strength of 8.0 pounds.

Example 36

A product was prepared in a manner similar to Example 28 except that the binder was polyethylene, and it was applied from a latex at 4.5% concentration. After drying, the impregnated mat was pressed for 10 minutes at 175° C. and 1,245 lbs./sq. in. using 0.030" shims; and the cellulose acetate pore-former was finally extracted with acetone. The leather-like product was 0.029" thick and weighed 1.48 oz./sq. ft. It had a leather permeability of 14,216 and a tongue-tear strength of 5.2 pounds.

Example 37

A mat comprising 1.688 parts of 0.01", 3 denier/filament polyhexamethylene adipamide staple and 4.125 parts of 0.01", 3 denier/filament acetate staple was preheated 15 minutes at 65° C. and impregnated with 16.3 parts of a hot 10.34% solution in toluene of chlorinated polyethylene of 27.5% chlorine content. The solvent was allowed to evaporate, and the impregnated mat was pressed 10 minutes at 190° C. and 1,450 lbs./sq. in. After extraction of the cellulose acetate pore-former, the product had a leather permeability of 3,531, a water liquid resistance of 21,584 flexes, and a Schiltknecht flex life of 8,000.

Example 38

A mat was prepared in a manner similar to that described in Example 28; and the ethylene/vinyl acetate 2.36/1 copolymer binder, dispersed at 7.2% concentration in toluene, was employed. After drying, the impregnated mat was pressed for 10 minutes at 180° C. and 1245 lbs./sq. in. using 0.030" shims. After extraction of the cellulose acetate pore-former, the product was 0.026" thick and weighed 0.9 oz./sq. ft. The product had a leather permeability of 19,430, a resistance to liquid water penetration of 18,000–24,000 flexes, and a tongue-tear strength of 15 pounds.

Example 39

A mat comprising 1.688 parts of 0.01" 3 denier/filament polyhexamethylene adipamide staple and 4.125 parts of 0.01", 2.5 denier/filament polyvinyl alcohol staple was prepared by the procedure described in Example 27. This was impregnated with 26.65 parts of 6.33% latex of a vinylidene chloride-acrylonitrile copolymer/dioctyl phthalate 75/25, dried, pressed 10 minutes at 140° C.

and 1,450 lbs./sq. in.; and the polyvinyl alcohol pore-former was extracted with warm water.

The product had a leather permeability of 17,228, a water penetration resistance of 586 flexes, and a Schiltknecht flex life of 6,000.

Example 40

A mat prepared as described in Example 28 was impregnated with a dispersion of neoprene (poly-2-chloro-1,3-butadiene)/zinc oxide/magnesium oxide/phenyl-beta-naphthylamine 100/10/10/2 at 7.2% concentration in benzene to give a structural fiber/binder/pore-former ratio of 22.5/22.5/55. The freshly impregnated mat was submerged in methanol, dried, pressed for 40 minutes at 155° C. and at 1,245 lbs./sq. in., using 0.030" shims; and finally the cellulose acetate pore-former was extracted with acetone. The weight of the extracted product was 1.41 oz./ft., and its thickness was 0.028". It had a leather permeability of 8,638, a water liquid penetration resistance of 165 flexes and a tongue-tear strength of 10 pounds.

The following example illustrates use of the synthetic leather compositions of the present invention in the fabrication of shoe uppers.

Example 41

In order to fabricate shoes from the synthetic leather compositions of the present invention, composite sheets consisting of fibers of polyhexamethylene adipamide, cellulose acetate, and a copolyester made from ethylene glycol and 60 mol percent of terephthalic acid and 40 mol percent of sebacic acid were prepared. In general, the initial non-woven water vapor-impermeable fiber sheets were made by carding the mixed fibers together and then hot-pressing at 500 lbs./sq. in. at 170° C. the carded fibrous mat to form a composite sheet. In all cases, the fibers were 2.5" in length and 3 denier/filament.

To prepare the non-woven fibrous impermeable sheets, the three fibrous components were blended on a Garnet card and were collected in the form of a bat or web of the desired thickness by wrapping the primary thin web from a doffer comb around a collecting drum a suitable number of revolutions. As indicated in Table II, some of the mats were formed from two webs of the same composition; and some of the mats were composed of two different webs. In one of the mats, an additional quantity of binder polymer was introduced in the upper layer of the mat by assembling a homogeneous film on top of the two webs. It should be noted that this did not remain in the form of a film in the final product, but was pressed entirely into the fibers and existed merely as an additional binder in the composition. The complete assembly of webs with or without film was laminated between cellophane and subjected to heat and pressure to melt the binder and make it flow into the fibrous webs. All of the compositions were cooled under pressure and extracted at room temperature in acetone. In Table II, the samples coded Ae–Ee have the same composition as samples A–E except that the initial fibrous impermeable mats were embossed with heat and pressure at a slightly lower temperature than that at which they were made, the embossing being carried out before extraction of the cellulose acetate fibers. This procedure represents an outstanding advantage of the process of the present invention whereby a synthetic leather composition with an embossed surface may be prepared by carrying out the embossing step prior to extraction of the pore-forming fiber. Obviously, embossing after extraction compresses the capillary structure of the compositions and decreases the water vapor permeability.

It will be noted that leather permeability values in the following table were measured at 23° C. and 80% relative humidity (R. H.), and this only applies to the examples in this table.

TABLE II

Code	Wright Ratio of Structural Fiber/Binder/Pore-Former			L. P. V. Grams/100 sq. meters/hr. at 80% R. H. and 23° C.	Tongue-Tear, Pounds	Thick-ness (inches)	Tenacity (p. s. i.)	Elonga-tion (percent)	Modulus (p. s. i.)
	Nylon ¹	T/10 ²	Cellulose Acetate						
A-----	1	1	3	13,088	24.3	.031	1,839	93.3	11,377
B-----	1	1	2	4,818	18.4	.031	3,205	102	22,153
C-----	1	1	4	13,522	16.8	.045	1,508	109	5,771
<i>Three-Layer Composition</i>									
(Top)-----	1 Mil Continuous T/10 45/55 ³			9,216	15.2	.037	1,772	105	7,098
(Mid)-----	1	1	3						
(Bot)-----	1	1	4						
Ae-----	(Embossed Surface)		3	14,348	18.0	.032	1,804	100	8,412
Be-----	(Embossed Surface)		2	8,839	21.0	.026	1,776	86.1	12,786
Ce-----	(Embossed Surface)		4	16,181	12.9	.033	1,050	84	6,718
<i>Three-Layer Composition</i>									
(Top)-----	1 Mil of Continuous T/10 45/55			11,550	-----	.029	1,490	100	7,453
(Mid)-----	1	1	3						
(Bot)-----	1	1	4						
	(Embossed Surface)								

¹ Polyhexamethylene adipamide.² Copolyester of ethylene glycol and 60 mol percent terephthalic acid and 40 mol percent sebacic acid.³ Copolyester of terephthalic and sebacic acids in the stated ratio, with ethylene glycol.

All of the synthetic leather compositions indicated in the above table were fabricated into shoe uppers, two pairs of men's shoes being fabricated from each composition. The shoes were worn for a period between 400-3000 hours, and all wearers testified that the shoes were more comfortable than shoes fabricated from various types of genuine leather. In general, embossing was found to increase the abrasion resistance of the shoe uppers.

The following examples mainly illustrate the use of

structural fibers of greater length, e. g., 2"-2.5", and show the superior tear strength of the resulting synthetic leather compositions as compared to various types of genuine leather.

Examples 42-49 are presented in tabular form in Table III, the preparation of these synthetic leather compositions being carried out in accordance with the general procedure described in Example 41. It will be noted that tear strengths of the compositions in the following table

TABLE III

Example	Weight Ratio			Structural Fiber			Binder	
	Structural Fiber/Binder/Pore-Former			Nature	Denier Filament	Length (Inches)	Nature	Used As
Control-----	Brown topgrain (upholstery) cowhide-----							
Do-----	Red Morocco finish topgrain upholstery cowhide-----							
Do-----	Yellow topgrain heifer hide (shoe upper)-----							
Do-----	High quality cotton duck (army tents, tarpaulins).-----							
42-----	20/18.5/61.5-----			Nylon*	3	2-2.5	Polyethylene film	
43-----	12.5/12.5/75-----			do-----	3	2-2.5	T-10**	Staple fiber (1.5", 7 den./fla.)
44-----	20/20/60-----			do-----	3	2-2.5	T-10**	do-----
45-----	20/20/60-----			do-----	15	2-2.5	T-10**	do-----
46-----	20/20/60-----			do-----	1.5	1.5	T-10**	do-----
47-----	20/20/60 top film of chlorosulfonated polyethylene as additional binder.			do-----	3	2.5	T-10 film with top film of chlorosulfonated polyethylene (0.002")	
48-----	27/18/55-----			Polyethylene Terephthalate.	3-4	2	Polyethylene film	
49-----	25/24/51-----			do-----	3-4	2	do-----	do-----

Example	Pore-Forming Fiber			Wt. of Extracted Product oz./yd. ²	Thickness of Extracted Product (Inches)	Tenacity, #/in./oz. yd. ²	Trapezoidal Tear Strength, #/oz./yd. ²	Tongue-Tear Strength, #/oz./yd. ²	LPV, g./100 sq. meters/hr.	Percent Elongation At Break
	Nature	Denier Filament	Length (Inches)							
Control-----				20	0.039		0.607	0.208	1,447	
Do-----				21	0.045		1.54	0.22	1,104	
Do-----				25			1.90	0.48	12,000-16,000	34
Do-----						9.25	1.5			
42-----	Cellulose Acetate.	3	1.5	9.68	0.028	6.57	7.67		20,816	69
43-----	do-----	3	1.5	4.29	0.0194	2.57	5.67			43
44-----	do-----	3	1.5	4.01	0.0135	5.78	6.29			46
45-----	do-----	3	1.5	4.2	0.0133	2.88	2.89		17,526	53
46-----	do-----	3	1.5	3.15	0.0127	4.15	3.14		17,549	62
47-----	do-----	3	1.5	6.05	0.0167	3.52			7,210	52
48-----	do-----	3	1.5	3.91	0.0114	3.61	4.5		20,772	54
49-----	do-----	3	1.5	9.58	0.023	5.12	6.05		15,815	82

* nylon = polyhexamethylene adipamide.

** T-10 = copolyester of ethylene glycol and 60 mol percent terephthalic acid and 40 mol percent sebacic acid.

are expressed in terms of trapezoidal tear strength in lbs./oz./sq. yd. This test is described in Federal Specification CCC-T-191a dated October 5, 1945. For the sake of comparison, the trapezoidal and tongue-tear strengths (both expressed in lbs./oz./sq. yd.) are given for three different types of genuine leather. For these samples, the ratio of trapezoidal to tongue-tear strength ranges from 3 to 7. Hence, there appears to be no constant conversion factor.

It is to be understood that the foregoing examples are merely illustrative and that the present invention broadly comprises forming a compact, essentially impermeable and continuous, composite sheet by hot-pressing a composition comprising a structural fiber component, an extractable pore-forming fiber component, and a binder material, the proportion of pore-forming fiber, based upon the total volume of the sheet, being from 40-70%, the weight ratio of structural fiber to binder material being from 1/2 to 2/1, and thereafter forming interconnecting pores having essentially the shape of the pore-forming fibers in the sheet by extracting the pore-forming fiber.

Fibers of nylon, i. e., synthetic linear polyamides such as polyhexamethylene adipamide, polyhexamethylene sebacamide, polycapromide and interpolyamides, etc., are outstanding for use as the structural fibers in the synthetic leather compositions of the present invention. The use of nylon structural fibers produces an extracted composition having high tear strength, tensile strength, softness and flex life. Polyethylene terephthalate homopolymer and copolymer fibers are also considered to be good structural fibers; and other natural and synthetic fibers which may be employed include polyacrylonitrile, acrylonitrile copolymers, cellulose acetate, viscose, polyvinyl acetals, cotton, wool and glass fibers. The length of the structural fiber may be varied depending upon the general strength properties required. As illustrated in the foregoing examples, structural fibers as short as 0.01" may be employed; but structural fibers having a length of about 1.5" give a product of substantially optimum strength properties. Using structural fibers longer than 1.5" imparts little additional strength to the present synthetic leather compositions; but, as mentioned hereinbefore, it may be convenient to use longer fibers; and the use of longer structural fibers, e. g., up to 8", is within the intended scope of the present invention. On the other hand, structural fibers less than 0.01" in length add little to the strength of the sheet over that of a sheet composed wholly of the binder polymer.

It should be emphasized that the structural fiber component should not be excessively softened at the flow temperature of the binder material and should be insoluble in the solvent used to extract the pore-forming fiber.

The pore-forming fiber must be a workable staple fiber; that is, it should be adaptable to making bats. In this form, the pore-forming fiber is randomly disposed; and extraction thereof results in the formation of a network of interconnecting capillaries or pores. Furthermore, the pore-forming fiber must not be excessively softened at the flow temperature of the binder and must be readily extractable from the composite sheet with a solvent which is substantially inert, i. e., has no solvent action, to the structural fiber and the binder material. As illustrated in the foregoing examples, cellulose acetate is readily extractable using acetone and some grades of polyvinyl alcohol as readily extractable with water. Other suitable pore-forming fibers are those of sodium alginate, potassium metaphosphate polymer glass, and carboxymethyl cellulose.

The choice of a solvent for extracting the pore-forming fiber from the initial impermeable sheet depends upon the particular pore-forming fiber and the nature of the structural fiber and the binder material. The solvent should be one in which the pore-forming fiber is readily soluble;

and it should be substantially inert, i. e., have no solvent action, toward the structural fiber and the binder material. The duration of the extraction step depends upon the weight of the pore-forming fiber in the initial sheet, the thickness of the sheet, the solubility of the pore-forming fiber in the solvent, the temperature of the extracting liquid, and the degree of agitation.

As illustrated in the foregoing examples, products of satisfactory leather permeability may be formed using pore-forming fibers as short as 0.01", e. g., 0.01" cellulose acetate flock. However, a considerable increase in leather permeability is realized when longer pore-forming fibers are employed. For example, increasing the length of the pore-forming fiber from 0.01" (Example 16) up to a length of 0.25" (Example 17) produces a substantial increase in the leather permeability of the resulting product. However, as illustrated by comparing Examples 17 and 18, an increase in pore-forming fiber length from 0.25" to 0.5" resulted in substantially no increase in the leather permeability of the resulting sheet.

As illustrated in Examples 19-24, variations in the denier of the structural fibers and pore-forming fibers appear to have little effect upon leather permeability. On the other hand, it has been found that decreasing the thickness of the pore-forming fiber results in the formation of a synthetic leather sheet having improved resistance to penetration by liquid water. On the other hand, fibers which are finer than 1 denier are difficult to process on standard textile machinery; and, when used as structural fibers in the present compositions, the fibers are too rigidly immobilized by the binder to give optimum strength, e. g., tear and tensile. In other words, the fibers of greater denier tend to shift within the binder under flexing or tearing, this action making the product more durable. Finer fibers, however, are rigidly held by the binder. Furthermore, fibers having a denier less than 1/2 have so much exposed surface, i. e., ratio of surface area to core volume is high, and are so soft that they no longer behave as normal textile staples. On the other hand, fibers coarser than 16 denier are extremely harsh and more closely resemble bristles.

It is in the binder material that the interconnecting capillaries or pores are formed upon extraction of the pore-forming fibers, the interconnecting capillaries or pores having the shape of staple fibers. Furthermore, the binder material holds together and is reinforced by the structural fibers. The binder material may be selected from a great variety of soft, elastic, initially thermoplastic, synthetic polymers which may be classified generally as elastomers, as set forth by H. L. Fisher (Industrial and Engineering Chem., August 1939, page 942). The following polymers are preferred: N-methoxymethyl polyhexamethylene adipamide, copolymers made from ethylene glycol, terephthalic acid and sebacic acid of the general types disclosed and claimed in copending applications U. S. Serial Nos. 150,811 and 150,812, filed March 20, 1950, in the name of M. D. Snyder, polyethylene and its derivatives, plasticized polyvinyl chloride, plasticized vinyl chloride/vinyl acetate copolymers, natural rubbers, synthetic rubbers such as neoprene (2-chloro-1,3-butadiene polymer) and various other compositions containing vinyl chloride polymers or copolymers. Various other specific synthetic linear polymers which may be employed as a binder material with or without plasticizers include polyvinyl acetals, such as polyvinyl butyral or laural, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene/vinyl acetate copolymers, vinylidene chloride/acrylonitrile copolymers, polyethylene terephthalate, etc., or any tough, pliable polymeric material which is at least initially thermoplastic and which melts or flows at a temperature below the deformation (softening) temperatures of the structural fiber and pore-forming fiber. By the term "initially thermoplastic" is meant that the binder material must melt and flow under the conditions of the hot-pressing

step. When the binder material is in the form of individual fibers, the length of the fiber has no effect upon the properties of the extracted sheet, provided that the binder fibers have been uniformly dispersed throughout the composition before heat and pressure are applied.

In describing the binder material as a tough, pliable, at least initially thermoplastic, polymer, the following more specific requirements apply to those binder materials that are preferred:

1. The tensile strength should be at least 500 p. s. i.
2. The elongation must be at least 100%.
3. Materials not having a tensile strength and elongation greater than the above minimum specifications are satisfactory if the product of their tensile strength and elongation (where 100%=1) is at least 1,000.
4. The modulus must not be more than 25,000 p. s. i. and, preferably, not more than 5,000 p. s. i.

The binder material may be incorporated into the initial impermeable composite sheet in a variety of ways, several of which are illustrated in the foregoing examples. As illustrated in Example 2, the binder material may be in the form of fibers which may be carded along with the structural fiber and the pore-forming fiber to form a composite sheet by pressing the carded mixed fibers at elevated temperatures. Examples 1 and 7 illustrate mutual coagulation of a mixed dispersion of structural fibers, pore-forming fibers and binder polymers. Example 16 illustrates formation of a fibrous mat of a mixture of structural and pore-forming fibers followed by impregnation of the mat with a binder polymer in an aqueous dispersion. Other techniques of incorporating the binder material include impregnation of a fibrous mat with a binder polymer in solvent solution and impregnation of a fibrous mat with a binder polymer in the form of a powder or a homogeneous sheet. Other techniques of incorporating a binder material with the fibrous components (structural and pore-forming fibers) of the initial sheet include hot melt impregnation, impregnation by calendering or by spraying the binder material from aqueous dispersion or solvent solution onto one or both sides of a fibrous mat, followed by heat and pressure to impregnate the fibrous portion of the sheet with the binder material. Regardless of the technique employed to form a composite sheet, the sheet is consolidated prior to extraction by pressing at a temperature which is above the flow temperature of the binder and below the softening temperature of the structural fiber and pore-forming fiber. The pressure used is sufficient to cause the binder to flow and thoroughly impregnate the fibrous components of the sheet.

On the basis of numerous types of actual wearing comfort tests, it has been ascertained that membranes, e. g., leather and synthetic leather, exhibiting a leather permeability of 2,000 to 10,000 gms./100 sq. meters/hr. would provide wearing comfort equivalent to that obtained with glazed leathers and heavy shoe upper leathers. Furthermore, permeabilities of 10,000 to 22,000 were found to provide adequate wearing comfort equivalent to that obtained with the lightest shoe leathers.

In general, the wearing comfort of boots, shoes, gloves, etc., is determined or evaluated by measuring the leather permeability of the material from which the article is fabricated. With synthetic leather compositions made by the process of this invention, the leather permeability is substantially directly dependent upon the proportion of pore-forming fibers in the initial impermeable sheet. It is to be understood that the initial sheet, i. e., before extraction of the pore-forming fibers, is substantially continuous and vapor-impermeable. As mentioned hereinbefore, generally satisfactory comfort for boots and shoes is obtained when the shoe upper material has a leather permeability of at least 2,000 gms./100 sq. meters/hr. in an atmosphere of 23° C. and 90% R. H. Expressed in terms of one of the critical limitations of the present invention, it has been found that the total volume of

voids, i. e., interconnecting pores produced by extraction of the pore-forming fiber, should be no less than 40% of the total volume of the porous sheet to give at least satisfactory wearing comfort. Hence, since the densities of the components, i. e., structural fiber, binder material and pore-forming fiber, of the composite are substantially the same, this means that the proportion of the pore-forming fiber should be at least 40% of the total volume of the initial composite sheet. On the other hand, the foregoing examples clearly illustrate that the strength of the synthetic leather compositions of this invention drops off appreciably when the volume of the pore-forming fiber in the initial unextracted structure is substantially greater than 70% of the whole. This means that the strength of the synthetic leather compositions of the present invention is substantially below optimum when the total volume of voids in the final composition is greater than 70% of the whole. Resistance to penetration to liquid water is also unduly decreased at greater than 70% pore-former. The optimum volume of voids or pores in the final composition appears to be from 50-60%. As illustrated in the foregoing examples, the value of leather permeability increases as the total volume of voids increases; but the amount of void space is limited by the ultimate strength desired. For example, kid leather has a tongue-tear strength of only 3.15 pounds; and coated fabrics, for example, a woven cotton fabric coated with N-methoxymethyl polyhexamethylene adipamide, which have been successfully fabricated into shoes, have a tongue-tear strength of 2.62 pounds. On this basis, the very minimum tongue-tear strength of synthetic leather compositions is in the neighborhood of one pound (tongue-tear) although at least a tongue-tear of 3 to 5 pounds is preferred.

As mentioned hereinbefore, the prevailing problem in the production of a synthetic leather having satisfactory wearing comfort is that of preparing a sheet material of satisfactory tear strength, tenacity, flex life, softness, coupled with the ability to transpire water vapor and air. In addition to the direct effect of pore-former content upon leather permeability, it has been found that the weight ratio of structural fibers to binder material is also a critical factor in the preparation of a comfortable material of satisfactory strength. As illustrated in Examples 1, 5 and 6, optimum tear strength is obtained when the weight ratio of structural fibers to binder material is between 1/2 and 2/1. Synthetic leather compositions of this invention in which the weight ratio of structural fibers to binder material is outside this range possess tear strengths substantially below the optimum. This is surprising and is not predictable on the basis of prior art on the preparation of impermeable non-woven sheets.

In addition to possessing optimum tear strength when the ratio of structural fibers to binder fibers is within the above specified limits, it is surprising that the present synthetic leather compositions are more durable in general service than conventional coated fabrics made from the same fiber and binder, i. e., film-former, material. For example, a woven nylon fabric coated with a typical binder polymer of this invention does not possess the unique combination of tear strength, tensile strength, softness, and flex life, which are characteristic of the synthetic leather compositions of this invention. Furthermore, the coated fabrics are substantially impermeable to air and water vapor. In addition, the formation of a synthetic leather composition by extraction of a pore-former fiber results in producing a composition which is generally superior to all types of known synthetic leathers, especially with respect to the combination of tear strength, flex life, tensile strength, pliability and water vapor and air permeability. In general, the present synthetic leather compositions surpass all previous leather substitutes and, frequently, even natural leather itself.

The process of the present invention is exceptionally versatile with respect to preparing a synthetic leather

composition of the desired internal structure and surface texture. As mentioned hereinbefore, embossed sheets may be readily and efficiently produced by employing embossing rolls or pressure-applying surfaces during composition and fusing of the combination of structural fibers, binder and pore-forming fibers. Hence, embossing may be carried out in conjunction with a necessary step in the process; or it may be carried out immediately thereafter under conditions of lower temperature and pressure than employed in the fusing step. Embossing the extracted composition results in substantially decreasing the permeability of the structure and is generally to be avoided.

Another outstanding advantage of the present process is that the cross-sectional structure of the present synthetic compositions may be tailored for the desired end use by laminating or fusing different plies of one or more of three basic components together, the binder component usually being in fiber, powder or film form. On the other hand, initial fibrous mats composed of a mixture of the structural and pore-forming fibers may be carded and thereafter impregnated with the binder material by any of the methods mentioned hereinbefore. Examples 2, 3 and 41 illustrate laminating various plies containing one or more of the three basic components together in order to control the "face-to-back" concentration of structural fiber, binder material and pore-former. For example, the top ply of the initial unextracted composition may be composed entirely of the binder polymer in the form of a homogeneous film. The middle ply may be composed of various amounts of the structural, binder and pore-forming fiber; and the bottom ply may be composed essentially of the structural fiber. Such a structure after lamination and extraction of pore-former would form a synthetic leather composition having a relatively smooth or non-fiber-like upper surface (usually referred to as the "skin" side); and the bottom side would be substantially fibrous (usually referred to as the "flesh" side). It is obvious that the concentration of the structural fiber, binder material and pore-former may be varied from the face to the back of the sheet within reasonable limits by employing the general practices of the present invention.

An additional advantage of the present invention is that it provides a synthetic leather having a unique combination of tear strength, tensile strength, softness, pliability, flex life and ability to transpire water vapor and air. A further advantage is that it provides a process of preparing such synthetic leather compositions especially useful in fabricating boots, shoes, gloves, etc., wherein the properties may be tailored to the desired end use. A still further advantage is that it provides an economical process of preparing a synthetic leather which is equal or superior to the various types of genuine leather.

As many widely different embodiments may be made without departing from the spirit and scope of this invention, it is to be understood that said invention is in no way restricted except as set forth in the appended claims.

We claim:

1. The process of forming non-woven porous fibrous sheet which comprises forming a non-woven fibrous sheet comprising essentially structural fibers from the group consisting of staple fibers of synthetic linear polyamide, polyethylene terephthalate, polymers of acrylonitrile, polyvinyl acetals, regenerated cellulose, cotton and wool, from 40% to 70% by volume based on the total volume of the sheet, of pore-forming fibers selected from the group consisting of polyvinyl alcohol, cellulose acetate, sodium alginate and carboxymethyl cellulose, and a soft elastomeric binder material having a flow temperature below the deformation temperature of said fibers, the weight ratio of structural fibers to binder material being within the range of from 1:2 to 2:1, hot pressing said sheet at a temperature above the flow temperature of the binder and below the deformation temperature of said fibers, and thereafter extracting said pore-forming fibers from the sheet with a liquid which is a solvent for said pore-forming fibers and a non-solvent for said structural fibers and binder material whereby said structural fibers are substantially uniformly distributed throughout said porous sheet.

2. The process of claim 1 in which the structural fibers are a synthetic linear polyamide.

3. The process of claim 2 wherein the length of the synthetic linear polyamide fibers is within the range 0.01" to 8.0" and the length of the pore-forming fibers is within the range of 0.01" to 2.5".

4. The process of claim 1 wherein the pore-forming fibers are cellulose acetate.

5. The process of claim 1 wherein the pore-forming fibers are polyvinyl alcohol.

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