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FLEXIBLE LEATHERLIKE SHEET MATERIAL

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This invention relates to novel flexible leather-like sheet materials and to methods of manufacturing the same. It provides a strong, flexible, plump sheet materials having toughness, high resistance to tear, stitch-holding strength, multi-dimensional extensibility, and pliability, and which, if desired, can be surface-finished as may leather to a high gloss, grain, or matte appearance. In my material these properties are combined to provide characteristics found heretofore only in natural leather.

Natural skin from which leather is prepared consists essentially of proteinaceous fibers and a small proportion of a gelatinous binding material. The physical characteristics of these leather fibers differ somewhat, depending upon the source of the skin, but, in general, the fibers are of varying diameters and each is composed of many fine sub-fibers. Even though individual leather fibers are weak compared to the usual natural textile fibers, a leather structure possesses a surprising composite tensile strength due, it is believed, to the tangled yet fiber-free arrangement of its fibers. These fibers are so fitted around each other that the application of stress tightens and locks them in their respective positions, yet the structure is free enough to permit the fibers in some degree to slip, twist, and turn as they tighten, permitting stresses to be distributed progressively over an increasing number of fibers as the leather gives or deforms under load.

The extensibility of leather appears due in part to the flexible nature of the protein fiber and more particularly to the ability of the fibers to adjust their positions without suffering breakage. While the fibers may be closely packed, particularly at the surface, the leather retains a considerable degree of porosity and flexibility, due, it is believed to the maintenance of inter-fiber spaces and fiber freedom even in closely packed areas.

The high cost of natural leather has led to various attempts to provide substitute materials which have to some extent replaced leather for certain uses. While some of these substitutes may even excel leather in a single property, such as tensile strength, other equally important qualities are missing or have been sacrificed to achieve this end. Primarily because the fibrous structure of leather has until now defied approximation, no one has heretofore devised a product which combines to any appreciable degree the unique properties of natural leather.

It is the principal object of this invention to provide flexible sheet materials having the desirable characteristics of natural leather and a fibrous organization functionally approximating that of leather.

The flexible leather-like sheets of my invention may be described as a reticulate structure consisting essentially of an integrated association of intercurled and interlocked unspun fibers having artifically induced kinks, bends, and twists flexibly locally joined by elastic articulations with an elastomeric material dispersed about and between the fibers, and voids within the structure so that fibers are free to move, that is, to twist or turn, to straighten, or to bend or kink further, under stresses tending to elongate, deform, compress or bend the structure.

It is believed that the leather-like properties of the unique products of this invention are due primarily to the peculiar arrangement and relationship to one another of the fibers of the new materials. The degree of fiber entanglement may not be so high nor so compact as in natural leather, but the fibrous arrangement is remarkably similar in that the fibers are curled, kinked, looped and twisted in all directions and are entangled and frictionally interlocked one with another. The materials are further similar in that the elastomeric material substantially contributes to the strength and integrity of the sheet somewhat as the gelatinous material in some natural leathers contributes to their characteristics.

Without the elastomeric material, the fibers of my sheet preferably are free of attachment to one another, the integrity of the sheet deriving from the entanglement of the fibers. I have found that a remarkably leather-like, tough, yet flexible product is obtained by the combination of my fibrous sheet and a limited amount of an elastomeric material so as to leave substantial voids, pores, or vacuoles. It is believed that the elastomeric material provides resilient articulations between fibers and that the presence of the voids further permits unbending of the fibers and relative movement thereof whereby the sheet accommodates itself to stress. Thus, as in natural leathers, there is a cooperation of the fibers, by virtue of the integrated yet fiber-free arrangement, to distribute load stresses evenly and progressively, producing in my products unusually high tensile strength, stitch-holding strength, two-way stretch, conformability, and tear-resistance. The plumpness, suppleness, extensibility, and leather-like feel of my flexible sheet materials are thought to be due to and dependent upon the fiber freedom provided as described heretofore.

The fibers of my novel leather-like products are preshrunk and have little or no tendency to become adhesive in water, so that, unlike leather, my products are substantially shrinkproof and characterized by a suppleness and flexibility which is unaffected by drying from a wet state. Furthermore, my products are much less susceptible to attack by heat or microorganisms than are protein materials which comprise natural leather. The products of my invention can be manufactured in a uniform and continuous sheet, thus eliminating inconsistencies in quality and waste in cutting operations such as are encountered in the use of natural leathers, which vary greatly in size, quality and shape and in many instances have weak spots because of hair follicles or scars resulting from injuries to the animal or from diseases to the skin of the animal from which the leather is prepared. It is to be understood that the novel products of my invention possess a combination of characteristics not known heretofore, and although a practical standard of comparison is provided by natural leather, my products are not imitations thereof.

The substitutes for natural leather which are known in the art consist of continuous, resinous films, colored and grained in visual imitation of leather, usually formed on and supported by a fibrous base, such as paper, woven cloth, or a garnetted web. Despite their utility for some purposes, all of these imitations are deficient in one or more characteristics, primarily because of wide differences between their fibrous structures and the fiber arrangement in natural leather as described above, which have led effort in the direction of a superficial imitation of the appearance of natural leather. In paper-based materials the fibers are short and relatively straight; they are held in relatively close-packed arrangement by paper-maker's bonds. Poor flexibility and very low tear strength are among the resulting deficiencies. Woven-base artificial leathers particularly suffer from the inherently poor extensibility of spun yarns; adequate anchorage and smoothness of the coating are difficult or impossible to obtain. Saturated garnetted cotton webs may be strong but are dense, inelastic, nonconformable and have not been found suitable as replacements for natural leather. Wool felt artificial leathers have enjoyed little commercial success because of the high cost of the raw materials and great difficulties in saturation.

My novel leather-like products are manufactured by incorporating in my fibrous sheet, as hereinabove and hereinafter described, an elastomeric or rubber material which serves to improve the already appreciable strength and integrity of the fibrous sheet while still permitting a substantial degree of freedom of individual fiber movement, drying, and, if desired, thereafter applying to the material one or more finish coats and any chosen grain design.

Any natural or synthetic elastomer (unvulcanized or

vulcanized) such as natural rubber, polyisobutylene, butadiene-styrene copolymer (Buna-S), polychloroprene, butadiene-acrylonitrile copolymer (Buna-N), isobutylene-butadiene copolymer (butyl rubber), plasticized polyvinyl chloride, plasticized polyvinyl butyral, and mixtures thereof, employed in a suitable solution or dispersion, is applicable to my invention. The term "elastomer" includes by commonly accepted definition macromolecular materials which exhibit long-range elasticity at ordinary room temperatures. The choice of the particular elastomer to be employed will depend to a large extent on the proposed end use of the product.

When the elastomeric or rubber material is to be applied from a dispersion, the elastomeric or rubber material may include in addition to the latex, a dye and/or a pigment serving to impart a desired color to the product; one or more plasticizers as dibutyl phthalate or glycerine; an agent, such as carboxymethyl cellulose, by means of which the viscosity of the formulation is controlled; a material for adjusting the stability of the latex, e. g., ammonium hydroxide, ethyl amine; a material, such as a zinc ammonium chloride complex, which promotes coagulation of the latex during the drying stage; an inert filler, such as clay or a colloidal silica; and an antioxidant. If it is desired to modify the properties of the elastomeric material by vulcanization it is necessary to include in the dispersion a vulcanizing agent, usually sulfur, an accelerator, for example, sodium diethyl dithiocarbamate, and, if desired, a reinforcing material such as zinc oxide. When the elastomeric material is applied by means of a solution, plasticizers, dyes, and/or pigments, fillers, and an antioxidant are usually included in addition to the solvent, which may be naphtha, toluol, or the like; if vulcanization is desired, a common vulcanizing agent, an accelerator and a reinforcing material may be added.

The incorporation of the elastomeric material in the fibrous mass may in general be accomplished by any of the standard techniques or combinations thereof. For example, a sheet of my fibrous material may be passed through a bath containing the elastomeric material and then through nip rolls adjusted to give the sheet the desired amount of pickup; or a solution or dispersion of the elastomeric material may be sprayed or flooded onto the fibrous sheet while it is preferably supported on a moving belt and passed through nips, if desired. If the elastomeric material is within a suitable viscosity range, it can be knife-coated, or spread-coated onto the sheet. In order to "set" the elastomeric material, the treated sheet may be subjected to drying cans, an oven or heated tunnel, or to any other means calculated to remove excess moisture or solvent.

Since the desirable properties of my product derive from the flexible, local, elastic articulations between and among the fibers, it is important that the elastomeric material be distributed throughout the fibrous structure of my leather-like sheet. Normally the mechanical force employed to adjust the pickup will suffice to secure a substantially uniform distribution of the impregnant, but depending on the viscosity of the solution or dispersion of elastomeric material and the nature of the solvent or dispersing liquid, it may be desirable to use wetting agents or even to reverse the fibrous sheet and repeat the impregnation.

It is essential to take notice of the fact that as the amount of elastomeric material is increased appreciably beyond 75% (on the total weight of fiber and elastomer), the void space in the structure is so reduced that the fibers of the saturated sheet no longer have the freedom of movement necessary to provide fully the combination of leather-like properties heretofore described. Thus, the product lacks the requisite porosity and is insufficiently conformable for many purposes, representing essentially nothing more than a sheet of rubber reinforced with fibers. Similarly, if the percentage of elastomeric material is reduced below about 20% of the total weight of fibers and elastomer, other desirable leather-like qualities are substantially lost. Within the indicated 20–75% range on elastomer content, from about 38 to 87% of the volume of the sheet structure may be accounted for by voids, while the average total elongation at break ranges from 35 to 150%. Preferred products of this invention comprise the elastomer in an amount equivalent to from 40 to 60% of the combined weight of the fiber and elastomer.

The soft, flexible, leathery sheet materials of this invention find wide application where suede-like characteristics are useful, for example, as an interliner in women's coats, in the fabrication of novelties such as women's belts, tobacco pouches, and hand bags, or as a decorative material with or without an embossed surface.

My products are especially adapted for the preparation of surface-finished leathery products and when so finished are useful in the manufacture of wallets, shoe findings, quarter linings, luggage, upholstery and like products in which highly surface-finished natural leather also is employed.

In applying surface finishes to either or both surfaces of my novel leather-like materials I have found that the techniques commonly used in finishing natural leathers generally may be employed. Water-carried pigment finishes which consist essentially of acrylic ester polymers or protein materials, natural resins, gums and waxes, combined with dispersed pigments and dissolved dyestuffs may be applied and, if desired, topped by a clear lacquer coating. Lacquer finishes normally comprising cellulose nitrate, a gum or resin, a suitable plasticizer such as castor oil or dibutyl phthalate, all dissolved in a suitable solvent, are among those frequently used. Color may be imparted to such surface finishes by means of suitable pigments or dyes. A bond-coat consisting, for example, of butadiene-acrylonitrile copolymer, is commonly applied to the sheet material before it is knife-coated with the lacquer. Any number of lacquer coats may be employed depending on the effects desired. Vinyl esters such as polyvinyl chloride and polyvinyl acetate and copolymers thereof are also used following application of a bond-coat, and provide a tough, durable, extensible surface coating and an excellent appearance for the products of my invention. These synthetic films may be calendered onto my sheet materials, or they may be prepared in situ by spread-coating or knife-coating, and subsequently drying or fusing as may be required.

In such surface-finished sheet materials of the invention, the coating of the finished surface, in which are embedded at least those fibers or parts of fibers which are at or near the surface or surfaces of the sheet, provides my materials with surface characteristics and appearances similar to those of natural leather after the addition of finish-treating coats. The distinctive grain patterns of natural leathers, such as morocco, alligator, salmon, and others can be reproduced by embossing the pattern on such surface-finished, novel, leather-like sheet materials. Usually the embossing is the final step in manufacture, but in some cases a spray finish is applied after the desired grain pattern has been impressed in the material.

Leathery suede-like, moisture and air permeable materials of the invention having an average elongation of about 98%, an average tear strength of about 5.5 pounds, an average tensile strength of about 30 pounds per inch, and having calculated voids of about 71%, may be made by passing a sheeted fibrous body 0.045" thick and weighing 175 grams per square yard through a bath of a formulated natural rubber latex composition consisting of

270 lbs. centrifuged natural rubber latex (60% solids)
12.3 lbs. zinc ammonium complex: 10% zinc chloride
5.5 lbs. ammonium hydroxide (28% NH_3)
3.66 lbs. ethyl amine
60 lbs. colloidal silica dispersion (30% solids)
5 lbs. dispersed tan pigment (50% solids)
257 lbs. water

then between squeeze rolls so that the sheet has a wet pickup of 330% of its original weight, and finally over drying cans maintained at a temperature of about 255° F. wherein the latex is set and dried. The dried product may be used, for example, in the novelty trade, or, if a more limp material is required, as for example, in ladies' coat interliners, the above sheet may be worked in a hot soap solution containing about 3% of a good grade textile soap and thereafter dried. If a more abrasive-resistant gloss-surfaced material is desired, for example, as an upholstery material, it may be obtained by applying a synthetic resin such as pyroxylin, and thereafter graining with embossing plates.

If a particularly plump, porous and resilient leathery product is desired for use, for example as a quarter lining, where stitches inserted under normal sewing tensions should not protrude above the surface plane but should be substantially countersunk in the leather, a fibrous sheet may be treated with an elastomeric material containing a milled elastomer, e. g., pale crepe, dissolved in a suitable

solvent. The elastomeric material may also contain other compatible ingredients as, for illustration, pigments, fillers, viscosity adjusters, plasticizers, and vulcanizing agents.

Flexible, leather-like materials of the invention resistant to the common hydrocarbon or chlorinated hydrocarbon solvents and particularly suitable for surface-finishing with a plastic film, such as a vinyl polymer film, may be prepared by selecting a composition containing Buna-N for the elastomeric material. Using the process described heretofore, a formulation is applied consisting of

244 lbs. butadiene-acrylonitrile latex (35% solids)
6.8 lbs. 65% dibutyl phthalate emulsion
45 lbs. clay dispersion (50% solids)
8.9 lbs. glycerine
20 lbs. 2½% carboxymethyl cellulose (2½% solids)
180 lbs. water

The liquid pickup is adjusted to 400%. After drying, the leather-like sheet material may be surface-finished as by combining it with a pre-heated sheet of vinyl polymer film on hot calender rolls, the temperature of the calender rolls being such as to soften the film to an extent assuring firm bonding of the film to the sheet. The surface-finished material may then be embossed to provide a leather grain, or it may be plate-polished to provide a patent leather, the character of the fibrous arrangement of my sheet material providing an appearance of depth only found heretofore in patent leather made from natural leather.

Elastomers other than natural or synthetic rubbers may be employed in the practice of my invention. For example, the following formulations may be applied to my fibrous sheets by the process heretofore described, the pickup adjusted to about 350% and the saturated sheets dried on steam cans. The sheet treated with formulation B is further heated in an air-circulating oven for ten minutes at 300° F.

A

300 lbs. D-1000 latex (60% solids)—a polyvinyl butyral dispersion distributed by the Monsanto Chemical Company and containing 100 parts polyvinyl butyral to 40 parts ricinoleate ester.
3.6 lbs. dispersed black pigment
300 lbs. water

B

400 lbs. Geon 576 latex (55% solids)—an ester-plasticized polyvinyl chloride latex distributed by the B. F. Goodrich Chemical Company.
6.6 lbs. water-dispersable red pigment
50 lbs. dioctyl phthalate
334 lbs. water

From the foregoing it can be readily seen that the products of my invention have little in common with the prior art leather substitutes in the manufacture of which the primary object obtained was to simulate simply the surface appearance of natural leather rather than its fundamental fibrous structure, whereas my new leather-like materials are adaptable to many of the end uses of natural leather because they are amazingly functionally similar to natural leather in basic structure as well as in appearance.

This application is a continuation of my application Serial No. 145,919, filed February 23, 1950, and now abandoned.

Having described my invention, I claim:

1. A flexible leather-like sheet having a substantially smooth leather-like surface and consisting essentially of an integrated reticulate association of intercurled and interlocked unspun cotton fibers and an amount of a rubber material equivalent to from 20–75% of the total weight of the sheet, said fibers having artifically-induced kinks, bends, and twists, and being flexibly joined together by said rubber material dispersed about and between the fibers and voids throughout the structure, these voids accounting for between about 38 and 87% of the volume of the sheet, the fibers being free to straighten or to bend or kink further under applied load stresses tending to elongate, deform, or compress the structure.

2. A flexible leather-like air and water permeable sheet having a substantially smooth leather-like surface and consisting essentially of an integrated reticulate association of intercurled and interlocked unspun cotton fibers and a rubber material present in an amount equivalent to from 20–75% of the total weight of the sheet, said fibers having artifically-induced kinks, bends, and twists, being flexibly joined together by said rubber material, dispersed about and between the fibers and voids throughout the sheet structure, these voids accounting for between about 38 and 87% of the volume of the sheet, and being free to straighten or to bend or kink further under applied load stresses tending to elongate, deform, or compress the sheet.

3. A flexible leather-like sheet having a substantially smooth leather-like surface and consisting essentially of an integrated reticulate association of intercurled and interlocked unspun cotton fibers and a rubber material in an amount equivalent to from 40–60% of the total weight of the sheet, said fibers having artificially-induced kinks, bends, and twists, being flexibly joined together by said rubber material, dispersed about and between the fibers and voids throughout the sheet structure, these voids accounting for between about 50 and 87% of the volume of the sheet, and being free to straighten or to bend or kink further under applied load stresses tending to elongate, deform, or compress the sheet.

4. A flexible leather-like conformable sheet having a substantially smooth leather-like surface and having a multi-directional extensibility of at least 35% and consisting essentially of an integrated reticulate association of intercurled and interlocked unspun cotton fibers and a rubber material in an amount equivalent to from 20–75% of the total weight of the sheet, said fibers having artificially-induced kinks, bends, and twists, and being flexibly joined together by said rubber material dispersed about and between the fibers and voids throughout the structure, these voids accounting for between about 38 and 87% of the volume of the sheet, the fibers being free to straighten or to bend or kink further under applied load stresses tending to elongate, deform, or compress the structure.

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