

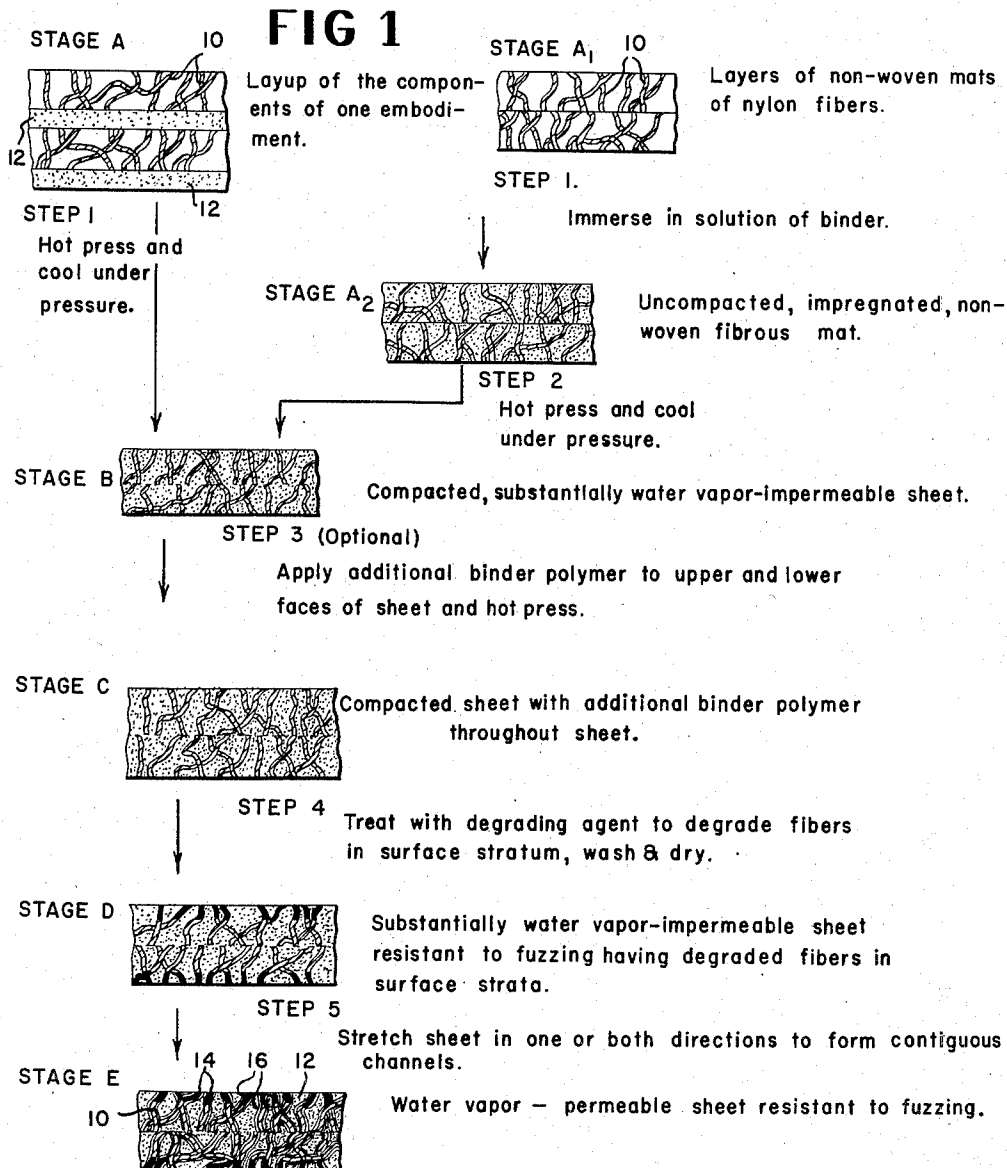
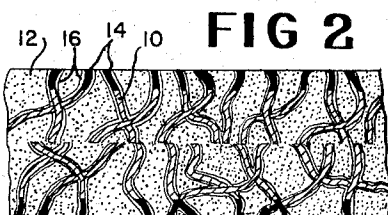
Aug. 6, 1957

I. SWERLICK

2,801,674

PROCESS FOR PREPARING A PERMEABLE SHEET MATERIAL AND PRODUCT

Filed June 21, 1955



INVENTOR

ISADORE SWERLICK

BY *Herbert M. Wolfson*

ATTORNEY

1

2,801,674

PROCESS FOR PREPARING A PERMEABLE SHEET MATERIAL AND PRODUCT

Isadore Swerlick, Kenmore, N. Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Application June 21, 1955, Serial No. 517,020

22 Claims. (Cl. 154—34)

This invention relates to leather replacement materials, and more particularly to non-woven sheet materials wherein matted, structural fibers are bound together by an extensible, polymeric binder.

Leather replacement materials have had a long history dating from the days of pyroxylin-coated, fibrous materials to the vinyl-coated, woven fabrics available today. Recently, leather replacement materials have been developed which are not only cheaper than genuine leather and prior art synthetic leathers but can be tailored to various end uses by controlling their processes of manufacture. These materials comprise matted, structural fibers bound together by a polymeric binder. They are generally prepared in three steps:

1. A non-woven mat of interlaced fibers is formed from staple fibers by suitable means such as techniques used in wool carding or paper making.

2. The mat is impregnated with a thermoplastic binder polymer so that each individual fiber is completely surrounded by the binder.

3. The impregnated mat is pressed, usually at an elevated temperature, to form a consolidated or integrated sheet structure.

The properties of the sheet material may be controlled by the particular binder and fibers used, the length and denier of the fibers and the location of special fibers in the original non-woven mat. Permeability to water vapor may be controlled by the degree of consolidation in the third step or by adding a fourth step which involves a chemical or physical treatment of the consolidated structure.

These leather replacement materials, despite improving on prior art materials in terms of properties and cost, suffer from an important shortcoming. They are not "scuff-proof." An unsightly fuzz resulting from fibers being pulled from the structure by abrading or scuffing tends to form on the surface of the sheet material. Since there are many applications such as shoe uppers, gloves, etc., where this condition cannot be tolerated, these materials have failed to gain wide public acceptance.

It is an object of this invention to provide a new sheet material of the type in which matted, structural fibers are held together by an extensible, polymeric binder. Another object is to provide such a material having much greater scuff resistance than possessed by heretofore known sheet materials of this type. A further object is to provide a new sheet material having high scuff resistance as well as softness, high tear strength, water repellency and, if desired, vapor-permeability. A still further object is to provide a process for preparing such materials. Other objects will appear hereinafter.

The above objects are accomplished by using embrittled or degraded fibers in the surface layer of a sheet material composed of a non-woven mat of structural fibers and an extensible polymeric binder. Preferably, the structure comprises a sheet material of 30% to 70% non-woven matted structural fibers and 70% to 30% of

2

an extensible polymeric binder binding the fibers together, the sheet having a surface layer of degraded fibers, and in the case of the permeable sheet, the sheet also having channels substantially contiguous with a major portion of the fibers throughout the thickness of the sheet.

The process for preparing the sheet material comprises plying a plurality of non-woven mats of fibers having a non-woven mat of degradable fibers in the surface layer; impregnating the mats with an extensible polymeric binder; pressing the impregnated mats to form a compacted structure; degrading the fibers in the surface layer of the compacted structure; and to form a vapor-permeable, scuff-resistant sheet material, breaking a substantial portion of the fibers away from the binder to form channels substantially contiguous with a major portion of the fibers. Alternatively, degradable fibers may be used throughout the structure and the degrading treatment controlled to degrade only the fibers in the surface layer.

For some purposes it may be desirable to make both surfaces of the sheet material scuff resistant. It is understood that the sheet material of this invention can have degraded fibers in both surface layers.

The degradable fibers for the surface layer or layers are preferably selected from the group consisting of polymeric materials having amide, aliphatic ester, and ether linkages. Most outstanding are fibers of nylon, viscose rayon and cellulose acetate. The fibers become degraded or embrittled by treatment with degrading agents. For nylon, viscose rayon and the like, aqueous solutions of zinc chloride, ferric chloride, stannic chloride, hydrochloric acid and ferric nitrate may be used as degrading agents; for cellulose acetate, a mixture of acetone and water may be used; and for polyesters such as polyhydroxyacetic ester and the like, water alone may be used.

The term "contiguous channels" as applied to the vapor-permeable sheet material, refers to channels or pores adjacent to portions of fibers throughout the structure. The channels are not necessarily completely annular. In some cases, the channel may spiral around part of the length of the fiber or may take the form of a "hairline crack" substantially parallel to or immediately adjacent to the fiber. They are formed by breaking away fibers from the binder, particularly at points where fibers cross or otherwise contact each other.

Three processes for forming contiguous channels are described in more detail in three copending applications. In U. S. Serial No. 318,732 filed November 4, 1952, to V. L. Simril, now Patent No. 2,757,100, a process is described wherein non-extensible structural fibers are used with a relatively extensible binder. Stretching the structure in one or two directions results in contiguous channels. In U. S. Serial No. 325,689 filed December 12, 1952, to J. C. Richards, now abandoned, contiguous channels are formed by first swelling the fibers followed by deswelling (or shrinking) to break the fibers away from the binder. In U. S. Serial No. 430,550 filed May 18, 1954, to H. R. Mighton, the previous alternative methods are combined into a single method for forming contiguous channels.

Figure 1 is a flow diagram of a representative process for preparing the preferred sheet material.

Figure 2 is an enlarged cross section of the final sheet material.

Stage A in Figure 1 represents a "layup" or composite of the essential components of one embodiment of the sheet material. About four layers of non-woven mats of nylon fibers 10 are placed in "cross-grain" fashion, one over the other so that the "grain" of each mat is substantially perpendicular to the "grain" of adjacent mats. Non-woven mats can be prepared by the techniques

known to paper making or wool carding or they may be prepared by deposition from an air stream on a screen. Homogeneous films or sheets of polyethylene 12, the binder polymer, are placed between each layer of mats. In the first step, the composite as illustrated in stage A is placed between two layers of non-heat-sealing cellophane (not shown) and hot pressed at a temperature sufficient to cause the binder polymer 12 to flow but not sufficient to fuse or transpose the nylon fibers 10 to any appreciable extent. The resulting compacted structure, as represented by stage B, is a binder polymer sheet reinforced with structural fibers.

Stage B may also be reached by the alternative procedure shown in stages A₁ and A₂. Stage A₁ represents layers of non-woven mats of nylon fibers 10 plied in cross-grain fashion as previously described. In the first step the mats are impregnated with the binder polymer by immersing them in a solution of polyethylene in a volatile solvent such as toluene, and solidifying the polyethylene. Alternatively, the mats of stage A₁ may be conducted through a dispersion of polyethylene in a non-solvent medium. Stage A represents the uncompacted, impregnated, non-woven fibrous mat. In the next step, the second step, the composite undergoes the hot pressing treatment previously described to form stage B, the compacted structure of a binder polymer sheet reinforced with structural fibers.

The next step, step 3, is an optional step and involves applying additional binder polymer to the upper and lower faces of the sheet followed by hot pressing. This step is an effort to distribute binder around all the fibers by filling any voids that might exist after step 2. The additional binder polymer may be applied by spraying or immersion or as thin sheets followed by pressing. The result shown in stage C is substantially the same sheet as that of stage B with additional binder polymer throughout the sheet.

The sheet is then conducted through an aqueous bath containing 60% zinc chloride at a temperature of 60° C. The zinc chloride solution tends to degrade the nylon fibers making them brittle. The time for this step, step 4, is controlled to limit the effect to the surface strata of the sheet. The sheet is then washed and dried. The resulting sheet is shown in stage D and may be used in applications where water vapor-permeability is not desired. Such uses include: draperies, shower curtains, book bindings, brief cases, luggage, table covers, etc.

However, to form synthetic leathers permeable to water vapor, the next step, step 5, is applied to the sheet of stage D. This step broadly involves breaking a substantial portion of the nylon fibers away from the polyethylene binder to form contiguous channels along a major portion of a substantial number of the fibers. Specifically, the sheet shown in stage D is stretched from 10% to 50% in one or two directions. The structural fibers, being less extensible compared to the relatively extensible binder polymer, break away from the binder polymer leaving the contiguous channels. As an alternative procedure the sheet may be dipped in water at a temperature above the softening temperature of the binder to swell the fibers. By then drying the sheet at a temperature below the softening temperature of the binder, the fibers shrink and tend to break away from the binder leaving the contiguous channels. These two alternative methods for forming contiguous channels may also be combined in a single method for the most effective results, i. e., stretching, followed by swelling-deswelling. In any case the resulting sheet shown in stage E, or the enlarged cross section shown in Figure 2, is formed. The sheet is composed of non-woven structural fibers 10 throughout a polymeric binder 12 with degraded fibers 14 in the surface of the sheet. The interconnecting channels 16 contiguous with the fibers provide water vapor-permeability

in the sheet material yet do not destroy its liquid repellency.

The leather replacement sheets may range in thickness from 15 mils to 50 mils with the surface stratum varying anywhere from 2% to 33% of the total thickness of the sheet. The outstanding result achieved in the prepared sheet is the failure of the sheet to produce surface fuzz after 100,000 scuffing strokes compared to prior art products without the described surface layer which produce fuzz after about 25 scuffing strokes.

Other specific embodiments of the invention are illustrated in the examples which follow. In these examples all percentages are by weight unless otherwise stated. The following tests were used to determine the properties of the products:

1. *Eccentric wheel scuff test*.—Scuff resistance was determined in a test instrument composed of two wheels. One was a non-rotatable wheel, 6 inches in diameter and 1 inch wide. The second wheel was a 4 inch diameter, 1 inch thick felt disk mounted so as to rotate about an off-center axis. The smaller wheel was so arranged that at its maximum displacement, it abraded strongly against the large non-rotatable wheel. The sample to be tested was placed on the periphery of the non-rotatable wheel. A single rotation of the off-center wheel was referred to as a scuff.

2. *Eraser scuff test*.—This was a simple test for rapidly evaluating the ability of the surface of structures to resist fuzzing upon being subjected to abrasion. A rubber eraser was merely rubbed against the surface of the sheet as one would do in erasing pencil marks on a sheet of paper and the result observed.

3. *Leather permeability measurement*.—This test was carried out substantially as described by Kanagy and Vickers in Journal of American Leather Chemists Association 45, 211-242 (April 19, 1950). Briefly, a 3 inch diameter crystallizing dish was filled with 12 mesh calcium chloride and covered with a membrane of the substance under test. The dish was inverted and suspended in an atmosphere of 90% relative humidity and a temperature of 23° C. and weighed at intervals. The increase in weight was a measure of the moisture vapor-permeability of the substance under test.

EXAMPLE I

Crimped staple fibers of polyhexamethylene adipamide (nylon), 2½ inches long and 3 denier/filament, were carded to form a web according to the wool carding technique. The web was cut into smaller mats and 4 layers of mats were plied in cross-grain fashion to form a composite structure. The composite was placed between screens and immersed in an aqueous solution of wetting agents, the solution comprising 2% octyl sodium sulfosuccinate and 2% of a sodium salt of an alkyl benzene sulfonate. The structure was squeezed through a two-roll wringer and permitted to dry.

The composite was then impregnated with from about 50% to about 70% by weight of the binder polymer by immersing in an aqueous dispersion of plasticized vinyl chloride polymer. The dispersion contained the following ingredients:

500 parts of a dispersion containing about 50% vinyl chloride polymer
300 parts of a dispersion containing about 50% dioctyl phthalate
50 parts of a dispersion containing about 50% black pigment
275 parts of water

The total percent solids was, therefore, 34.5% and the percent plasticizer was 35.2% of the total solids. About 0.3% of sodium alginate was used in the dispersion to prevent loss of polymer during subsequent dipping for gelling the polymer.

After immersion, the composite structure was allowed to drain and again was squeezed through the two-roll

5

wringer. The binder polymer was then gelled by dipping the impregnated composite structure in a solution containing 50% acetic acid in methanol. Acid and salt were removed by washing with water and excess water was pressed out of the structure.

The structure was dried at a temperature below 95° C.; placed between sheets of cellophane and Bristol board; and pressed at 500 pounds per square inch and at a temperature of about 150° C. The consolidated fiber/binder structure was then immersed in an aqueous solution containing 60% zinc chloride at a temperature of 60° C. The time of immersion was varied as shown in the ensuing table. The structure was then immersed in water to wash away zinc chloride and any products resulting from the reaction with zinc chloride.

In the following table, Table I, the properties of the structures treated with zinc chloride solution are compared to a structure that did not undergo the treatment.

TABLE I

Nylon fibers/vinyl chloride polymer binder

Test	Percent by wt. binder	Time of Degradation Treatment, minutes	Eraser Test	Scuff Test
Control.....	57	none	fuzzed...	fuzz after about 25 scuffs.
A.....	64	22	no fuzz...	no fuzz after 100,000 scuffs.
B.....	71	5	do....	short fuzz after 100,000 scuffs.
C.....	53.3	15	do....	no fuzz after 100,000 scuffs.

¹ Additional vinyl chloride polymer was added to the surface of the sheet and a second hot pressing followed.

The above structures were then stretched about 25% in two directions to impart vapor-permeability to the structures. The leather permeability value for all structures was well above 3,000 grams/100 square meters/hour while the fuzzing characteristics remained substantially as shown in Table I. Furthermore, the zinc chloride treatment showed no appreciable effect on the remaining properties, such as tensile strength, tear strength, elongation, etc., when compared to the stretched control structure.

EXAMPLE II

A composite structure of 4 layers of mats was prepared from nylon fibers substantially in the manner described for Example I. The structure was impregnated with from about 50% to 60% of its weight of a polymeric binder by immersing in an aqueous dispersion of plasticized neoprene. The dispersion contained the following ingredients:

- 500 parts of a dispersion containing about 50% neoprene
- 300 parts of a dispersion containing about 50% polyethylene glycol di-2-ethyl hexoate
- 20 parts of a dispersion containing about 50% zinc oxide
- 12 parts of a dispersion containing a polyoxyethylated fatty alcohol as a stabilizer
- 32 parts of a dispersion containing 50% of a curing agent for neoprene
- 50 parts of a dispersion containing 50% black pigment
- 385 parts of water

The total percent solids was, therefore, 35% and the percent plasticizer was 33% of the total solids.

After immersion, the composite structure was allowed to drain and again squeezed through the two-roll wringer. The binder polymer was then gelled by immersing the impregnated composite structure in a solution containing 50% acetic acid in methanol. Acid and salt were removed by washing with water and excess water was pressed out of the structure.

The structure was dried at a temperature below 95° C.

6

to prevent the neoprene binder from curing. Thereafter, the composite structure was placed between sheets of cellophane and Bristol board and pressed at 1,000 to 1,500 pounds per square inch and a temperature of about 150° C. and held for sufficient time to cure the neoprene binder. The consolidated fiber/binder structure was permitted to cool under pressure and then immersed in a solution containing the degrading agent. The particular degrading agent, the temperature of treatment and the time of treatment are given in the ensuing table. The structure was then immersed in water to wash away the degrading agent and any products resulting from the reaction.

In the following table, Table II, the properties of structures treated with a degrading agent are compared to a structure that did not undergo the treatment.

TABLE II

Nylon fibers/neoprene binder

Test	Percent by wt. binder	Degrading Treatment	Eraser Test	Scuff Test
Control.....	58.5	none.....	fuzzed badly, no fuzz...	fuzz after 25 scuffs.
A.....	58.5	10% HCl—80° C.—1 minute.	do....	do....
B.....	58.5	10% HCl—80° C.—2 minutes.	do....	do....
C.....	58.5	10% HCl—80° C.—2½ minutes.	do....	do....
D.....	58.5	10% HCl—80° C.—3½ minutes.	do....	do....
E.....	58.5	10% HCl—80° C.—surface treated only.	do....	do....
F.....	61	10% HCl—90° C.—½ minute.	do....	no fuzz after 100,000 scuffs.
G.....	58	60% ZnCl ₂ —60° C.—5 minutes.	do....	Do.
H.....	59.5	60% ZnCl ₂ —60° C.—10 minutes.	do....	Do.
I.....	58.2	60% ZnCl ₂ —60° C.—2½ minutes.	do....	Do.
J.....	58.5	60% ZnCl ₂ —60° C.—10 minutes.	do....	Do.
K.....	59.8	60% ZnCl ₂ —60° C.—15 minutes.	do....	Do.
L.....	58.7	60% ZnCl ₂ —60° C.—20 minutes.	do....	Do.
M.....	50	50% Fe(NO ₃) ₃ —50° C.—3 minutes.	do....	do....

The above structures were stretched from 30% to 40% in one or two directions, A through D being stretched in one direction, the others being stretched in two directions. The leather permeability value for all structures was well above 2,000 grams/100 square meters/hour while the fuzz characteristics remained substantially as shown in Table II. The degrading treatment showed no appreciable effect on the remaining properties such as tensile strength, tear strength, elongation, etc., when compared to the stretched control structure.

EXAMPLE III

A composite structure of 50% polyethylene and 50% nylon fibers was prepared directly by hot pressing alternate layers of a non-woven fibrous mat of the nylon fibers and layers of the polyethylene film at a temperature of 140° C. and a pressure of 500 pounds/square inch. The consolidated fiber/binder structure was then immersed in an aqueous solution containing 10% hydrochloric acid at a temperature of 90° C. The time of immersion was varied as shown in the ensuing table. The structure was immersed in water to wash away excess hydrochloric acid solution and any resulting products of chemical reaction.

In the following table, Table III, the properties of structures treated with the degrading agent are compared to a control that did not undergo the treatment.

7

TABLE III

Nylon fibers/polyethylene binder

Test	Time of Treatment, Minutes	Eraser Test	Scuff Test
Control.....	none	fuzzed badly..	fuzz after 25 scuffs.
A.....	5	no fuzz.....	no fuzz after 100,000 scuffs.
B.....	10	do.....	Do.
C.....	15	do.....	Do.

The above four structures were stretched about 30% in two directions in accordance with the process described in U. S. Serial No. 318,732, filed November 4, 1952, to V. L. Simril. The resulting leather permeability values for all structures were well above 2,000 grams/100 square meters/hour while the fuzz characteristics remained substantially as shown in Table I. The hydrochloric acid treatment showed no appreciable effect on the remaining properties of the treated structures when compared to the control structure.

EXAMPLE IV

Crimped staple fibers of nylon, 2½ inches long and 3 denier/filament, and rayon, 1½ inches long and 1.5 denier/filament (50/50 by weight), were carded, plied, impregnated with from 50 to 60% by weight of vinyl chloride polymer and treated with a 60% zinc chloride solution at 60° C. as described for Example I.

In the following table, Table IV, the properties of the structures treated with zinc chloride solution are compared to an untreated control.

TABLE IV

Nylon and rayon fibers/vinyl chloride polymer binder

Test	Percent by wt. binder	Time of Treatment, Minutes	Eraser Test	Scuff Test
Control.....	58	none	fuzzed badly..	fuzz after 25 scuffs.
A.....	54.2	20	no fuzz.....	no fuzz after 100,000 scuffs.
B.....	55	20	do.....	Do.
C.....	50	20	do.....	Do.

The above structures were stretched about 20% in two directions in accordance with the process previously described. The resulting leather permeability values for all structures were well above 3,000 grams/100 square meters/hour while the fuzz characteristics remained substantially as shown in Table IV. The remaining properties of the structures were unaffected by the degrading treatment.

EXAMPLE V

A composite structure of 50% neoprene and 50% rayon fibers was prepared and treated in accordance with the procedure described in Example II. The degrading treatment was a 60% zinc chloride solution at 55° C. for 25 minutes. The resulting structure was "scuff-proof" as shown by no fuzz in the eraser test. After stretching the structure 10% in two directions, the leather permeability value was 4,666 grams/100 square meters/hour while there was no change in the surface fuzzing characteristics.

EXAMPLE VI

Crimped staple fibers of nylon, 2½ inches long and 3 denier/filament, and rayon, 1½ inches long and 1.5 denier/filament (50/50 by weight), were carded, plied, impregnated with 50 to 60% neoprene and formed into a composite structure as described in Example II. Two samples were treated with zinc chloride solution, two with ferric nitrate solution, one with ferric chloride solution and one was untreated. The details of the treatment and the results are presented in the following table.

8

TABLE V

Nylon and rayon fibers/neoprene binder

Test	Percent by wt. binder	Degrading Treatment	Eraser Test
Control.....	55	None.....	fuzzed badly.
A.....	57	60% ZnCl ₂ -90° C.-2 minutes.....	no fuzz.
B.....	55.5	60% ZnCl ₂ -90° C.-1½ minutes.....	Do.
C.....	50	50% Fe(NO ₃) ₃ -50° C.-8 minutes.....	Do.
D.....	51.3	50% Fe(NO ₃) ₃ -50° C.-3 minutes.....	Do.
E.....	47	35% FeCl ₃ -75° C.-8 minutes.....	Do.

EXAMPLE VII

Fibers of cellulose acetate, 2½ inches long and 3 denier/filament, were combined with neoprene in the manner described for Example II to form a composite structure containing 50% neoprene. The structure was treated with an acetone-water mixture containing 55% acetone at room temperature for 5 minutes. The treating solution was washed away with water. The resulting structure did not fuzz in the eraser test. After stretching 50% in two directions, the structure had a leather permeability value of 11,157 grams/100 square meters/hour and there was no change in the surface fuzzing characteristics.

EXAMPLE VIII

A non-woven matted structure of two inner layers of nylon fibers and two outer layers of cellulose acetate fibers was impregnated with vinyl chloride polymer to form a composite structure containing 62.5% of the vinyl chloride polymer in the manner described for Example I. The structure was treated with an acetone-water mixture containing 50% acetone for 6 minutes at room temperature. The treating solution was washed away with water. The resulting structure did not fuzz in the eraser test.

EXAMPLE IX

Non-woven matted structures containing in one case 50% nylon fibers and 50% cellulose acetate fibers and in the second case 75% nylon fibers and 25% cellulose acetate fibers with cellulose acetate fibers in the top layers of both structures were impregnated with vinyl chloride polymer in the manner described for Example I to form a composite structure containing 50% of the vinyl chloride polymer. The structures were treated with an acetone-water mixture containing 55% acetone for 10 minutes at room temperature. The resulting structures showed no fuzz in the eraser test. After stretching both structures between 20 and 25% in two directions, both structures showed leather permeability values of about 3,850 grams/100 square meters/hour and there was no change in the surface fuzzing characteristics.

EXAMPLE X

A non-woven matted structure of 50% nylon fibers and 50% cellulose acetate fibers with cellulose acetate fibers in the top layer was impregnated with neoprene in the manner described for Example II to form a structure containing 59.1% neoprene. The structure was treated with an acetone-water mixture containing 55% acetone for 13 minutes at room temperature. The resulting structure did not fuzz in the eraser test and after stretching 50% in two directions had a leather permeability value of 2,496 grams/100 square meters/hour with no change in the surface fuzzing characteristics.

EXAMPLE XI

A non-woven matter structure was prepared containing polyethylene terephthalate and nylon fibers with nylon fibers in the top layer. In the first case the mat was impregnated with vinyl chloride polymer in the manner of Example I to form a structure containing

58.3% of the vinyl chloride polymer. In the second case the mat was impregnated with neoprene in accordance with the procedure of Example II to form a structure containing 38.5% neoprene. Both structures were treated with a solution of 60% zinc chloride at 90° C. for 1½ minutes. After washing and drying, neither structure fuzzed in the eraser test. After stretching 20% in both directions, the structures displayed leather permeability values of over 10,000 grams/100 square meters/hour with no change in the fuzzing characteristics.

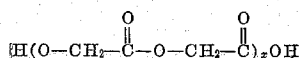
It is understood that the preceding examples are merely illustrative of specific preferred embodiments.

The invention broadly resides in using embrittled or degraded fibers in the surface layer of a sheet material composed of matted structural fibers bound together by an extensible polymeric binder. The same degradable fibers may be used throughout the structure with degrading being limited to the surface layer. Degrading would be controlled by the time and temperature of the treatment and by the concentration and type of degrading agent. An alternative structure is suggested by some of the examples wherein the fibers used for the surface layer are different from those used throughout the remaining portion of the structure. A degrading agent is used which only affects the fibers in the surface layer. Thus, "overtreatment," where the degrading agent penetrates below the surface layer to weaken the structure, is prevented. Mixtures or blends of fibers may also be used for certain purposes. Thus, when a swelling-deswelling treatment is used for imparting permeability, it is advantageous to combine rayon, which reacts to a mild swelling-deswelling treatment, with nylon which provides strength but does not react substantially to the treatment.

Most fibers of synthetic and natural origin may be used as degradable fibers. However, in some cases the degrading agent required may be so potent that it becomes very difficult to locate a binder material that will not also be affected by the degrading treatment. Among the more useful fibers, besides those disclosed in the examples, are:

1. Synthetic linear polyamides such as polyhexamethylene sebacamide, polycapraamide and interpolymers, in short, those disclosed in U. S. Patents 2,130,523, 2,252,555, 2,285,009, 2,252,257 and 2,430,860, which are degraded by the treatments suggested for polyhexamethylene adipamide (nylon) fibers.

2. Polyhydroxyacetic esters of the general form:



polyethylene sebacate, polyethylene adipate which may be degraded with water.

3. Other synthetic linear condensation polymers such as polyesters, polyesteramides, and mixtures or blends thereof such as the dibasic acid/diamine or amino acid polyamides, the dibasic acid/diol or hydroxy acid/polyesters or the intermixed polyester/polyamide products described in greater detail in U. S. Patents 2,071,250, 2,071,251, 2,071,253, 2,130,948, 2,224,037, 2,572,844 which may require a harsher degrading agent such as sulfuric acid.

4. Cellulose esters and ethers such as cellulose acetate propionate, cellulose acetate butyrate, ethyl cellulose, benzol cellulose, etc., which require treatment with acetone for degrading.

5. Polymers of vinyl chloride alone or copolymerized with vinyl acetate or with acrylonitrile which may be degraded by dimethylformamide.

6. Natural fibers such as cotton, wool and silk which may be degraded by sulfuric acid.

The denier and length of the staple fibers are not critical to the invention. The length may vary from

.01 inch up to 8 inches or greater and the denier may vary from 1 to 16 denier per filament. The longer fibers, 0.5 to 4 inches long, are preferred since they provide improved tensile strength and improve extensibility in the finished sheet material. The heavier deniers are also preferred since they make the sheet material tougher and more durable. The denier may also affect the efficiency of the treatments for degrading and imparting permeability. In general, as denier increases the rate of penetration of any liquid used for treatment will decrease.

Degrading polymeric materials involves reducing their molecular size and in the case of oriented polymeric fibers, deorienting the molecular structure. By reducing molecular size and deorienting an oriented molecular structure, the material becomes drastically embrittled, the tensile strength of degraded fibers being no more than 75%, usually 50% or less of the strength of the original fibers. The desired depth of the surface layer or layers, which is the depth of degrading, may vary from 2 to 33% of the total thickness of the sheet and will depend on the particular end use. For instance, materials used for shoe uppers require a deeper layer than those used as drapery materials because of the harsher scuffing treatment received by shoe uppers in use. In all cases, the depth should be kept to the minimum necessary for the particular use. Otherwise, the structure may be weakened and its leather permeability value reduced. The depth can be determined by experiment and will vary with the fibers used, the binder used, the degree of consolidation achieved during pressing, the degrading agent used and the time and temperature used for the treatment.

It is important to degrade the fibers after consolidation with the binder. Direct treatment of the fibers prior to consolidation, while it can be done, is much too difficult to control. In fact, it has been found necessary that the structure comprise at least 30% binder, preferably at least 40%, in order to provide a sheet material whose surface fiber can be degraded in a controllable manner and by a continuous process. A top limit of 70% binder or 30% fibers in the sheet is set to maintain sufficient fiber reinforcement in the sheet material for strength.

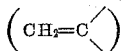
The degrading treatment may be accomplished in any suitable manner. Immersion of the sheet material in the degrading solution and spraying or otherwise applying solution on the sheet material are two methods which have been used.

The embrittled fibers may be "chipped" from the surface layers at any time following the degrading treatment. In the case of the vapor-permeable sheet this is most conveniently accomplished by abrading the sheet after forming the contiguous channels.

The critical factor in selecting the polymeric binder is that it should be chemically different from the structural fibers. A convenient rule is that the binder be incompatible in the melt with the structural fibers. Otherwise, the structures are usually deficient in drape, hand, flex life and tear strength. Furthermore, the binder should flow at a temperature at least 50° below the deformation temperature of the structural fiber and, as a film, exhibit a tensile strength of at least 500 pounds/square inch, an elongation of at least 100% and a tensile modulus no greater than 25,000 pounds/square inch. A binder fulfilling these requirements may be described as tough, pliable and initially thermoplastic.

A number of thermoplastic materials useful as binder materials are classified as elastomers and are disclosed by H. L. Fisher in Industrial and Engineering Chemistry, August 1939, page 942. In the most preferred sheet materials of this invention, the polymeric binder will be a linear addition polymer. Because of their availability and particularly their low cost and desirable polymer properties, the most outstanding are the vinylidene polymers and copolymers including both the monoene and

diene types. This class of polymers is characterized by having in each polymerizable monomer as the only polymerizable ethylenic unsaturation, terminal ethylenic groups wherein the terminal carbon is a methylene carbon, i. e., those containing one or more vinylidene



groups. Specific examples of such polymers include the various vinylidene hydrocarbon polymers such as butadiene/styrene, polyethylene, polyisobutylene, polyisoprene, both synthetic and natural; the various negatively substituted polymers such as the vinylidene halide including vinyl halide polymers, e. g., polyvinylidene chloride, polyvinyl chloride and polyvinyl fluoride; derivatives of such polymers as halogenated vinyl and vinylidene polymers, e. g., chlorinated polyethylene, and chlorinated polyvinyl chloride; the various vinylidene polymers wherein one or both of the indicated free valences of the 2-carbon of the vinylidene group are bonded directly to carboxyl groups or groups hydrolyzable to carboxyl groups either directly to the acyl carbon or to the oxy oxygen thereof, such as polymers of various vinylidene esters, including vinyl acetate and ethylidene diacetate; vinylidene carboxylic acids and their derivatives such as acrylic acid, acrylonitrile, and methacrylamide.

Also included in this most preferred group are the various copolymers of such vinylidene monomers, including specifically the various monoene and diene copolymers of this class such as 2,3-dichlorobutadiene-1,3/2-chlorobutadiene-1,3 copolymers; the various monoene/vinylidene copolymers such as the commercially important vinyl and vinylidene chloride copolymers, e. g., vinyl chloride/vinyl acetate, vinyl chloride/vinylidene chloride, and vinyl chloride/vinyl acetate/acrylonitrile copolymers; the various vinylidene hydrocarbon negatively substituted vinylidene copolymers, e. g., ethylene/vinyl acetate and the hydrolyzed products therefrom; ethylene/vinyl chloride, and butadiene/acrylonitrile copolymers.

In the case of those binder components containing in combined form appreciable proportions of diene monomers, particularly the vinylidene diene monomers, it is frequently desirable to have present in the solution, dispersion, or bulk treating material, whichever is used, suitable amounts of chemical agents for effecting under controlled conditions, after the fiber has been impregnated with the binder and the whole mat suitably compacted, the cross-linking of the diene copolymer component. The agents for effecting such controllable cross-linking are well known in the rubber art. In the case of the diene hydrocarbon polymers and copolymers, the presence of mercaptans and/or sulfur in the diene polymer composition provides cross-linking by disulfide formation. In the case of negatively substituted diene polymers and copolymers such as the 2-chlorobutadiene-1,3 (chloroprene) polymers, the presence of metallic oxides such as zinc or magnesium oxides provides cross-linking by removal of halogen.

Various polyesters containing terephthalic acid or derivatives thereof as essential components are also useful as binder polymers, there including polyethylene terephthalate and copolyesters made from ethylene glycol, terephthalic acid and sebacic acid of the general type described and claimed in United States Patents Nos. 2,623,031 and 2,623,033 in the name of M. D. Snyder. Polyamides useful as a binder polymer include N-methoxymethyl polyhexamethylene adipamide and other similar polymers disclosed and claimed in United States Patent No. 2,430,860. Also included among useful binder polymers are the polyvinyl acetals, such as polyvinyl butyral, polyvinyl laural, etc. Included among various elastomeric polymers which may be employed as binders in the present invention are the polyurethanes which are essentially reaction products of (1) an organic polyisocyanate or polyisothiocyanate with (2) a compound obtainable by reacting (a) one or more polyhydric alcohols with

(b) one or more polycarboxylic acids (either in the presence or absence of one or more monocarboxylic acids). Specified products of this type are described and claimed in United States Patent No. 2,333,639 to R. E. Christ and W. E. Hanford. Other types of elastomeric polymers which may be used as binders include reaction products of polyalkylene ether glycols and organic diisocyanates.

In many instances, it is desirable to have appreciable proportions of plasticizers for the binder polymers in the binder composition. This is particularly important in the case of the vinylidene resins. Plasticizers provide high pliability and desirable drape in products that might otherwise be too stiff. This is particularly true of the higher molecular weight, negatively substituted vinylidene polymers and copolymers, such as the vinyl chloride/vinylidene chloride and vinyl chloride/vinyl acetate copolymers. Suitable examples of plasticizers include the higher molecular weight mono- or dicarboxylic acid/alcohol or/polyolesters such as glycerol mono-oleate, glycerol sebacate, dioctyl phthalate, and ethylene octanoate; or the lower molecular weight polyesters and polyesters such as the polyalkylene oxides and their esters, e. g., polyethylene oxide, methoxypolyethylene glycol; and the lower molecular weight condensation polyesters such as polyethyleneglycol adipate.

The binder polymer employed in the surface stratum may be different from the binder in the internal strata of the sheet. This might be desirable to obtain a flexible structure with a hard top layer. To obtain an integral structure, the binder polymer in the top layer must be compatible with and chemically similar to the binder employed in the lower layers of the composite. A typical lay-up might consist of alternate layers of films of polyisobutylene and non-woven fibrous mats with polyethylene in the top layer.

Another method of obtaining a flexible structure with a hard top stratum would be to use the same binder polymer throughout but with different contents of plasticizer in the various strata. For example, the top stratum may be composed of a binder without plasticizer and the lower strata may contain varying amounts of a plasticizer. Such a structure will have a relatively hard surface stratum, but with high flexibility due to the plasticized internal strata.

Color can be imparted to the sheet material of this invention by incorporating dyes or pigments in the polymeric binder or, preferably, by dyeing the structural fibers prior to forming the initial composite with the binder. Another method is to apply a special color coat, about 2 to 4 mils thick, which contains a pigment, a polymeric binder and a plasticizer. The binder may be different from that used in the basic sheet material. A typical color coating may comprise 100 parts of polymeric binder, 70 parts of plasticizer and 40 parts of the pigment. When using a color coat, it may also be desirable to apply a "depth" coat about 0.5 mil thick. The depth coat usually contains binder and plasticizer wherein the plasticizer content is lower than in the color coat and in the remaining structure. A top coating called a "gloss" coat, about .01 to 2 mils thick, may be applied over the color and depth coats. This coating is normally transparent, a typical formulation comprising 100 parts of binder polymer, 33 parts of polymethylmethacrylate, 6.6 parts of silica and 1.4 parts of stearic acid. These three coats may be made permeable if desired by suitable means heretofore known in the art.

The advantage of the product lies in the high scuff resistance attainable without sacrificing tear strength, tensile strength, flex life or extensibility. The process is relatively easy to control and can be modified to tailor the product for particular end uses. The process is also easily adapted for continuous operation. Most important, the product is economical to produce and the process requires relatively little time.

The product, vapor-permeable or impermeable, can

be substituted in substantially all leather applications: the impermeable material in handbags, shoe soles, book bindings, luggage, brief cases, table covers, etc.; the vapor-permeable material in gloves, shoe uppers, etc.

As many different embodiments of this invention may be made without departing from the spirit and scope thereof, it is understood that the invention is not limited except as defined in the appended claims.

The invention claimed is:

1. A sheet material comprising matted structural fibers and an extensible polymeric binder binding said fibers together, wherein the fibers in the surface layer only are degraded.

2. A sheet material as in claim 1 composed of 30% to 70% structural fibers and 70% to 30% binder.

3. A sheet material as in claim 1 wherein the fibers for the surface layer are selected from the group consisting of polymeric materials having amide, aliphatic ester and ether linkages.

4. A sheet material as in claim 1 wherein the fibers for the surface layer are selected from the group consisting of nylon, viscose rayon and cellulose acetate.

5. A sheet material as in claim 1 having channels substantially contiguous with a major portion of the fibers throughout the thickness of said sheet.

6. A sheet material as in claim 5 composed of 30% to 70% structural fibers and 70% to 30% binder.

7. A sheet material as in claim 5 wherein the fibers for the surface layer are selected from the group consisting of polymeric materials having amide, aliphatic ester and ether linkages.

8. A sheet material as in claim 5 wherein the fibers for the surface layer are selected from the group consisting of nylon, viscose rayon and cellulose acetate.

9. A process for preparing sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of degradable fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; and degrading the fibers in the surface layer only of the compacted structure.

10. A process as in claim 9 wherein the degradable fibers are selected from the group consisting of polymeric materials having amide, aliphatic ester and ether linkages.

11. A process as in claim 9 wherein the degradable fibers are selected from the group consisting of nylon, viscose rayon and cellulose acetate fibers.

12. A process for preparing sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of nylon fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; and treating the structure with an aqueous solution of an agent selected from the group consisting of zinc chloride, ferric chloride, stannic chloride, hydrochloric acid and ferric nitrate to degrade the nylon fibers in the surface layer only of the compacted structure.

13. A process for preparing sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of viscose rayon fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; and treating the structure with an aqueous solution of an agent selected from the group consisting of zinc chloride, ferric chloride, stannic chloride, hydrochloric acid and ferric nitrate to degrade the viscose rayon fibers in the surface layer only of the compacted structure.

14. A process for preparing sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of cellulose acetate fibers being in the

surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; and treating the structure with a mixture of acetone and water to degrade the cellulose acetate fibers in the surface layer only of the compacted structure.

15. A process for preparing permeable sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of degradable fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; degrading the fibers in the surface layer only of the structure; and breaking a substantial portion of the fibers away from the binder to form channels substantially contiguous with a major portion of the fibers.

16. A process as in claim 15 wherein the fibers in the surface layer are different from those in the remaining portion of the structure.

17. A process as in claim 15 wherein the fibers are the same throughout the structure and degrading is limited to the surface layer of the structure.

18. A process as in claim 15 wherein the degradable fibers are selected from the group consisting of polymeric materials having amide, aliphatic ester and ether linkages.

19. A process as in claim 15 wherein the degradable fibers are selected from the group consisting of nylon, viscose rayon and cellulose acetate fibers.

20. A process for preparing permeable sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of nylon fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; treating the structure with an aqueous solution of an agent selected from the group consisting of zinc chloride, ferric chloride, stannic chloride, hydrochloric acid and ferric nitrate to degrade the nylon fibers in the surface layer only of the structure; and breaking a substantial portion of the fibers away from the binder to form channels substantially contiguous with a major portion of the fibers.

21. A process for preparing permeable sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of viscose rayon fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; treating the structure with an aqueous solution of an agent selected from the group consisting of zinc chloride, ferric chloride, stannic chloride, hydrochloric acid and ferric nitrate to degrade the viscose rayon fibers in the surface layer only of the structure; and breaking a substantial portion of the fibers away from the binder to form channels substantially contiguous with a major portion of the fibers.

22. A process for preparing permeable sheet material which comprises plying a plurality of non-woven mats of fibers, a non-woven mat of cellulose acetate fibers being in the surface layer; contacting said mats with an extensible polymeric binder; pressing the mats in contact with the binder to form a compacted structure; treating the structure with a mixture of acetone and water to degrade the cellulose acetate fibers in the surface layer only of the structure; and breaking a substantial portion of the fibers away from the binder to form channels substantially contiguous with a major portion of the fibers.

References Cited in the file of this patent

UNITED STATES PATENTS

2,647,297	Battista	Aug. 4, 1953
2,715,588	Graham et al.	Aug. 16, 1955
2,719,802	Nottebohm	Oct. 4, 1955
2,730,479	Gibson	Jan. 10, 1956