IMPROVED COLLAGEN FIBER SHEET MATERIAL

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Fig. 1

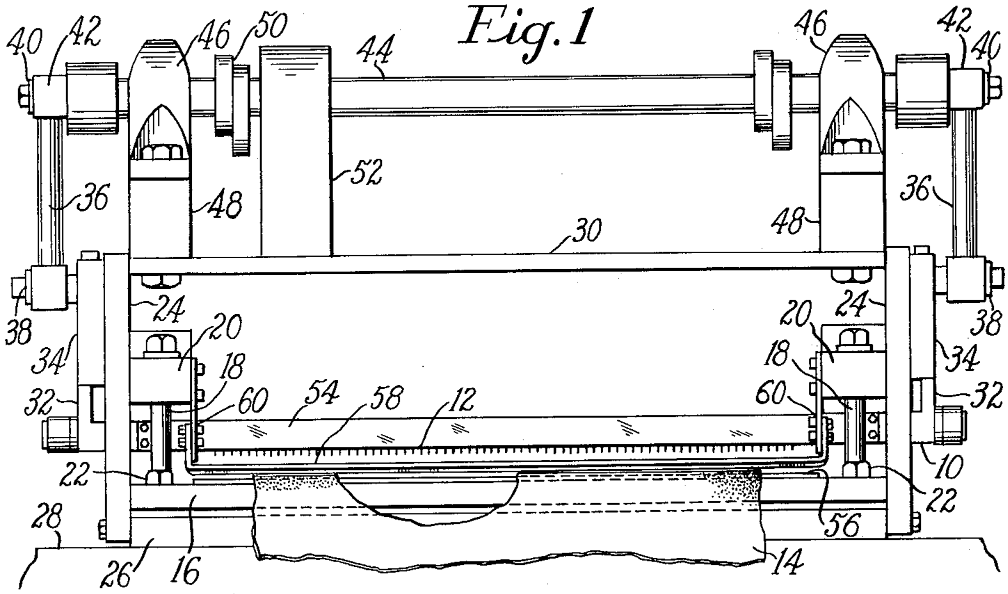



Fig. 2


Fig. 3

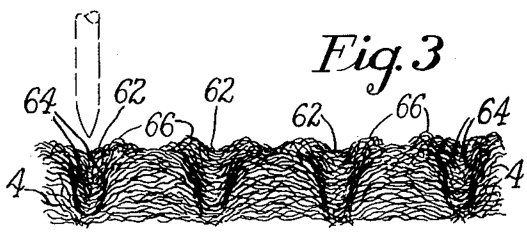



Fig. 4

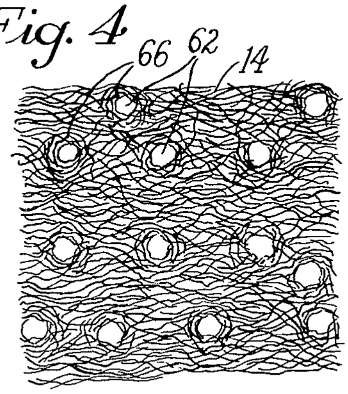
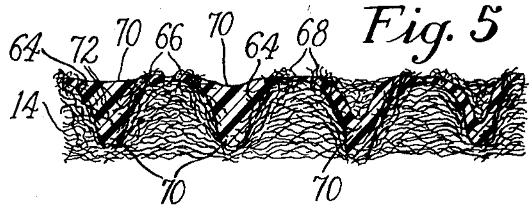



Fig. 5

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# IMPROVED COLLAGEN FIBER SHEET MATERIAL

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This invention relates to an improved collagen fiber sheet material.

Skin-like or leather-like sheet material has been prepared by a process disclosed in the United States patent application Serial No. 691,728, filed Oct. 22, 1957, entitled "Collagen Fiber Masses and Methods of Making the Same," in the names of John H. Highberger and Robert A. Whitmore, and now U.S. Patent No. 2,934,447. In that process, hide or skin material, preferably chemically treated to resist surface hydration, as by lightly tanning with formaldehyde, is subdivided into fibers in the presence of water. The resultant fiber dispersion is combined with a collagen solution and spread in a layer; and the layer is then treated to precipitate collagen from solution as fibers. The precipitated collagen fibers bind together the collagen fibers of the dispersion, and, after removal of fluid from the layer, the product is a sheet formed of a network of collagen fibers and resembling animal skin. The sheet may be tanned to a leather-like product.

The leather-like sheet material is tough and strong, and for many purposes is an adequate replacement for natural leather. However, where the sheet is subjected to repeated sharp flexing there may be a tendency for the sheet to pipe, that is, to separate or split parallel to the plane of the sheet.

It is a feature of the present invention to eliminate or reduce the tendency to pipe of sheets formed of collagen fibers. It is a further feature to form a leather-like sheet with improved softness, plumpness and surface texture.

It is a feature of the present invention to provide a sheet material having superior characteristics from collagen fibers in which the arrangement of the collagen fibers reproduces more closely the internal arrangement of collagen fibers of natural skins and hides.

We have found that the physical properties of sheet material formed of collagen fibers may be improved by penetrating the fibrous sheet as with needle points over substantially the entire area of the sheet at closely spaced points to form very small crater-shaped holes in which fibers of portions of the sheet immediately surrounding the holes have been displaced from the position in which they were prior to forming the holes. It appears that the displaced fibers have a substantial effect in resisting delamination tendencies of the sheet.

In one form of treatment, the sheet of collagen fibers, after having been subjected to the penetration step, is wiped with a fluid hardenable polymer composition which enters the holes and solidifies in the holes to lock the sheet firmly against delamination.

The invention will be described further in connection with the drawings forming part of the disclosure, in which:

FIG. 1 is an elevation of a device which may be used in forming holes in a collagen fiber sheet, portions of the collagen sheet being broken away for purpose of clarity;

FIG. 2 is a diagrammatic cross section on an enlarged scale of a collagen fiber sheet before forming holes therein;

FIG. 3 is a diagrammatic cross section on an enlarged scale illustrating the fiber arrangement of a collagen fiber sheet after forming holes therein according to the present invention;

FIG. 4 is a diagrammatic cross section taken on the line 4—4 of FIG. 3 illustrating the fiber arrangement of a collagen fiber sheet after forming holes therein according to the present invention; and



FIG. 5 is a diagrammatic cross section on an enlarged scale illustrating the fiber arrangement of a collagen fiber sheet after forming holes therein and also illustrating the keying action of a plastic deposited in the surface of such sheet.

The manufacture of sheet material formed of intertwined collagen fibers for treatment according to the present invention may be carried out by procedure such as disclosed in the application of John H. Highberger and Robert A. Whitmore, Serial No. 554,557, filed December 21, 1955, entitled "Improvements in Collagen Fiber Masses and Methods of Making the Same," and now U.S. Patent No. 2,934,446, or in the application by the same inventors, Serial No. 691,728, above referred to. As described more fully in those applications, skin or hide material such as limed unhaired hide, pickled hide, or unlimed hide is washed, subdivided into pieces, preferably not smaller than one inch, and preferably chemically treated as by limited formaldehyde tannage to reduce the swelling tendency of the collagen fibers of the skin or hide. The treatment, which should be sufficient to provide a minimum of at least 1/10% of combined formaldehyde based on the dried weight of the fibrous material and preferably not over 2%, brings the skin or hide material to a condition in which it can be reduced most effectively to its separate fibers.

The hide material, preferably chemically treated, is placed in a water bath and subjected to a mechanical device involving relatively moving surfaces which exert a shearing action for pulling or tearing the hide material into its constituent fibers and forming a pulp or suspension of the fibers in water.

The procedure of the applications referred to includes as a next step the admixture of a collagen solution to the suspension, forming the mixture into a sheet, and subsequent precipitation of collagen fibers from the solution. The product including precepitated collagen fibers is markedly superior to products obtained by simple deposition of a sheet of the collagen fibers, but for some purposes simple sheets of collagen fibers may be treated in accordance with the present invention and will give useful products.

In forming collagen solution for use in the preferred process, young mammalian skin, suitably calfskin, is washed, roughly ground and dispersed in an aqueous acid bath at a pH of from 2 to 4.5. Usable acids include formic acid, acetic acid, propionic acid, citric acid, phosphoric acid, hydrochloric acid, sulfuric acid and other common organic and mineral acids which do not precipitate protein. The skin material is allowed to stand at a temperature below 25° C. and preferably near 0° C. for from 12 to 48 hours. The acid bath containing skin material is then preferably passed through a mechanical device to subject it to severe shearing action which brings the product to a pasty condition in which a high percentage of the collagen of the original skin material appears to be in solution.

The pasty mass including the dissolved collagen is brought to a temperature below 5° C. if not already at that temperature and is adjusted by addition of a salt and neutralizing agent, if necessary, such that when the pasty collagen solution is combined with the fiber dispersion the resultant mixture will have a pH of from 5.2 to 9.5, preferably about 7.5, and will have an ionic strength in the range of from 0.1 to 0.5.

The fibers and collagen solution are thoroughly mixed at a temperature of from 0° to 5° C. and the mixture is worked into a sheet as by rolling the mass to a determined thickness or by pressing a mass of the material to a determined thickness. The formed sheet is then raised to a temperature which may be up to 37° C. until the collagen in solution is precipitated as fibers. The precipitated fibers cooperate with and apparently build onto existing collagen fibers to form a fine intertwined fiber network. The sheets may then be dried suitably by solvent or freeze drying techniques. The dried sheets may then be tanned in a tanning bath either mineral tanning, e.g. chrome, or vegetable tanning, in accordance with known skin or hide tanning procedure. Alternatively the wet sheets may be pressed to remove excess water and put directly in an aqueuos tanning bath.

Either before or after the tanning step the collagen fiber sheet material preferably in dry condition is treated to impress holes in closely spaced relation over the entire surface of the sheet.

A suitable device for impressing holes in collagen fiber sheet material is shown in FIG. 1 but other devices may be used or the holes may be impressed manually. The device shown comprises a reciprocating needle bar **10** carrying one or more rows of needles **12** and movable to carry the needles into and out of hole forming engagement with a collagen fiber sheet **14** supported on an adjustable bed member **16**. The bed member **16** is supported by bolts **18** extending down through supporting blocks **20** with their lower ends threaded into the bed member **16**. The bed member is adjusted by turning the bolts into or out of the threaded holes in the bed member **16** and is locked in the determined position by the lock nuts **22**.

The bed member supporting blocks **20** are carried on slotted uprights **24** forming part of a frame including an elongated base plate **26** extending beneath the bed member **16** and resting on a surface **28**, the slotted uprights **24** and a transverse plate **30** at the upper ends of the uprights **24**. The needle bar **10** extends through the slotted uprights **24** with its ends fixed in slide members **32** movable in guides **34** secured to the outer face of the uprights **24**.

The slide members **32** are reciprocated in the guides **34** by connecting rods **36** journaled at one end on pins projecting from the slide members **32** and on the other end on the pins **40** on crank arms **42** at opposite ends of the shaft **44**. The shaft **44** is mounted for rotation in bearings **46** mounted on blocks **48** secured to the transverse plate **30**. Counterweight members **50** are mounted on the shaft **44** to balance the crank arms **42**, connecting rods **36**, etc.; and the shaft **44** is driven by suitable means such as a drive pulley (not shown) within the housing **52**.

In the device shown, the needles **12** are clamped in place, with their points projecting evenly, between the needle bar **10** and a clamping plate **54**. The needles **12** are simple pointed needles comparable to the traditional steel phonograph needle. Preferably, the needles **12** are spaced closely, for example, from about ⅛" to about ½" apart, in order to make a large number of holes with each stroke; but it will be understood that they may be spaced much farther apart if desired.

To protect the needle points **12** and provide a surface over which the collagen fiber sheet will slide readily, a sheet **56** of nonadhesive plastic, which may be about 1/16" thick, is diposed on the upper face of the bed member **16** between the bed members and the needle bar **10**. The sheet may be made of any suitable plastic such as polytetrafluoroethylene, polyethylene or the like and may, if desired, be provided with preformed holes or slots (not shown) to receive the needles **12**, although this is not strictly necessary since the needles **12** will penetrate the plastic without harm.

A holddown bar **58** is provided to prevent lifting of the collagen fiber sheet **14** when the needles **12** are lifted after being forced into the collagen fiber sheet. As shown in FIG. 1, the holddown bar **58** extends parallel to and above the bed member **16** near to the row of needles **12**. The bar **58** is supported at its ends by brackets **60** bolted to the supporting blocks **20** on the uprights **24**. It has been found desirable to form this bar **58** with the edge adjacent the row of needles springy to hold the collagen fiber sheet **13** resiliently against the plastic sheet **56** on the bed member **16**.



Operation of the device involves applying power to rotate the shaft **44** and reciprocate the needle bar **10**; and feeding collagen sheet material **14** between the holddown bar **58** and the bed plate **16** and under the needles **12**. At each stroke of the needle bar **10** a row of holes **62** is formed in the collagen fiber sheet material **14**. It is preferred to pass the collagen sheet material **14** back and forth beneath the needle bar **10** several times at a relatively fast pace rather than to move it slowly in a single direction since several passes will provide a random distribution of needle holes rather than a regular alinement of holes. Desirable products have been obtained where there were as few as 600 and as many as 6000 holes per square inch in the collagen fiber sheet material. Also, there is some indication that somewhat better rearrangement of the collagen fibers is effected where there is pressure tending to move the collagen sheet edgewise while the needle is projecting down through it. However, this last factor does not appear to be critical.

The bed member **16** may be adjusted to provide that the reciprocating needle bar causes the needle points to enter only partially into the collagen fiber sheet, or where a more deeply indented surface is desired or where increased porosity is sought, the bed member may be so positioned that the needle points pass through the collagen fiber sheet **14**. The holes **62** formed by the needle points are crater-shaped, that is, substantially larger at the point of entrance than at further points in the hole (see FIGS. 3 and 4). In some instances where there is pressure tending to move the sheet **14** relative to the needle bar **10** while the needle point is in the collagen fiber sheet **14**, the material around the hole may be pulled toward one side.

As shown more clearly in the enlarged sketch of the fiber structure in and surrounding a crater, fibers **64** initially at the surface of the sheet, as in FIG. 2, are pulled down and extend transversely of the general plane of the sheet **14**, as illustrated in FIG. 3, and markedly increase the resistance of the sheet to delamination. That is, in the sheet as formed from the mixture of fiber dispersion and collagen solution, the fibers of the dispersion are initially at only a fairly slight angle to the plane of the sheet because of their length and because of the flow of the mixture in being spread as a sheet. When the collagen fibers are precipitated and water removed from the sheet, the sheet shrinks in thickness which reduces even more the angle of the fibers **64** to the plane of the sheet (see FIG. 2) so that except for the fibers precipitated from the collagen solution which are randomly oriented, there are only a limited number of fibers oriented to resist separation of the fiber sheet along planes parallel to the sheet. The fibers **64** forced into an angled relation to the surface of the sheet **14** by penetration of the needle points (see FIG. 3) augment the fibers otherwise at an angle to the sheet to resist delamination.

A further advantage of the displacement of fibers **64** by the penetration of needles is that the fibers are forced sideways away from the center of the holes **62** to form compacted rings **66** (see FIG. 4), the upper edges of the rings being raised slightly above the general level of the sheet **14**. These closely spaced compacted rings **66** interrupt the uniformity of the sheet **14** to prevent or markedly retard the spread of such separations in the plane of the sheet **14** as may develop. It will be observed that the net effect of needle penetration of the collagen fiber sheet **14** is closely parallel to the natural arrangement of collagen fibers in skins and hides where the collagen fibers are intertwined in a three-dimensional arrangement formed in the slow growth of individual collagen fibers and the strict uniformity of the fiber structure is interrupted by sweat glands, pores and hair follicles extending into the skin.

In the collagen fiber sheet prepared with the penetration treatment, there is also obtained the advantage of a large number of open pores, comparable to the pores of the sweat glands and hair follicles of natural skin, which aid in taking up tanning material, plumping or softening agents, dyes, finishes, etc.

For sheet materials which are to be subjected to severe service it has been found that a further improvement in resistance to delamination is obtainable by depositing a plastic material **68** in the holes **62** of the sheet. The plastic material in the holes provides a keying action which holds the fibers **64** against slipping relative to each other so that separation along planes parallel to the plane of the sheet does not take place readily. The plastic deposit may be provided by spreading, as by brushing or spraying, a fluid hardenable polymer material on the surface of the sheet into which the needles have penetrated. The fluid polymer material is preferably wiped with a sponge, knife or squeegee to remove undesired excess of material from the exposed portions of the sheet and to force the fluid polymer material into the holes **62**. The polymer material is then allowed to harden. The polymer material in the holes serves in some measure as a multitude of small bodies **70** serving as keys or rivets permanently anchoring together the fibers against delamination along planes parallel to the sheet.

Suitable fluid polymer compositions include aqueous emulsions or latices of polymeric resinous materials and volatile organic solvent solutions of polymeric materials. Aqueous emulsions which have been found useful include emulsions of the polymers and copolymers of ethyl and methyl esters of acrylic and/or methacrylic acids, emulsions of polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, polyvinyl acetal and latices of various natural and synthetic rubbers and combinations of the above. It has been found that the natural and synthetic rubber latices may be blended with emulsions or latices of resinous polymers with which they are compatible and will serve as solid plasticizers. An aqueous emulsion or latex or a volatile organic solvent of a low molecular weight polysulfide (Thiokol LP) is particularly desirable in this regard in that it produces a noncontinuous film which facilitates penetration of moisture and also serves as a wash-resistant plasticizer to give desired softness and stretch. In the emulsions it has been found that 5% solids emulsions are most suitable but higher solids content emulsions may be used. Any desired weight of coating material may be used, but about 10% coating material based on the weight of the fiber has been found to give a very desirable product.

When an aqueous emulsion or latex of a resinous material is applied to a collagen fiber sheet which has been subjected to the penetration treatment, the water component causes swelling of the collagen fibers and allows the ends **72** of some of the displaced fibers around the holes **62** to move out and project into the holes **62**. The projecting ends **72** are embedded in the resin deposited from the emulsion or latex and are held firmly in the resin when it solidifies. These ends of the fibers, being strongly anchored, strengthen the sheet against disrupting forces. The swelling of the collagen fibers also reduces the diameter of the holes **62** and may close the holes at their narrower points.

Volatile organic solvent solutions useful in treatment of the needled collagen fiber sheet material include solutions of such resins as polyesters, alkyds, epoxide resins, polysulfite resins, nitrocellulose, cellulose acetate, polyurethanes and polyamides. Useful coating compositions may contain from 20% to 30% by weight solids.

The treated collagen fiber sheet with or without subsequent treatment with fluid resin may be finished, as by



plating, pressing or embossing, to provide any desired surface character.

The following example is given as of possible assistance in understanding the invention; but it is to be understood that the invention is not limited to the specific materials or conditions shown in the example:

*Example*

43 lb. of salt calfskin scraps were unhaired, washed, and added to 120 lb. of water containing a commercial $H_3PO_4$ and 138 cc. of acetic acid. After stirring the hide in, the pH was 3.1. The bath was allowed to stand six days with occasional stirring. At the end of this time the scrap material was well swollen and the pH was 4.0. The scraps were cooled with cold water, drained, and run through a mill comprising closely spaced, relatively moving rough plates, i.e. a Bauer mill, several times with the plates set close. The milled product weighed about 100 lb. To this were added 20 lb. of water containing 42 cc. of mixed acid (138 cc. of acetic acid and 54 cc. of phosphoric acid). After stirring and standing briefly the pH of the mix was 3.8. The mix was then sent through the Bauer mill again and 40 additional lb. of water and 100 cc. of the same acid mixture were added and stirred in. After standing overnight the pH of the mix was 3.7. 20 lb. of water, 92 cc. of the same acid mixture were added to the mix and the mix was then sent through the Bauer mill using close set, fine plates and came out as a smooth pasty mass at pH 3.7. In this mass a high proportion of the collagen initially present was in solution.

Pickled split cowhide trimmings were washed and brought to a pH of 8.5 by addition of sodium hydroxide. The trimmings were cut to approximately 1″ pieces and 50 lb. of the trimmings were placed in a Hollander type paper beater with 150 lb. of water to give a solids content of about 5%. The beater was operated for ½ hr. at the end of which time the pH was readjusted to 8.5 and 300 cc. of 37% formaldehyde were added. The beating was continued for 5 minutes and the resultant slurry was allowed to stand for 2 hrs. then discharged onto screens and drained overnight. The drained material was passed through rubber squeeze rolls to bring its solids concentration to about 25%. The squeezed material was then put back in the beater and water added to bring the solids content in the beater to about 5%. The beater was operated for one hour with the beater knife close to the bed plate (0.003″ to 0.005″ clearance). The slurry was then removed from the beater, drained overnight and squeezed through rubber rollers to give a fibrous mass of about 26% solids.

To 2700 grams of the slurry from the Bauer mill at from 0° to 5° C. there were slowly added in a worm type mixer 2600 grams of the drained and squeezed fiber, 2700 cc. of water and 93 grams of $K_2HPO_4$. After mixing for one hour a mix of the mixture was placed on a polyethylene sheet, covered with a sheet of polyethylene terephthalate resin and spread by rolling and working to a thickness of about 0.1″.

The sheet was then warmed to 37° C. and held at this temperature for 2 hours. The sheet was then immersed in a 1% vegetable tanning solution (wattle) for 16 hrs. The sheet was then withdrawn from the tanning solution, soaked in water for 4 hrs. and then transferred to a 5% aqueous solution of glycerine and soaked for an additional 4 hrs.

The sheet was removed from the glycerine solution bath and stretched out on a board and fastened in stretched condition. The stretched sheet was allowed to dry almost to completion and was then sprayed with a 10% solution of oleic acid in isopropyl alcohol. Approximately 100 cc. were sprayed on a sheet 18″ x 28″. The sheet was then allowed to dry overnight.

The sheet was then passed beneath a reciprocating bar carrying needles on its lower surface and the sheet manipulated beneath the needle bar to provide an average of about 1500 perforations in the sheet per square inch. The diameter of the holes was found to be from about 0.1 to about 0.2 mm. when examined under a microscope.

After the needling treatment a 20% solids solution of a butadiene acrylonitrile copolymer latex was spread on the surface of the sheet. The latex contained 5% of a wetting agent (Triton 200) and 5% resin solids on the weight of the dried sheet were spread on. The wetting agent insured rapid wetting and penetration of the needling holes of the sheet. The sheet was dried and thereafter a conventional acrylic resin emulsion finish, e.g. a Primal finish, was spread on the surface of the sheet and allowed to dry.

Thereafter the sheet was finished by conventional procedure, including application of a commercial base coat containing pigment, wax and resin. The sheet was embossed by the usual commercial embossing procedure and finally a coat of an aqueous dispersion of shellac was applied as a top coat and the sheet was plated.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. A delamination-resistant sheet comprising collagen fibers in the water-bonded association in which they are deposited from an aqueous dispersion of collagan fibers, a surface of said sheet being formed with from 600 to 6000 very small crater-shaped holes per square inch,



the upper ends of said holes being from 0.1 mm. to 0.2 mm. across, the fibers originally in said holes forming the walls of said holes.

2. A delamination-resistant sheet comprising collagen fibers in the water-bonded association in which they are after deposition from an aqueous dispersion of collagen fibers and drying, a surface of said sheet being formed with from 600 to 6000 crater-shaped holes per square inch, the upper ends of said holes being from 0.1 mm. to 0.2 mm. across, the fibers originally in said holes forming the walls of said holes, and resin solidified in said holes further reinforcing said sheet against delamination.

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