United States Patent Office 3,285,775
Patented Nov. 15, 1966

3,285,775

PENETRATION OF COLLAGEN FIBERS THROUGH INCLUSION OF PROTECTIVE COLLOID

Shu-Tung Tu, Ipswich, and Janet Appleton, Beverly, Mass., assignors to United Shoe Machinery Corporation, Flemington, N.J., and Boston, Mass., a corporation of New Jersey

No Drawing. Filed June 14, 1965, Ser. No. 463,922
11 Claims. (Cl. 117—140)

This application is a continuation-in-part of the copending application Serial No. 256,225 of Shu-Tung Tu, one of the present inventors, entitled "Leather-Like Material and Method of Making the Same," which was filed February 5, 1963, and is now U.S. Patent No. 3,223,551, said application being a continuation-in-part of the earlier filed application Serial No. 170,225 of Shu-Tung Tu, filed January 31, 1962, and having the same title, said earlier filed application now being abandoned.

This invention relates to an improvement in the manufacture of collagen fiber based material and particularly to an improved method for the manufacture of a strong leather-like material.

In the copending application referred to above there is disclosed the manufacture of a leather-like material in which undissolved collagen fibers are associated with a layer of intermeshed fibers by introducing an aqueous suspension of collagen fibers into an intermeshed fiber mass. The collagen fibers in suspension are slightly swollen and of microscopic size, and are retained within the intermeshed fibrous mass and caused to associate with each other as a larger collagen fiber structure extending through the intermeshed fibrous mass to reinforce those fibers against displacement.

Achievement of best results by the process of the prior application calls for a careful balance between using a pH value displaced enough from the isoelectric point of the collagen fibers to secure good penetration ability and securing good collagen fiber retaining ability through use of a pH value as close to the isoelectric point as will permit effective entry of the collagen fibers in suspension into the intermeshed fiber mass. With some collagen fiber suspensions, achievement of good penetration and good collagen fiber retention is achieved only within a narrow range of pH values, in some instances only 0.1 pH unit. Such close pH control is difficult to achieve particularly in larger operations and in many instances best collagen retention must be sacrificed in the interests of better penetration.

It is an object of the present invention to provide a method for introducing and retaining collagen fibers into a mass of intermeshed fibers under conditions allowing a broader range of pH values and a greater latitude in the character of the collagen fibers for securing effective penetration and high collagen fiber retention.

To this end and in accordance with a feature of the present invention an aqueous collagen fiber suspension is prepared and there is added to the suspension a small percentage of hydrophilic protective colloid material. Surprisingly, even though the viscosity of the collagen fiber suspension is increased, rapid and uniform penetration is secured even at pH values close to the isoelectric point, while at the same time there is also achieved excellent collagen fiber retention within the intermeshed fiber mass.

A suspension of microscopic size collagen fibers for use

in the present process may be formed according to the procedure and conditions set forth in the copending application above-referred-to. That is skin material preferably is lightly tanned to an extent comparable to 1/10% to preferably not over 3% of combined aldehyde such as formaldehyde, glutaraldehyde or glyoxal based on the dried weight of the skin material. From about 1% to about 8% by weight of small skin pieces is placed in water in a beater similar to a paper beater and beating is carried out at a pH preferably of from 2 to 8. Beating at pH 5 to 8 appears to give a particularly desirable action in forming short fibers of microscopic size for penetration into intermeshed fiber masses. The beating of the skin material is carried to an extent to form distinct non-colloidal fibers which have a length of from about 0.001 mm. to not over about 4 mm. in length, preferably not over 1 mm. in length. The suspension obtained is then adjusted in pH above or below the isoelectric range of the collagen fibers to effect "swelling" of the fibers. The term "swelling" in the sense here intended refers to the phenomenon that the surfaces of the fibers become slippery and the fibers increase in thickness and decrease in length but remain as distinct fibers.

It has now been found that the requirements for control to secure optimum penetration and retention of collagen fibers in an intermeshed fiber mass may be made much less exacting by combining a small percentage of a hydrophilic protective colloid with the collagen fiber suspension. Depending on whether the collagen fiber suspension is to be caused to penetrate the intermeshed fiber mass on the acid side or on the alkaline side of the isoelectric point of the collagen, the protective colloid will be chosen for its ability to cooperate with the collagen fibers under the pH conditions selected. A wide variety of protective colloid materials have been found useful. Gelatin which has been disclosed for use in the prior patent application, above referred to, operates as a protective colloid material and is desirable because of its similarity to collagen and its desirable moisture absorption and transmission characteristics as well as its ability to be hardened and preserved by the tanning agents customarily used in treating the product of the present invention. Other hydrophilic protective colloid materials which form viscous solutions with water, particularly carbohydrate gums such as guar gum, Irish moss (carrageenan), Kelzan (a polysaccharide gum), locust bean gum, gum tragacanth and methyl cellulose. Other protective colloids which have been useful include ammonium salts of carboxyvinyl polymer (Carbopol 960), water soluble polyelectrolytes such as the interpolymer of methylvinylether and maleic anhydride (Gantrez AN), and others. Some of these materials are more effective than others and particularly guar gum appears to have outstanding ability to aid penetration and reduce the sensitivity of the collagen fiber suspension to minor pH changes so that effective control of penetration conditions is more readily achieved.

In general at least about 1% of the protective colloid material is used to give substantial improvement; but it is preferred to use from 5% to 10% by weight of protective colloid based on the weight of the collagen fibers in suspension.

Penetration of a collagen fiber suspension into an intermeshed fiber mass and retention of the collagen fibers by the intermeshed fibers is affected by the character and extent of swelling of the collagen fibers which depends

on the pH of the suspension and the extent of tanning of the collagen, and is also affected by the concentration of the collagen fibers in the suspension and the openness of the intermeshed fiber mass.

A useful degree of swelling of the suspended collagen fibers is obtainable at pH values about 0.5 of a pH unit outside the isoelectric range of the collagen fiber. Where the collagen fiber is obtained from hides which have been limed, the isoelectric range may be from about 4 to 5.5 while with hides which have not been limed the isoelectric range may be from about 7 to about 8. Ordinarily limed hides which are more readily available will be used and the following description sets forth conditions particularly useful with fibers from limed hides. Adjustment of pH values for use with fibers from other hide materials can be made readily by chemists. On the acid side of the range the pH of the suspension of collagen fiber from limed hide will ordinarily be kept in the range of from about pH 0.5 to about pH 3.5 and most desirably from about pH 2 to about pH 3.0. The higher portions of this range are used with the more highly swelling acids such as formic acid, acetic acid, citric acid, phosphoric acid and others.

Effective swelling above the isoelectric range has been obtained in a suspension of collagen fiber from limed hide at a pH in the range of from about pH 6.0 to about pH 12 and more desirably from about pH 8 to about pH 10. The fiber suspension may be brought to this range by addition of alkaline reagents such as sodium hydroxide, trisodium phosphate, potassium hydroxide and various other alkaline hydroxides and salts which do not form insoluble compounds with the collagen.

Penetration ability decreases and retention of the fiber increases with increase in the extent of tanning. It has been found generally desirable to use collagen fiber tanned to an extent corresponding to about 0.2% to about 1.1% formaldehyde by weight based on the weight of the collagen fiber. Thus, it has been found that with a formaldehyde content of 0.2% by weight based on the weight of the hide material, the fiber suspension at the important pH range penetrates well into a given fiber batt but that retention of the fibrous material in the batt is barely acceptable. Where the formaldehyde content is 1.1% by weight based on the weight of the hide material and where no protective colloid is used, a proportion of the fibers may be retained on the surface of the same fiber batt to which the suspension is applied and the penetration properties are poor. Within this range and preferably at a formaldehyde content of from about 0.4 to about 0.6% by weight based on the weight of the hide material and with close control of the pH of the suspension, suspensions penetrate well and the fibers are retained effectively within the fiber batt. It is desirable that the fibers have been swollen to a controlled degree and it is believed that one effect of this swelling is a plasticizing of the fibrous collagen material enabling the fibers to move effectively through the interstices in the fiber batt. Higher tanning agent contents restrain the extent of swelling to reduce the ability of the fibrous material to enter the batt; and if no tanning agent is used, there is not only an undesirable increase in viscosity which makes it difficult to use it to penetrate a fiber batt but the fibrous material is not retained well by the fibers of the batt.

There is some indication that, at least with the more highly tanned collagen fibers, for example, fibers containing from about 0.6% to about 0.8% by weight formaldehyde based on the weight of the fibers, the "swelling" may occur primarily at the surfaces of the fibers. This offers the advantage that the fibers develop a surface character allowing the fibers to slip relative to one another and to the fibers of the mat so that the fibers will penetrate the fiber mat, while the volume of individual fibers is not greatly increased so that the ultimate quantity of collagen fiber solids on a dry fiber basis which can be introduced into a mat to fill the interstitial spaces in the mat may be greater with the more highly tanned fibers than with the less tanned fibers. It is believed that the protective colloids added to a collagen fiber suspension become associated to some extent with the collagen fiber surfaces to provide a slip effect to aid penetration of fibers, for example, fibers tanned to the higher ranges, which might not be sufficiently swollen for effective penetration.

The ability of suspended fibers to penetrate an intermeshed fiber mat depends also on the retained openness of a mat during application of the collagen fiber slurry or suspension. Fiber mats which retain a high degree of openness may be penetrated with collagen fiber suspensions with a degree of tanning and under pH conditions giving a relatively low penetrating ability which would not effectively enter less open fiber mats. It is possible to form fiber mats filled with collagen fibers by adjusting the penetrating ability of the collagen fiber suspension through careful control of extent of tanning and pH conditions relative to the retained openness of the fiber mat. However, the precision of control required is much less where protective colloid material is included in the suspension.

In addition to the factors of extent of tanning and pH control which exert a primary effect on the penetration ability, a limited control over penetrating ability can be obtained by adjusting the collagen fiber solids content of a suspension. That is, suspensions of collagen fibers with relatively low penetrating ability may penetrate more effectively where the collagen fiber solids content is reduced to a relatively low percentage. Suspensions having collagen fiber solids contents of at least 0.5% preferably from about 1% to about 5% are preferred from the standpoint of securing a good penetration and the introduction of a desired high collagen fiber solids content into a fiber mat with desirable efficiency in time and amount of suspension handled. It will be understood that it is possible to operate somewhat outside those ranges; but, for example, the use of a lower solids content suspension entails the separation of collagen fiber from a large volume of liquid; and use of a higher solids content suspension may require an undesirably open mat or result in uneven penetration.

The use of protective colloids is more important with high collagen fiber content suspensions. As discussed above suspensions having a higher content of collagen fibers tend to penetrate intermeshed fiber masses less effectively than do low collagen fiber content suspensions so that as discussed above undesirably open mats have been required or uneven penetration has been secured. Surprisingly the protective colloid materials appear to have proportionately greater effectiveness with the higher collagen fiber content suspensions and thus increase the efficiency of the process and insure high collagen fiber retention within the intermeshed fiber mass. It has also been found that particularly with relatively open intermeshed fiber masses, the presence of a protective colloid will, with some collagen fiber suspensions, allow some degree of penetration into the intermeshed fiber mass even within the isoelectric range. The uniformity and character of penetration are ordinarily not particularly good within the isoelectric range; but the ability to enable such penetration indicates the special nature of the association and illustrates the extent to which the use of protective colloids has reduced the rigid pH control requirements.

Protective colloid action ordinarily involves an electrical charge effect on the particles which prevents their association. A majority of the protective colloids listed above are relatively rich in alcoholic OH groups which tend to develop a net negative charge at the surface of the particle. Also in addition the protective colloid molecule is swollen and hydrated by the water and there is some indication that the water of the swollen molecule may have some effect in establishing hydrogen or hydration bonding between the colloid molecule and the hydrated surface of

the collagen fibers. Particularly in alkaline media, the result of such association is a high negative charge on the associated collagen fiber and protective colloid which tends to keep the collagen fibers apart and resist premature tangling or packing together of collagen fibers in the course of penetration into an intermeshed fiber mass. The electrical charge effect is supplemented and assisted by the covering or masking of portions of the collagen fibers by hydrated colloid material on its surface which also tends to prevent tangling or packing of the fibers. A further action is a marked increase in the viscosity of the collagen fiber suspension which slows down movement of the fibers relative to each other in the suspension medium and thus reduce the frequency and speed at which collagen fibers approach each other to reduce the tendency to tangle or pack. Viscosities below about 400 cps. result in barely noticeable improvement and preferred viscosities are from about 1500 cps. up to viscosities which interfere with easy handling. Finally colloid material on the surface of the collagen fibers is slippery and may serve to help the collagen fibers to move into an intermeshed fiber mass.

The above discussion is advanced as of possible assistance in understanding the invention; but it is to be understood that patentability does not depend upon the correctness of the explanation advanced for the advantages obtained.

A wide variety of intermeshed fiber materials both woven and nonwoven may be used for association with collagen microscopic fiber suspensions. Ordinarily nonwoven fiber materials are preferred because of their greater variety of thicknesses, densities and openness to penetration by the suspensions. Thus, the fibers may be nylon, polyacrylic ester fibers (Orlon), polyester fibers (Dacron), polypropylene fibers, wool, extruded cellulosic fibers such as viscose or cellulose acetate and others. It has been found that best results are secured when the fibers are hydrophobic. In this connection a batt of longer collagen fibrous material which has been treated for example, by chrome tanning or other treatment to decrease its affinity for water may be used. Also natural cotton fiber preferably treated to decrease its affinity for water is also usable.

Since an important aspect of the present invention is the manufacture of leather-like products, the intermeshed fiber materials are preferably in the form of relatively thin batts in which the fibers are in a relation providing relatively large interstitial spaces. The fiber batts preferably although not necessarily have been subjected to a treatment as with barbed needles to improve the intermeshing of the fibers. A fiber density and relation which have been found very satisfactory are those in nylon fiber batts having densities of the order of 4 oz. per sq. yd. at a thickness of 0.15" and 6 oz. per sq. yd. at a thickness of 0.175". It is preferred that the fibers be relatively fine and fall in the range of from 1 to 5 denier with 3 denier being satisfactory. Another highly satisfactory material is a polypropylene fiber batt having a density of 7 oz. per sq. yd. and a thickness of 0.2".

Penetration of the suspension of swollen collagen microscopic fibers into an intermeshed fiber mass may be effected in a variety of ways. Thus, a fiber batt may be immersed in a suspension, suitably a relatively low solids suspension of the order of 1% to 3% by weight solids. The rate of impreganation may be increased by use of a vibrator. Another procedure involves disposing the fiber batt on a screen and forcing the suspension in with the aid of pressure or suction. Suspensions having a solids content of for example, from about 1% to about 5% by weight solids may be used in this procedure. Still other procedures are available including spreading the suspension on the surface of the batt and working it in.

Products having a higher collagen content at the surface may be formed by first treating the fiber batt with a collagen suspension having good penetrating ability and thereafter treating the batt with a suspension having a lower penetration ability. If desired suspension may be applied from alternate sides.

When the intermeshed fiber mass impregnated with collagen fiber is treated to reduce swelling either by pH change, extraction with water or solvent or the like as described more fully in the copending application above-referred to, there is an observable association of the fibers into substantially aligned relationship. It appears that as association of the individual fibers preceeds, a larger collagen fiber structure is reaggrevated from a multitude of the microscopic fibers and is comparable to native larger collagen fibers extending through the intermeshed fiber mass.

Reduction of the acid or alkali content of the collagen microscopic fiber material within a fiber mass and removal from the fibers of the water of swelling may be effected by subjecting the fibrous mass to extraction with distilled water or a water-miscible volatile organic solvent such as acetone and other ketones, and lower alcohols such as methanol, ethanol and isopropanol to bring the pH to the isoelectric range. Treatment of the fiber batt with an aqueous solution of a buffer salt such as an acetate or phosphate buffer system is also effective to bring the pH to a value in the range of about 3.5 to about 6 at which reaggregation of the collagen microscopic fibers will occur with removal of the swelling water from the fibers. It is desirable in the use of buffer systems to use a solution having an ionic strength of about 0.2. Reaggregation may also be effected by treating the fiber batt with a 10% aqueous ammonium sulfate solution which effects a deswelling of the fibers.

The fiber batt is compacted and reduced in thickness in the course of penetration by the suspension and reaggregation of the collagen material so that, for example, starting with a 4 oz. per sq. yd. nylon fiber batt with an initial thickness of 0.15", after penetration by suspension and reaggregation of the collagen material, the thickness will have reduced to from about .015 to about .03". Correspondingly, a sheet prepared from a 6 oz. per sq. yd. nylon batt having an initial thickness of 0.175 will form a sheet about 0.04 inch in thickness. This reduction in thickness is due in considerable measure to the action of the suspension in being forced into the batt. A further action which influences the reduction in thickness is the pulling together of the collagen material by water bonding; and this factor may range from very slight where water is extracted from the sheet by solvent to relatively large where a substantial portion of the water is removed by evaporation.

The sheet material is preferably subjected to tanning with mineral tanning agents such as chrome tanning liquors or with vegetable tanning agents. Because of the collagen deswelling action of mineral tanning agents such as chrome tanning agents it is possible to effect both reaggregation and tanning with such agents. Conventional leather tanning procedures may be used and the tanning may be carried out either in an aqueous tanning medium or a solvent type tanning medium.

The following examples are given to aid in understanding the invention and it is to be understood that the invention is not restricted to the particular materials, proportions or procedures set forth therein.

EXAMPLE I

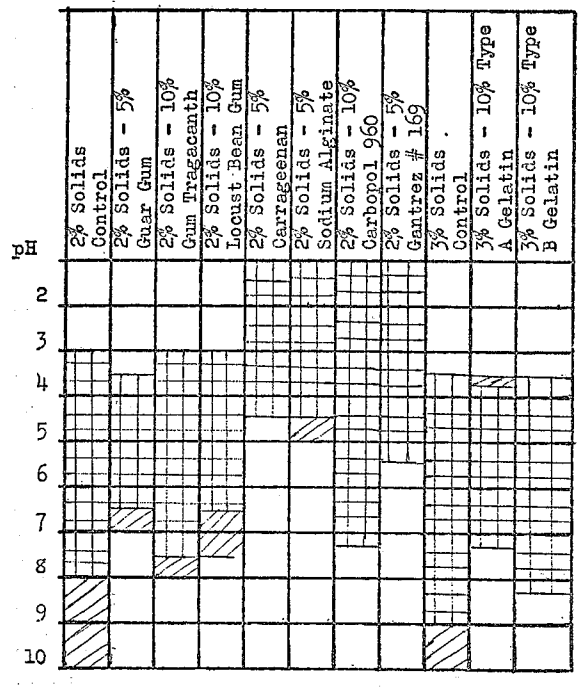
Pickled hide splits were washed and 35% of the washed material was introduced into a drum along with a buffer made of 1200 ml. of glacial acetic acid, 1000 gms. of sodium hydroxide and 1000 ml. of a 37% solution of formaldehyde. 80 lbs. of water were added and the drum was rotated for 21 hours. The splits were then drained, washed for one hour, hosed and drained for one-half hour and then cut into approximately one inch

pieces. The formaldehyde content of the material at this time was about 0.26% by weight based on the weight of the dry collagen. The chopped material was then introduced into a Hollander type paper beater and made up to a 200 lb. batch by addition of water. The pH of the material in the beater at this time was about 5.4. The beater was operated until about 4 kw. hours of energy had been supplied to the beating operation. At this time, 250 cc. of an emulsifying agent were added and beating continued for three minutes to emulsify the fat content of the split material. The resulting emulsion was drained off. Half of the split material was then put back in the beater along with 80 lbs. of water and the beating was continued. The pH of the material was adjusted to approximately pH 7 by addition of 4 N solution of sodium hydroxide. After 4½ hours of beating the material was reduced to a suspension of collagen fibers having a length of about 0.2 to about 1 mm.

Quantities of the fiber suspension were withdrawn and made up with addition of water with and without protective colloid materials in solution to the solids contents and protective colloids contents shown in the following table. The percent of the protective colloid material given in the table is percent by weight based on the weight of the collagen fiber solids in the suspension so that, for example, a composition listed as "2% solids" and "5% guar gum" would contain 5% or 2% or $\frac{1}{10}$% of guar gum based on the weight of the suspension. Portions of the various suspensions were made up to a range of pH values from pH 2 to pH 10 by addition of acid or alkali and the portions were supplied to the surfaces of sections 7 oz. per sq. yd. mat of 3 denier polypropylene fiber mat to determine their abilities to penetrate the mats.

Penetration of the mats was effected by disposing the sections of mat on a filter bed provided with means for applying suction. When the portions of fiber suspension on the surface of the mat had been leveled with a rubber squeegee, suction was applied tending to pull the suspension into the mat.

Table I



In the above table, the portions of the pH range with latice cross hatching indicate areas in which penetration of the collagen fiber suspension into the intermeshed fiber mat was unsatisfactory and areas cross hatched in diagonal lines are portions of the pH range in which only fair penetration was secured. Uncross-hatched portions of the pH range indicate pH values at which good penetration of the suspension into the intermeshed fiber mat was obtained.

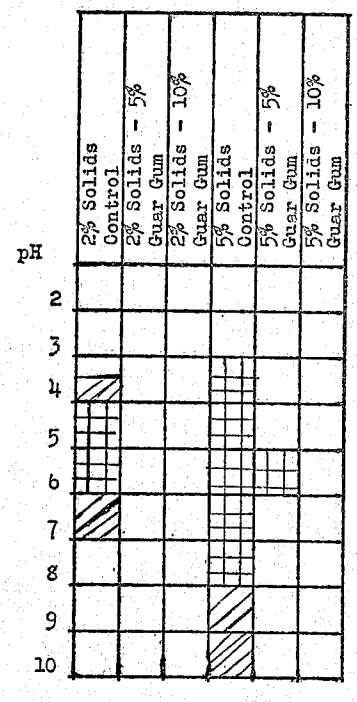
It will be observed that the collagen fiber suspensions not containing protective colloid material have relatively wide ranges of pH values in which the penetration ability is unsatisfactory and also have a substantial portion of the range in which the penetration into the intermeshed fiber mat is only fair. On the other hand suspensions in which a protective colloid material is present penetrate effectively into an intermeshed fiber mat at pH values unworkable with the simple collagen fiber suspension.

The fiber mats which had been penetrated by collagen fiber suspensions were reduceable to tough leather-like sheet materials by procedures such as shown in the copending application above-referred to. Such further processing might include drawing dry acetone through the impregnated mat to effect a reaggregation of the microscopic collagen fibers of the suspension and tanning the solvent dried sheet in a standard buffer chromium tanning liquor containing 0.5% chrome calculated as Cr_2O_3 and 1% of sodium formate and having a pH of 4. The sheets after removal from the tanning may be allowed to stand overnight in a covered receptacle and washed in water for three successive periods of 15 minutes. The sheets may then be dried and immersed in a 4% by weight solution of oleic acid in acetone for 1½ hours. On removal from the oleic acid solution and drying, the sheets had physical properties comparable to chrome tanned leather. The sheet material may be given any treatment to provide a suitable finish.

EXAMPLE II

Collagen fiber suspension prepared as in Example I was divided into portions and the portions were made up to different collagen fiber solids contents by addition of water, or by addition of water and solutions of a protective colloid, specifically guar gum to form the compositions listed in Table II. These portions were divided into sections, adjusted to pH values and used to impregnate intermeshed fiber mats following the procedure of Example I. In the results recorded in Table II, there will be observed that the first three columns involve penetration of a relatively open 2 oz. mat of intermeshed polypropylene fibers and use of a 2% collagen fiber solids suspension while the results recorded in the second three columns, involve use of a much denser mat namely, a 7 oz. mat of polypropylene fibers and a 5% collagen fiber solids content. As discussed hereinabove, penetration into a relatively open mat is more readily achieved than into a denser mat and the penetration ability of a collagen fiber suspension is less with higher solids content.

Table II



It is noted above that the 2% solids collagen fiber suspension without protective colloid was capable of penetrating the 2 oz. mat at pH values up to about 4 on the acid side although the penetration from about 3.6 to about pH 4 was only fair and that on the alkaline side of the isoelectric point of the collagen, the suspension would penetrate to a pH value down to about pH 6 although the penetration was only fair between pH 7 and pH 6. The 2% solids collagen fiber suspension containing either 5% or 10% of guar gum was capable of penetrating the 2 oz. mat over the entire range of pH values.

Under the more difficult penetrating conditions represented by a 5% collagen fiber solids suspension and a 7 oz. polpyropylene mat, the collagen fiber suspension with no protective colloid did not penetrate effectively on the acid side above a pH of about 3; and on the alkaline side of the isoelectric point penetration was only fair at pH's above 8 and no effective penetration was secured at pH values below 8. The inclusion of only 5% guar gum based on the weight of the collagen fiber solids allowed penetration into the mat at pH values below about 5 and above about 6; and the composition including 10% guar gum based on the weight of the collagen fiber solids was capable of penetrating the mat effectively over the entire pH range.

The mats which had been penetrated with collagen fiber solids could be converted to leather-like sheet materials by reaggregation of the collagen, tanning and finishing as noted in Example I.

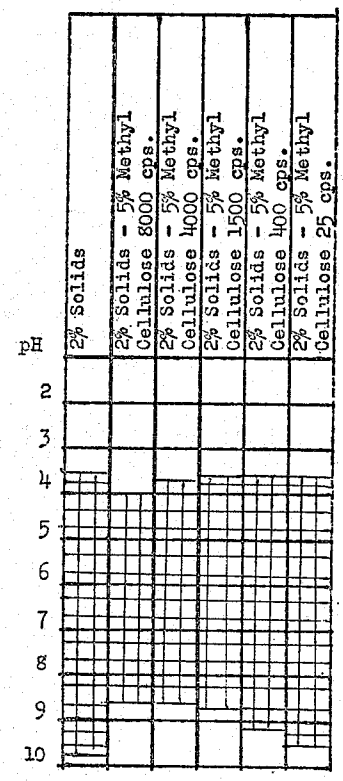
EXAMPLE III

Collagen fiber suspension was prepared as in Example I and divided into portions which were made up to compositions comprising 2% collagen fiber solids based on the weight of the compositions by addition of water and solutions of methyl cellulose as listed in Table III. These portions were divided into sections, adjusted to pH values and used to impregnate a needled mat of nonwoven three denier nylon fiber, the mat having a weight of 6 oz. per sq. yd.

As shown in the table, methyl cellulose of five viscosity types corresponding to decreasing molecular weights were made up. The viscosity figure given in the table is the viscosity of a 2% aqueous solution at 20° C. It will be observed that the effectiveness of the methyl cellulose in allowing penetration of the collagen fiber suspension after pH values closer to the isoelectric range decreases with lower viscosity solutions of the decreasing molecular weight protective colloid materials.

The mats penetrated by the collagen fiber solids could be converted to leather-like sheet materials by reaggregation of the collagen, tanning and finishing as noted in Example I.

Table III



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

1. The process of forming a tough, flexible material which comprises the steps of applying to intermeshed open fiber mass in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct, fine, collagen fibers of microscopic size to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension containing at least about 1% by weight of a hydrophilic protective colloid based on the weight of collagen fibers in said suspension, said protective colloid cooperating with said collagen fibers to resist packing together of said collagen fibers, and removing the swelling water from collagen fibers within said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

2. The process of forming a tough, flexible material which comprises the steps of applying to intermeshed open fiber mass in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen distinct, fine, short collagen fibers from 0.001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension containing at least about 1% by weight of a hydrophilic protective colloid based on the weight of the collagen fibers in said suspension, said protective colloid being associated with said collagen fibers to resist packing together

of said collagen fibers, and removing the swelling water from collagen fibers within said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

3. The process of forming a tough, flexible material which comprises the steps of applying to an intermeshed open fiber mass in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen, distinct, fine, short collagen fibers from 0.001 to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension containing at least about 1% by weight of a hydrophilic protective colloid based on the weight of the collagen fibers in said suspension, said protective colloid being associated with said collagen fibers to resist packing together of said collagen fibers, said suspension being caused to penetrate said intermeshed fiber in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and said collagen fibers, and removing the swelling water from collagen fibers within said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

4. The process of forming a tough, flexible material which comprises the steps of applying to an intermeshed open fiber mass in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen, distinct, fine, short collagen fibers from 0.001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH outside the isoelectric range of said collagen fibers and containing at least about 1% by weight of a hydrophilic protective colloid based on the weight of the collagen fibers in said suspension, said protective colloid being associated with said collagen fibers to resist packing together of said collagen fibers, said suspension being caused to penetrate said intermeshed fiber in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and said collagen fibers, and removing the swelling water from collagen fibers within said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

5. The process of forming a tough, flexible material which comprises the steps of applying to an intermeshed open fiber mass in penetrating relation an aqueous suspension containing from about 1% to about 5% by weight based on the weight of the suspension of swollen, distinct, fine, short collagen fibers from 0.001 mm. to about 4 mm. in length to carry said collagen fibers into the interstitial spaces of said intermeshed fiber mass, said suspension having a pH outside the isoelectric range of said collagen fibers and containing at least about 1% by weight of a hydrophilic protective colloid based on the weight of the collagen fibers in said suspension, said protective colloid being associated with said collagen fibers to resist packing together of said collagen fibers, said protective colloid being selected from the group consisting of carbohydrate gums, water-soluble polyelectrolytes, gelatin, glue and derivatives of these, said suspension being caused to penetrate said intermeshed fiber in quantity to provide from about 5% to about 90% by weight of collagen fibers based on the combined weight of said intermeshed fibers and said collagen fibers, and removing the swelling water from collagen fibers within said intermeshed fiber mass to reaggregate them into a larger collagen fiber structure within the interstitial spaces throughout said mass of intermeshed fibers to reinforce said intermeshed fibers against displacement.

6. The process of forming a tough, flexible material as defined in claim 5 in which said protective colloid is a carbohydrate gum.

7. The process of forming a tough, flexible material as defined in claim 5 in which said suspension contains from 5% to 10% by weight of protective colloid based on the weight of the collagen fibers in said suspension and said protective colloid is guar gum.

8. The process of forming a tough, flexible material as defined in claim 5 in which said suspension contains from 5% to 10% of protective colloid based on the weight of the collagen fibers in said suspension and said protective colloid is gelatin.

9. The process of forming a tough, flexible material as defined in claim 5 in which said suspension contains from 5% to 10% by weight of protective colloid based on the weight of the collagen fibers in said suspension and said protective colloid is methyl cellulose.

10. The process of forming a tough, flexible material as defined in claim 5 in which said suspension contains from 5% to 10% of protective colloid based on the weight of the collagen fibers in said suspension and said protective colloid is a water-soluble polyelectrolyte.

11. The process of forming a tough, flexible material as defined in claim 5 in which said suspension contains from about 5% to about 10% by weight of protective colloid based on the weight of the collagen fibers in said suspension and said protective colloid is a water-soluble polyelectrolyte interpolymer of methylvinylether and maleic anhydride.

References Cited by the Examiner

UNITED STATES PATENTS

2,015,865	10/1935	Muller	117—164
2,036,526	4/1936	Hagedorn et al.	117—164
2,040,511	5/1936	Bleyenheuft	117—164 X
2,238,839	4/1941	Watkins	117—165 X
2,405,978	8/1946	Pickles	117—140 X
2,411,818	11/1946	Weiss	117—164 X
2,663,989	12/1953	Schlatter et al.	117—165 X
2,838,363	6/1958	Vois	106—124 X
2,934,446	4/1960	Highberger et al.	162—151 X
2,973,284	2/1961	Semegen	117—138.8 X
2,979,410	4/1961	Parlour	117—165 X
3,013,936	12/1961	Iyengar	117—138.8 X
3,034,927	5/1962	Fairclough et al.	117—140
3,073,714	1/1963	Tu et al.	117—4 X

WILLIAM D. MARTIN, *Primary Examiner.*

T. G. DAVIS, *Assistant Examiner.*