FIG. 1.

FINE FIBERS

COARSE FIBERS

FINE FIBERS

FIG. 2.

SURFACE LAYER OF FINE FIBERS

ZONE OF INTERMINGLED FINE AND COARSE FIBERS

LAYER OF COARSE FIBERS

ZONE OF INTERMINGLED FINE AND COARSE FIBERS

SURFACE LAYER OF FINE FIBERS

INVENTOR

BOYNTON GRAHAM

BY

ATTORNEY
United States Patent Office

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NON-WOVEN SHEET MATERIAL

Boynton Graham, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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

Certain types of sheet material possessing outstanding properties have been prepared in which matted, structural fibers are held together by a polymeric binder. One type of such material which is disclosed and claimed in Graham and Picard U. S. application Serial No. 326,359, filed December 16, 1952, now Patent No. 2,715,591, uses undrawn or orientable fibers of synthetic linear polymers as the structural fibers. It possesses exceptionally high permanent elongation or extensibility with essentially no retractive tendencies, as well as great impact toughness. Another type of such material which is disclosed and claimed in Graham and Picard U. S. application Serial No. 326,360, also filed December 16, 1952, now Patent No. 2,715,598, is permeable and has a certain amount of interconnected void space distributed through it and combines the essential properties of genuine leather to a degree heretofore unattained in a synthetic product.

An object of the present invention is to provide a new sheet material of the type in which matted, structural fibers are held together by an extensible polymeric binder.

A further object is to provide such a material having much greater scuff resistance than possessed by heretofore known sheet materials of this type. A still further object is to provide a new sheet material having great scuff resistance combined with satisfactory tear and tensile strengths, flex-life, uniform extensibility, and uniformity of properties as a function of direction. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by forming sheet material comprising, by weight, 20% to 85% of non-woven, matted structural fibers and 80% to 15% of an extensible polymeric binder binding the fibers together, the sheet having a surface layer wherein the fibers are substantially all less than 0.2 denier/filament, and, preferably, less than 0.01 denier/filament, and a base layer wherein the fibers are substantially all greater than 1.0 denier/filament or greater.

It has been found that sheet material as characterized above not only has completely satisfactory tear and tensile strengths, flex-life, and uniform extensibility but possesses scuff resistance to a notable and unexpected degree. This latter attribute persists in the sheet material through the widest variations in the composition of the polymeric binder or the type of material used for the structural fibers and seemingly is accounted for by the combination of the extremely fine structural fibers at and near the surface of the sheet and the coarse fibers forming a base layer. If desired, sheet material highly scuff resistant on both sides can be obtained simply by providing a layer of fine fibers bound together with the polymeric binder on both sides of the so-called “base layer” of coarse structural fibers bound together with the polymeric binder.

In a preferred embodiment, the structural fibers comprise 30% to 70% by weight of the sheet material and the polymeric binder 70% to 30%, and the structural fibers are fibers of a synthetic linear condensation polymer.

The sheet material of this invention can be prepared in many different ways, using techniques well known in the art. The structural fibers in non-woven, matted form, i.e., in the form of webs, mats, or felts, are brought into intimate contact with the extensible polymeric binder by any suitable means such as impregnation from a solution or dispersion of the binder, or simple mixing where the polymeric binder is used in fibrous or particulate form. The mats can be prepared by a number of ways as by paper-making techniques, wool-carding, or deposition from an air stream. Usually, it is more convenient to prepare mats of the coarse fibers and fine fibers separately and then, either before or after impregnation with the binder, to ply them. Particularly, with respect to the mats of coarse structural fibers, several such mats can be prepared and piled to give a thicker, heavier, and stronger mat, and, subsequently, a thicker and stronger sheet material. An alternate procedure is to prepare the mat of coarse fibers and then form a layer or mat of fine fibers directly on the coarse fiber mat.

In the preparation of the mats, mixtures of fibers of various types can be used and the fibers can be of different lengths and diameters, always providing the structural fibers in the mat which is to form the base layer, are substantially all greater than 1.0 denier/filament and those in the mat which are to form the surface layer, are substantially all less than 0.2 denier/filament, and preferably, less than 0.01 denier/filament. Similarly, mixtures of binders can be used.

The present invention comprises both impermeable and permeable sheet material which latter may be a leather-like product of the type disclosed in the aforementioned U. S. application Serial No. 326,360. The type of product depends on the degree of consolidation achieved in the step wherein the matted structural fibers and binder are consolidated. If complete consolidation is achieved by either solvent or thermal means, the latter usually being high pressure, an impermeable material results. On the other hand, where incomplete consolidation is achieved by thermal means, a permeable material will be obtained. Conveniently, pressure is used in the partial consolidation and spacers or shims are employed to prevent complete consolidation.

Permeable sheet material can also be prepared in several different ways even though the structural fiber/binder mixture is completely consolidated. This can be done, for example, by incorporating a pore-forming fibrous or particulate component in the mixture and then, after consolidation of the fiber/binder by either solvent or thermal means, with or without pressure, extracting this pore-forming component by means of a preferential solvent therefor which is a non-solvent for the structural fibers and binder. This method of preparing a permeable product is more fully disclosed and claimed in Picard and Graham U. S. application Serial No. 301,603, filed July 29, 1952. Another method is to prepare consolidated sheet material of relatively extensible fibers thoroughly impregnated with a relatively extensible binder, and then stretching and finally relaxing the sheet material. This procedure is more particularly described and claimed in V. L. Simrul U. S. application Serial No. 318,752, filed November 4, 1952. Such material can also be prepared from consolidated sheet material of liquid swellable structural fibers and a binder.
therefore, by swelling the structural fibers, setting the binder while the fibers remain swollen, and finally drying to shrink the fibers. This procedure is more fully disclosed and claimed in J. C. Richards U. S. application Serial No. 325,689, filed December 12, 1952, now abandoned.

Although a solution or dispersion of polymeric binder or the polymeric binder in fibrous or particulate form will generally be used in preparing the sheet material of this invention, the polymeric binder can be used in film-form except in the instance where permeable sheet material is being prepared by incomplete consolidation. Piles of the fine and coarse structural fiber mats and the binder in film-form are simply consolidated using solvent or thermal techniques with or without applied pressure.

The permeable sheet material, no matter how achieved, constitutes a preferred embodiment of this invention since such material is of particular utility in the important leather replacement field where its superior wearing comfort, good tensile strength, and high scuff resistance makes it of particular significance. Because of the improved leather-like properties, especially the ability to breathe, the permeable sheet material will contain preferably, on a total weight basis, 50% to 70% of structural fibers and 50% to 30% of binder and will have a volume percent of interconnected void space uniformly distributed throughout which is at least equal to 3000 (weight percent fiber)−1−0.30 and no greater than 70%. Such sheet material is of outstanding value in the leather replacement field. A particularly preferred form of permeable sheet material which possesses the properties of genuine leather to an extraordinary degree and, hence, is useful in the extremely demanding leather garment field, is that containing, on a total weight basis, 50% to 60%, and especially about 50%, of structural fibers and 50% to 40%, and especially about 50%, of binder and having a volume percent of interconnected void space uniformly distributed throughout which is equal to 3000 (weight percent fiber)−1−0.25±0.5.

The impermeable sheet material having little or no interconnected void space is outstanding for uses where toughness, impermeability, and high scuff resistance are at a premium, such as in luggage, women's handbags, tarpaulin substitutes, beltings, shoe soles, and the like.

The permeable sheet material containing the above described uniformly distributed interconnected void space is outstanding for those uses where its ability to breathe is critical, e.g., protective clothing such as gloves, jackets, and especially shoe uppers.

The sheet material of this invention can vary in thickness from the thinnest material it is possible to make up to any thickness at all. However, it would be unusual to exceed a thickness range of from 1 mil to 500 mils and generally the sheet material will be considerably in excess of 25 mils in thickness. The so-called "surface layer" containing the fine fibers usually will range from 3 to 15 mils in thickness. In the case of the permeable sheet material, it will conventionally be of such thickness as to weigh between 5 and 20 oz./sq. yd. with the preferred material ranging in weight from 8 to 12 oz./sq. yd. The surface layer of the permeable material will usually range from 3 to 15 mils in thickness and, preferably, will be of the order of 6 mils in thickness.

While it is convenient to refer to "base layer" and "surface layer" in describing the herein considered sheet material, such layers are hardly visually noticeable in the finished material. Further, in the plying of mats of coarse and fine fibers or in otherwise preparing the matted structural fibers, a certain intermingling of coarse and fine fibers is practically inevitable. Thus, in discussing the thicknesses of layers above, it will be understood that the dividing line between layers may not be sharp and, more usually, the sheet material will comprise a surface layer of fine fibers and binder, a base layer of coarse fibers and binder, and between the two a narrow zone wherein coarse and fine fibers in mixture are distributed through the binder with the fine fibers predominating on the side adjacent the surface layer and the coarse fibers predominating on the side adjacent the base layer.

In the accompanying drawing there is illustrated more or less diagrammatically sheet material according to the present invention.

Fig. 1 is an enlarged cross section of an assembly of mats of coarse and fine fibers, separated from one another;

Fig. 2 is an enlarged cross section of the final sheet material showing the combined mats with a narrow zone indicated wherein the coarse and fine fibers are somewhat intermingled.

The sheet material illustrated in the drawing is specific to that embodiment of the invention where both the upper and lower surfaces of the sheet material have a layer of fine fibers. The invention is equally applicable to sheet material wherein only one of the two surfaces has a layer of fine fibers, that surface being the one exhibiting the improved scuff resistance.

The relative amounts of fine and coarse structural fibers can vary greatly in the instant sheet material and clearly will vary depending upon the relative thickness of the base and surface layers. In general, the fine structural fibers will be in the decided minority, e.g., from 5% to 30% of the total weight of structural fibers.

The sheet material of this invention whether permeable or non-permeable, can be prepared so as to exhibit uniform strength and extensibility in all directions or not, as desired, depending on the randomness or degree of order of the fiber components. Thus, sheet material wherein the structural fibers are random in their distribution with respect to each other will exhibit essentially uniform strength and extensibility in all directions. If, on the other hand, the structural fibers bear ordered relationships space-wise to each other, the sheet material will exhibit non-uniform extensibility and strength with the maximum amount of the former occurring in the direction in which the structural fibers are least ordered and vice versa for the latter.

The following examples in which all parts are by weight unless otherwise stated, illustrate specific embodiments of the invention. The Schiltknecht flexmeter values mentioned in the examples are the number of flexes a sample of the sheet material undergoes before surface cracking in the Schiltknecht flexmeter machine, which is described in detail in Bulletin #105 of Alfred Suter Co., 200 Fifth Avenue, New York, N. Y. Tongue-tear strength is reported in pounds and is a measure of the force necessary to continue an existing tear in the sheet material being tested. The values given are average values obtained in the manner of ASTM procedure D-39-39, using the Model TTB tester, manufactured by the Instron Engineering Corporation. Tensile strength is reported in units of lbs./sq. in. and represents the maximum load undergone by the sample under test when subjected to linear stress in the plane of the sample strip in the same type tester. Elongation values are reported as percentage of the original length and are obtained during the same test and represent the maximum elongation incurred in the strip sample being tested. Modulus values, which are also obtained with the same type tester in accordance with the ASTM test procedure D-638-46T, are expressed in units of lbs./sq. in. and actually represent the modulus of elasticity in tension, e.g., the stiffness. A higher modulus indicates a stiffer membrane.

Example 1

A dispersion of 4.1 parts of 19.3 micron diameter (three denier filament), half-inch long, polyhexamethylene oenadipamide fiber in 16,000 parts of water is formed into a mat by deposition on a wire screen according to paper-
making techniques, the screen dimensions being such as to give a dry weight of the mat of about 6 oz./sq. yd. After being dried, a similar mat was likewise prepared from a dispersion of one part of 0.1 micron diameter (0.0001 in. in diameter or less) non-permeable sheet materials which in the same apparatus exhibited excessive fuzzing after only about 25 scuffs. These various sheet materials exhibit on the average a Schilknecht flex-like of at least one million flexes before noticeable surface failure.

Example II

Three plied non-woven carded mats of 2½ inch long, 3 denier-filament polyhexamethyleneadipamide fibers were topcoated on one surface with a non-woven mat of fine denier (less than 0.01 denier/filament) polyhexa-
methyleneadipamide fibers, the fine diameter filaments constituting 17% of the total structural fibers by weight. The resultant plied mat was treated with the above-described wetting agent composition, dried, and impregnated with the above-described polychloroprene binder composition to a 62% weight level based on the total impregnated plied mat.

Example III

Sheet materials similarly prepared in which the fine diameter polyhexamethyleneadipamide fibers of the surface layer constituted 22% and 23% by weight of the total structural fibers and the polychloroprene binder composition constituted, respectively, 63% and 51% by weight of the total impregnated plied mats likewise exhibited excellent scuff resistance, but were less permeable than the material of Example II. After needle punching, respectively, 400 and 200 holes per square inch, the permeability of the sheet materials was found to be increased by, respectively, 200–300% and 100% while the scuff resistance remained essentially unchanged.

Example IV

Three non-woven fibrous mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were prepared, plied, treated with the above-described wetting solution, dried and then impregnated with a polychloro-
prene impregnating dispersion similar to that described previously but containing 25% solids. The thus im-
regnated plied mat was then plied with a non-woven mat of the fine denier polyhexamethyleneadipamide fibers which constituted 21% by weight of the total structural fibers, and the thus plied mat again impregnated with the 25% solids, polychloroprene impregnating dispersion. The total amount of the polychloroprene binder was 62.4% of the total impregnated plied mat. By this technique the total percentage of the binder in the surface layer was decreased but the strength of the base structure was maintained. The end product exhibited excellent scuff resistance.

Example V

Three non-woven fibrous mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were prepared and a surface layer of non-woven polyethylene terephthalate fibers less than 0.01 denier/filament was applied thereto, the latter constituting 20% by weight of the total structural fiber components. The thus plied mat was treated with the above referred to wetting agent solution, dried, and impregnated with the polychloroprene dispersion of Example II. After drying, it was found that the binder component represented 56.6% of the total composition. After pressing as before and stretching 40% in both dimensions of the plane of the plied mat there was obtained a permeable sheet material exhibiting excellent scuff resistance.

Example VI

A non-woven fibrous mat of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers was
plied with another such mat prepared from 1½-inch long fibers and the two plied mats finally plied with 2 mats of polyethylene terephthalate fibers less than 1.01 denier/filament, the latter constituting 47% by weight of the total structural fiber components. The thus plied mats were treated with a wetting agent, dried, and then impregnated with the polychloroprene dispersion of Example II to give 59.4% binder component by weight of the total product. After drying, pressing, and stretching 40% in each of the dimensions of the plane of the sheet, there was thus obtained a permeable sheet material exhibiting excellent scuff resistance.

Example VII

Three non-woven fibrous mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were plied and impregnated with the polychloroprene dispersion of Example II. A non-woven fibrous mat of the fine diameter (less than 0.01 denier/filament) polyethylene terephthalate fibers was similarly impregnated in a 25% solids dispersion of the same type. The plied impregnated three-layered composite was then combined, wrung together, set up, washed and dried. After pressing as before and stretching 40% in each of the two dimensions of the plane of the sheet product, there was obtained a permeable sheet material exhibiting excellent scuff resistance. The fine diameter structural fiber components and the end product contains 52.5% binder.

Example VIII

Three non-woven fibrous mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were plied and impregnated with the polychloroprene dispersion of Example II, set up, washed and dried. A non-woven mat of less than 0.01 denier/filament polyethylene terephthalate fibers (20.9% of the total fibers) was then placed over the base and the whole plied mat again impregnated to give a total of 80% binder in the end product. After drying and pressing as before and stretching 40% in each of the two dimensions of the plied mat, there was obtained a sheet material exhibiting excellent scuff resistance.

Example IX

Three non-woven fibrous mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were plied and a surface ply of non-woven polyhexamethylene adipamide fibers of less than 0.01 denier/filament was applied theroeto, the fine fibers constituting 30% by weight of the total structural fiber component. The thus plied mat was impregnated as before with the polychloroprene impregnating dispersion of Example II containing an added dispersed color pigment. The resulting impregnated mat was dried and pressed at 135° C. for 15 minutes using 150 mil shims. The pigment and binder amount to 57% by weight of the total sheet product which is permeable and exhibits excellent scuff resistance. The same results were obtained using varying proportions of the fine diameter structural fibers and pigments and binder composition with various size shims. The sheeet materials ranging from 53.3% to 63% pigment and binder and having from 12% to 18.2% of the fine diameter structural fibers, all exhibited excellent scuff resistance and varied in thickness from 80–150 mls. It is to be noted that a decrease in the thickness of the shims used in pressing lowers the permeability of the end sheet material appreciably with that obtained using 80 mil shims being essentially impermeable.

Example X

Two mats prepared as described in Example IX were placed back to back after impregnation and pressed under various pressures. They were then delaminated, i. e., split at the junction, to give two mats each having a smooth topside containing the fine denier fibers (31.4–34.9% of the total fiber component) and a fuzzy backside containing the large denier fibers. The matten which contained 52.5–50.2% pigment/binder exhibited excellent scuff resistance and varied in permeability depending upon the pressure used.

Example XI

Fibrous non-woven mats of 2½ inch long, 3 denier/filament polyhexamethyleneadipamide fibers were plied and a similar mat of less than 0.01 denier/filament fibers applied to the top thereof. These fine diameter fibers constituted 11.6% of the total structural fiber component. The thus plied mat was impregnated with 7.8 parts of 78% of a commercially available high molecular weight polyvinyl chloride and 5.2 parts of dioctyl phthalate in about 180 parts of a 2/98 dimethylformamide/tetrahydrofuran mixture to give 46.1% binder by weight of the whole. After impregnation, the binder was coagulated by immersing the impregnated mat in water. The dried impregnated mat was pressed at 50 lb./sq. in. and 140° C. for 2 minutes and then cooled under pressure to below 90° C. The mat, after pressuring, was swelled, swelled and stretched, and stretched to give a permeable sheet material exhibiting excellent scuff resistance and a flex-life of about 3½ million Schlichtmeck flexes. Essentially the same results were obtained using other mats and varying amounts of binder component, ranging from 45.1% to 48% by weight of the total with the fine diameter polyhexamethyleneadipamide fibers constituting from 16.5 to 18% of the total structural fiber component.

Example XII

Three mats of non-woven fibrous polyhexamethylene adipamide fibers 2½ inches long and 3 denier/filament were plied and a surface layer of less than 0.01 denier/filament polyethylene terephthalate fibers applied there-to—the latter constituting 14.2% by weight of the total structural fiber component. The thus plied mat was impregnated as described above in Example XI and the mat pressed, swelled, and stretched all as given there. The final product contained 46.1% by weight of the total binder component and exhibited excellent scuff resistance. The same results were obtained with another sheet material similarly prepared having 46.4% polyvinyl chloride/dioctyl phthalate binder whereas the fine diameter polyethylene terephthalate fibers comprises 11.8% of the total structural fiber component.

It will be understood that the above examples are merely illustrative and that the present invention broadly resides in sheet material comprising, by weight, 20% to 80% of non-woven structural fibers and 80% to 15% of an extensible polymeric binder fibers the fiberglass, the sheet material having a surface layer wherein the fibers are substantially all less than 0.2 denier/filament and a base layer wherein the fibers are substantially greater than 1.0 denier/filament. The structural fibers used in the sheet material of this invention can be of the widest variety, the only important limitation being that some fibers are not available for use as the fine structural fibers simply because they cannot be obtained in thicknesses of 0.2 denier/filament or less. Suitable fibers include fibers both of natural origin and synthetic origin, including rayon-type fibers, i. e., shaped cellulose derivative or regenerated cellulose fibers, and fibers from both the synthetic addition and condensation-type polymers, whether oriented or not. Blends of the various types of fibers can be used. The most outstanding sheet material is that wherein all the structural fibers are synthetic linear condensation polymers. An obvious qualification as to the structural fibers used is that they must be so selected with relation to the polymeric binder and the processing by which the sheet material is formed, that they will retain their entity in the final sheet material. In the case of sheet material pre-
pared by solvent techniques, this means that the structural fibers should not be soluble in the solvent used to effective addition polymerization of the binder/fiber mixtures although it is permissible that the fibers be partially swollen by the solvent. Also, in the preparation of permeable sheet material by solvent means, the structural fibers and the polymeric binder should not be soluble in the solvent used to extract the pre-mixed fibers or particulate components of the blend which is to be removed to form the requisite pores.

Where the sheet material is being made by thermal and/or pressure means, the structural fibers should preferably not melt or deform below about 500 °F., and most preferably about 200 °F., above the flow temperature of the polymeric binder. It is preferred that both the coarse and fine structural fibers be of the same type to simplify problems in selection of the binder.

Also, where permeable sheet material is to be prepared by solvent means, it is preferred the pore forming components be of the same type in both the mats forming the surface layer and the base layer of the sheet material. Because of undue adhesion caused by surface effects arising in the fine structural fibers, it is preferred not to use the thermal partial consolidation procedure for forming pores in the surface layer of the permeable type sheet material but rather to use the solvent extraction procedure for the surface layer with the base layer being prepared by either procedure.

Fibers of addition polymers suitable for use in this invention include the polyamide of ethylene, polymers and copolymers of the alpha-methylene-carboxylic acids and their derivatives and precursors thereof, including copolymers with other addition polymerizable monomers, e.g., acrylic, lonicylitrile polymers and copolymers. Because of their generally better fiber properties, e.g., higher strength, and the resultant superior properties of the mats prepared therefrom, the preferred structural fibers are the synthetic linear condensation polymers, whether orientated or unoriented but orientable, e.g., the polyamides, polymesters, polyetheramides, or mixtures or blends thereof, such as the dianodic acid/diamine or mono acid polyamides, the dianodic acid/diol or hydroxy acid/polyesters, or the intermixed polyester/polamide products by now well known in the art and described in greater detail in U.S. Patents 2,071,250, -251, -253, 2,130,948, 2,224,037, 2,572,844, and the like.

A particularly suitable class of such synthetic linear condensation polymers, because of good cold-drawability and the reader availability of intermediates necessary therefor, are the polyamides-prepare from the dianodic carboxylic acids, or amide-forming derivatives thereof, and essentially equimolar proportions of amino compounds having two amino hydrogen-bearing amine groups separated by divalent organic radicals, free of active hydrogen and preferably solely hydrocarbon in nature. Specific examples of such linear condensation polymers include polytetramethylenesbacamide, polyethyleneterephthalamide, and polydodecamethylene adipamide, including the especially preferred polyhexamethylenediamide. Also included are those polymers prepared from the amino hydrogen-bearing amino substituted carboxylic acids or amide-forming derivatives thereof, preferably those wherein the hydrogen-bearing amine group is on the terminal carbon of the carboxylic acid chain, e.g., the alpha-amino carboxylic acids, the epsilon-amino carboxylic acids, and the like. Specific examples of such polymers include poly-D- or L- or DL-amino, poly-D-, L- or DL-lactide, and the especially preferred poly epsilon-amino caproic acid.

Another similarly suitable group of synthetic linear, orientated condensation polymers are the polyster, i.e., those polymers containing a plurality of recurring intra-chain ester or acyloxy linkages, particularly those containing a plurality of recurring intra-chain carboxyester linkages. Specific examples of such polymers which can be prepared, for instance, by the intermolecular condensation between essentially equimolar proportions of dibasic acids and dihydroxy-hydrogen-bearing polyols, particularly those which apart from the carboxyl and hydroxy groups are solely hydrocarbon, include polydodecamethylene adipate, polyethylene sebacate, and polyhexamethylene oxalate.

Also included in this group of the linear condensation polymers are those prepared from the alcoholic hydroxyl hydrogen-bearing carboxylic acids, preferably those wherein the alcoholic hydrogen-bearing hydroxyl group is on the terminal carbon of the carboxylic acid chain, e.g., the alpha-hydroxy carboxylic acids, the epsilon-hydroxy carboxylic acids, and the like. Specific examples of such polymers include poly-D, or L, or DL-lactic acid, poly-D, or L, or DL-mandelic acid, and poly epsilon-hydroxy caprolactone acid.

While the relative thickness of the coarse and fine structural fibers goes to the heart of this invention, the length of the fibers is not critical and they can vary from as little as 0.01 inch (10 mls) up to 8 inches in length or greater. The fiber length is determined as much by the method of preparing the composite layers of fibers and the length of fiber conveniently available as by any differences in properties that can be effected in the resulting sheet material through the use of fibers of any particular length. For instance, papermaking techniques, which are the most preferable from the standpoint of quickness, convenience, high rate of production, and cheapness, are only applicable to fibers no longer than 0.5 inch. Similarly, air-blowing techniques, also both convenient and reasonably cheap, are usually limited to the use of fibers no greater than 1.5 inches in length. Fibers of greater length necessitate preparation of the non-woven mats by wool-carding techniques which are somewhat more costly and less convenient since this process can only produce non-woven mats of limited weight per pass. Despite this, the relatively longer fibers, i.e., those of at least 1.5 inches in length are the preferred coarse structural fibers because they give non-woven mats having greater form stability which is advantageous during the preparation of the sheet material and because they give tougher sheet material.

Further, as to the non-woven mats of fine structural fibers forming the surface layer of the sheet material, these fine fibers are generally formed by extruding and air-blowing on a screen target and unless conditions are carefully adjusted the fiber lengths will not be uniform. It is possible to form a surface layer of these fine structural fibers directly by using a non-woven mat of coarse structural fibers as the target instead of the conventional screen target.

All factors considered, including tensile strength and degree of extensibility of the finished sheet material, it is preferred that the non-woven mats of coarse structural fibers ranging from 0.5 to 4 inches long, more particularly, from 2.0 to 2.5 inches long, the fibers exceeding 1.0 denier/filament but being less than 60 denier/filament. For ease of handling and the greater pliability and toughness of the sheet material prepared therefrom, it is preferred to use coarse structural fibers of from one to nine denier/filament. Fine structural fibers in the approximate range of 0.05 inch up to 1.5 inches are preferable.

The polymeric binder is preferably chemically dissimilar to the structural fibers being used and also is preferably strong and pliable, especially the latter. The polymeric binder can be and often preferably a polycomponent structure, e.g., copolymers, frequently preferably plasticized. Because of the greater ease in handling, tensile strength and wear resistance arising from their use, it is preferred to use as the polymeric binder those synthetic polymers which are chemically dissimilar to the structural fibers; which flow at least 50 °F., and preferably at least 200 °F., below the deformation temperatur of the structural fibers; and which in film form
exhibit tensile strengths of at least 500, and preferably at least 1000 lb./sq. in., elongations of at least 100%, and preferably at least 200%, and moduli no greater than 25,000, and preferably no more than 5,000 lb./sq. in., with the product of said tensile strength and elongation being at least 100,000.

In the most preferred sheet material of this invention, because of greater strength, flex-life, and ease of handling, the polymeric binder will be a synthetic linear addition polymer of the above given set of properties and the structures therein will be formed from a synthetic linear condensation polymer. Frequently, when sheet material of higher plialibilities are desired, the binder will contain one or more modifiers, in particular plasticizers for the type binder component polymer being used. Other modifying agents equally well known in the art may also be present in the binder component, such as dyers, pigments, fillers, and the like.

The chemically dissimilar polymers useful as possible binder components include broadly synthetic addition polymers, synthetic condensation polymers which are not chemically similar to the binder polymer, and natural and modified natural products, e.g., cellulose acetate, cellulose acetate, cellulose cellulose, and the like. Because of their reader availability, better properties, and appreciably greater ease of handling, the addition polymers are preferred. A particularly outstanding group are the addition polymers containing in combined form the ethylenically unsaturated monomers including both the mono- and diene-type monomers. Suitable examples of such polymers include the lower monoene and diene solely hydrocarbon polymers such as polybutene-2, and the like; tetrafluoroethylene/ethylene; tetrafluoroethylene/chlorotrifluoroethylene, and the like.

Because of their reader availability and particularly their lower cost and more desirable polymer properties, the most outstanding group of these addition polymeric binders are the vinylidene polymers and copolymers, in- cluding both the monoene and diene types. This class of polymers is characterized by having in each polymerizable monoene therein involved 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 (CH=CH) groups. Included in this most preferred class are the great majority of commercially available addition poly- mers. Specific examples of such polymers include the various vinylidene hydrocarbon polymers such as buta- diene/styrene, polyethylene, polyisobutylene, polypolyisoprene, both synthetic and natural; the various negatively sub- stituted polymers such as the vinylidene halide including vinyl halide polymers, e.g., polyvinylidene chloride, poly- vinyl chloride, and polyvinylidene chloride; derivatives of such polymers such as the 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 the oxy oxygen thereof, such as polymers of the various vinylidene esters, vinyl acetate and ethylene diaceto; the vinylidene carboxylic acids and their derivatives such as acrylic acid, methyl methacrylate, acrylonitrile, and methacrylamide.

Also included in this most preferred group are the various copolymers of such vinylidene monomers, including specifically the various monoene/diene copolymers of this class such as the 2,3-dichlorobutadiene-1,3-2-chlorobutadiene-1,3 copolymers; the various monoene/vinyl- idene 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 sub- stituted vinylidene copolymers, e.g., ethylene/vinyl ac- e tate and the hydrolyzed products therefrom; ethylene/ vinyl chloride, and butadiene/vinylidene 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 chain-breaking agents for effecting under controlled conditions, after the fiber has been impregnated with the binder and the whole mat suitably partially consolidated, the cross linking of the diene copolymer com- ponent. These chemical systems for effecting such con- trollable crosslinking are well known in the rubber art and in the case of the diene hydrocarbon polymers and copolymers, normally function through a disulfide formed crosslink arising from the presence of mercaptans and/or sulfur in the diene polymer composition, and in the case of the negatively substituted diene polymers and copoly- mers, such as the 2-chlorobutadiene-1,3 (chloroprene) polymers and copolymers, normally function through halogen removal as affected by the presence in the diene polymer composition of appreciable quantities of metallic oxides such as zinc or magnesium oxides.

In many instances it is desirable to have present in the binder composition appreciable proportions of plastici zers, now well known in the art, for the binder poly- mers. This is particularly important in the case of the vinylidene resins, to prevent formation of products of too great stiffness, especially with the higher molecular weight, negatively substituted vinylidene polymers and copolymers, such as the vinyl chloride/vinylidene chlo- ride and vinyl chloride/vinyl acetate copolymers, so as to produce leather-like products of good drape and high pliability. Suitable examples of these include the higher molecular weight mono- or dicarboxylic acid/alcohol or/polyester monomers, the hydrolyzed products thereof, and ethylene octanoate; or the lower molecular weight polyesters and polyesters such as the polyalkylene oxides and their esters, e.g., polyethylene oxide, meth- oxypolyethylene glycol; and the lower molecular weight condensation polymers such as polyethyleneglycol adipate.

As pointed out previously, the critical factor in the choice of a preferred polymeric binder is the fact that is should not be chemically similar to the structural fiber. This is quite important since it has been found that where the polymeric binder is chemically similar to the structural fiber, the resulting sheet material, while occasionally adequate in tensile strength, is generally defi- cient in drape, hand, and flex-life and more importantly, is usually particularly deficient in tear strength. A con- venient rule for characterizing the chemically dissimilar polymeric binders is that they be incompatible in the melt with the structural fibers.

The sheet material of this invention has been described as comprising a surface layer of fine fibers and a base layer of coarse fibers. Where high scuff resistance is desired on both sides of the base layer, which is not usually the case, then a surface layer of fine fibers is provided on both sides of the base layer of coarse fibers. Manifestly, the present invention is equally ap- plicable to sheet material regardless of whether it has the surface layer of fine fibers on one or both sides of the base layer.

Color can be imparted to the sheet material of this invention by incorporating dyes or pigments in the polymeric binder, as previously mentioned, or by dyeing after finishing or using pre-dyed or pre-pigmented struc- tural fibers. Preferably, colored sheet material is pre- pared by the use of dyed or pigmented structural fibers or by incorporating the coloring material in the polymeric binder, particularly in the case of the permeable, leather-like sheet material, since the sheet material is then uni- formly colored throughout and thus, unlike colored natu-
natural leather, will not exhibit any marked or undesirable color change if scuffed or abraded.

An advantage of this invention is that it provides sheet material having great scuff resistance combined with satisfactory tear and tensile strengths, flex-life, and uniform extensibility. A particularly advantageous form of the invention is that wherein the sheet material exhibits leather-like properties, the great scuff resistance of the sheet material making it outstanding, particularly, for use in shoe uppers.

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

The invention claimed is:

1. Sheet material comprising, by weight 20% to 85% of matted structural fibers of synthetic linear condensation polymer bound together by 80% to 15% of an extensible polymeric binder of synthetic addition polymer which flows at least 50° F. below the deformation temperature of the structural fibers, from 5% to 50% by weight of said structural fibers being of fine size from less than 0.01 up to 0.2 denier per filament and the other structural fibers being of a coarse size from 1 to 60 denier per filament, said sheet having a surface layer of at least 3 mils in thickness wherein the fibers are substantially all of said fine size and a base layer wherein the fibers are substantially all of said coarse size.

2. Sheet material as set forth in claim 1 wherein said structural fibers of fine size are all less than 0.01 denier per filament.

3. Sheet material as set forth in claim 1 wherein said extensible polymeric binder is incompatible in the melt with the structural fibers.

4. Sheet material as set forth in claim 1 which contains a volume percent of interconnecting void space distributed therethrough at least equal to 3000 (weight percent fiber)^-1--30 and not greater than 70%.

5. Sheet material as set forth in claim 4 wherein the structural fibers comprise 40% to 60% by weight of the sheet and the polymeric binder comprises 60% to 40% by weight of the sheet.

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