United States Patent Office 3,194,865 Patented July 13, 1965

3,194,865

ACID DEPILATION AND EXTRUDABLE FIBRIL PRODUCTION FROM HIDE CORIUM

Paul V. Fagan, New Brunswick, and Emanuel R. Lieberman, Somerville, N.J., assignors to Johnson & Johnson, a corporation of New Jersey

No Drawing. Filed Oct. 1, 1962, Ser. No. 227,585
12 Claims. (Cl. 264—209)

The present invention relates to a method of treating hides and skins to prepare them for a subsequent conversion into a dispersion of swollen collagen fibrils for casing manufacture.

The collagen fibrils in bovine hides are arranged in bundles to form collagen fibers that vary in length and measure many thousand of Angstroms in diameter. Cowhide collagen fibers have been observed which measure about 10,000 to 20,000 Angstroms in diameter in the dehydrated state but larger collagen fibers measuring as much as 1,000 microns in diameter in their dehydrated state are believed to exist. Each collagen fiber contains hundreds or even thousands of fibrils, all bound together by a sheath. The collagen fibers in turn are organized into bundles of collagen fibers that are large enough to be seen by the naked eye and form the familiar fibers visible in hides of all sorts. For all practical purposes, cowhide tissue is the commercially available raw material from which collagen fibrils can be obtained.

Edible sausage casings may be manufactured by extruding a mass of undegraded acid swollen collagen fibrils through an annular orifice to form a tubular casing which can then be treated in a manner to dehydrate and deswell the individual collagen fibril units. When the collagen fibrils in the extruded casing lose their excess water of hydration by air drying, they cohere to form a translucent hyaloid substance in which the boundary line between individual fibrils cannot be distinguished.

To make a dispersion of swollen collagen fibrils suitable for extrusion, the hide must first be freed from all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands. This upper portion of the hide has been aptly designatetd the thermostat layer by Wilson, since it contains those organs concerned with the regulation of body temperature. These structures are made up of proteins of the class known as keratin. The class of protein known as collagen, on the other hand, is present in that part of the hide lying beneath the thermostat layer, known as the corium. In trying to separate the keratin from the collagen without damage to the collagen, it is important to recognize the differences in properties between these two kinds of protein. Both keratin and collagen can be destroyed by strong solutions of acids or alkalies, but acids destroy collagen more readily than they do keratin and alkalies destroy keratin more readily than they do collagen. For this reason, the separation has previously been effected in alkaline solutions.

If a calf skin is immersed in a solution containing one pound of caustic soda per gallon of water, the hair will be quickly dissolved, but the true corium will not be irreparably damaged for leather manufacture until after the hair is gone. Nevertheless the method is a dangerous one even in the manufacture of leather because strong alkali will rapidly degrade collagen. The pH value of such a solution is about 14.0. At this pH value, collagen is hydrolyzed and destroyed although hair and epidermis are more quickly destroyed.

Centuries ago, tanners discovered that a solution of lime might be used to separate hair from skin without much damage to the skin. The reason for this is that lime has a limited saturability. If one pound of lime

(calcium hydroxide) is put into a gallon of water, from 99.4 to 98.5 percent of it will remain undissolved because the solution becomes saturated at about 0.006 pound per gallon of water at boiling point and at about 0.015 pound per gallon of water near the freezing point. A saturated solution of lime has a pH value of about 12.5. It cannot be raised above this point by adding more lime because the excess will not dissolve.

Although lime treatment is quite suitable for leather manufacture, lime should not be used to dehair hides if the end product is to be an extruded casing. For although lime aids in the removal of hair and the epidermis layer, like most chemical reactions the liming of hides requires judgment and some compromise because the reaction of lime with keratin and collagen is not perfectly selective. The liming of hides is a very complicated reaction chemically which can effect the collagen fibrils that make up the hide in at least three ways:

(1) By deamidation and the minor destruction of the arginine residue resulting in an increase in free carboxylic groups.
(2) By breaking coordinate cross links between peptide bonds of adjacent peptide chains. This can result also in a greater up-take of cations, and
(3) Calcium hydroxide has a specific effect on collagen and a tendency to form complexes with hydroxy groups, which probably is connected with its low degree of ionization, its complexing power, and the bivalency of the cation.

The effects noted above may contribute to the inability of earlier workers in this field to produce edible sausage casings using limed hides as a starting material.

It is an object of the present invention, therefore, to remove the hair, epidermis layer, thermostat layer and all keratin substances from fresh hides without denaturing or adversely effecting the collagen fibrils that make up the hide corium.

In accordance with the present invention, bovine hides are dehaired in such a way that the corium is not adversely effected for its subsequent use in the preparation of swollen collagen fibrils for casing manufacture. This may be accomplished by soaking the hide in a dilute aqueous solution of a weak acid that has a dissociation constant between 1.0×10^{-5} and 1.0×10^{-3} in aqueous solutions. That one should in this manner be able to facilitate the removal of hair and epidermis without adversely effecting the collagen fibrils that make up the corium is all the more surprising in view of the known greater resistance of keratin to acid attack.

While the present invention is not to be limited by any particular theory, it is believed that the hairs are rendered removable from the skin by the dilute acid treatment because the acid swells and softens the corium of the skin, thus rendering the hairs removable from the follicles and the epidermis removable from the collagen-containing derma. Inasmuch as the subsequent treatment of the corium to produce swollen collagen fibrils for casings involves further swelling with similar dilute solutions of weak acids, the unhairing of the hides with such acid solutions is not adverse to the subsequent treatment of the corium and in some cases may contribute favorably to such subsequent treatment.

Weak organic acids which may be used in the practice of the present invention are those having a dissociation constant as indicated above among which may be named acetic, lactic, formic and citric acids. Particularly preferred is acetic acid which has a dissociation constant at 25° C. of 1.75×10^{-5}. Stronger acids such as citric acid may also be used but such acids result in a lower pH and increased swelling of the fresh hides. Too much swelling is a disadvantage since it results in a rigid, stiff hide that

is difficult to pass through the rollers of the splitting and dehairing machine.

The acidic aqueous solutions used may contain from 3% to 5% by weight of the organic acids described above, as required to give a pH of 2.3 to 3.7. At a pH above 3.7 it is necessary to treat the hides with the acid solution for a longer time and at a pH below 2.3 there is more danger of degrading the collagen. The acidic dehairing solution should be maintained at room temperature (about 70–75° F.) and the fresh hides are permitted to soak in the acid bath with occasional agitation for 100 to 150 hours. The soaking time in the bath may, of course, be reduced if the temperature of the bath is increased, but at elevated temperatures there will be some loss of the collagen due to acid hydrolysis and degradation.

The hides after this acid treatment are run through a defleshing machine and scraped on both sides to remove all hair epidermis and any adhering flesh. The cleaned corium so obtained is in a swollen condition because of solvation that occurs during the acid treatment. This swelling interferes with comminution and other mechanical handling of the skin during the preliminary stages of dispersing the collagen fibrils. It is necessary, therefore, after removal of the hair and epidermis to carefully neutralize and deswell the cleaned hide corium before proceeding further. During the neutralization step the cleaned hide corium is soaked in a weak aqueous alkaline bath at room temperature for about 12 hours. It is important to control the temperature and pH of the neutralizing bath to avoid alteration or degradation of the collagen. Moreover, the alkaline bath should not contain reagents, such as lime, or alkaline earth salts that might form an irreversible complex with the collagen. The alkaline bath may be prepared by dissolving ammonia or a soluble salt of a strong base and a weak acid, such as sodium bicarbonate, in water to give an alkaline pH below 10.0. Strongly alkaline agents must be avoided with regard to the ultimate use of the corium because the reagent used for neutralization and the ultimate pH of the neutralized skin are of substantial importance as they effect the subsequent condition of the acid swollen collagen fibrils in the mass to be extruded.

Following the neutralization step the cleaned hide corium is washed in water for 3 to 4 hours. The hide corium after neutralization and washing is in a deswollen condition and may be subdivided, using conventional grinding equipment, to a particle size that is readily dispersible in dilute acid solution.

It will be understood that the foregoing general description is exemplary and explanatory but does not restrict the invention. The process for dehairing fresh bovine hides may be more fully understood from the following description and example.

Forty steer hides, fresh from the slaughter house, are trimmed, fleshed, and placed in a drum bath with 3600 pounds of cold water (58° F.). The hides are drummed for 30 minutes and the wash water is discarded. An aqueous acetic acid solution is prepared in a paddle vat by adding to 3000 pounds of water at room temperature (70° F.) 111 pounds (3.7% by weight) of acetic acid. The washed steer hides are placed in the vat and the hides are agitated intermittently to insure that all sections of the hide surface contact the acid solution. The pH of the acetic solution increases from 3.2 to 3.5 after forty hours and the concentration of the acetic acid in solution at this time is 3.3% by weight. Intermittent agitation is continued and at the end of 90 hours the acid concentration has diminished to 2.1% by weight and the pH is 3.7. The hides are allowed to soak in the vat for five days and five nights (120 hours) with occasional agitation to assure uniform treatment of all hides. After the acid treatment the hides are scraped on both sides to remove hair, epidermis and other undesirable matter.

The cleaned hide corium is then loaded into a large drum having a capacity for forty hides and carefully

neutralized by washing for four hours at a temperature of 55–60° F. in a dilute alkaline solution containing eighty pounds of sodium bicarbonate in 4,000 pounds of water. The total time required for neutralization in this alkaline wash is approximately 12 hours.

The neutralized hide corium is next washed in an overflow bath for 3 to 4 hours in order to remove the salts formed during the neutralization step. The hide corium after this final wash is composed of substantially pure colagen fibrils free of all hair follicles and other extraneous matter. It may be comminuted and reswollen in acid solution to form a homogeneous mass of swollen collagen fibrils useful in the manufacture of extruded collagen casings, as disclosed, for example, in United States Patents No. 3,123,653 and No. 3,123,482.

Composites are prepared from five hides. The hide composites are then cut into ½ to 4 square inch sections and reduced to pulp by three passes through a meat grinder, each pass being a finer grind. The first and second passes are through 18 and 8 millimeter holes, respectively. The final grind is through holes 1.5 millimeters in diameter. It is important during the grinding process to keep the pulp below 20° C. This may be done by adding crushed ice to the hide sections as they are fed to the grinder.

The ground pulp is next diluted with tap water at 16° C. to give a smooth slurry containing 7.4% dry solids. This slurry (125 parts) is then treated with 125 parts of a 2.4% lactic acid water solution using an inline mixer to form a homogeneous mass of swollen colagen fibrils. It is important during this acid swelling step also that the temperature be maintained below about 25° C. The mixture so obtained contains 3.7% hide solids and 1.2% lactic acid. After the pulp is blended with acid, the mass of swollen collagen fibrils is further dispersed in a suitable homogenizer, fitted with a 2-stage valve and operated with a 1500 p.s.i. drop per stage. In the ultimate fluid mass of swollen colagen fibrils so prepared the individual fibrils are freed from the fiber bundles and fibers and released from the fiber sheaths. They take up all liquid and swell from an original diameter of the order of 300 A. to 1000 A. to a freshly swollen (one day old) maximum diameter of the order of 15,000 A.

Other mixtures prepared in similar manner may contain hide solids (in the above-described form of swollen collagen fibrils) as low as about 3% and as high as about 5%, the preferred concentration of hide solids being about 4%. If the concentration is less than 2.5% the mixture is so watery that coagulation after extrusion becomes virtually impossible, while a concentration exceeding 6% requires very high extrusion pressures due to increased viscosity and tends to formation of tough casings. The preferred concentration of lactic acid is about 1.2% but may be as low as about 0.50%.

The fluid mass of swollen collagen fibrils obtained by the method above described is filtered through a 7-mil filter screen to remove unswollen collagen and non-colagenous materials, and then extruded in the form of a tube, preferably in such a way as to impart some collagen fibril orientation transverse to the extrusion direction. The particular design and operation of the extruder constitutes no essential part of the present invention, but it has been found preferable to utilize the action of the extruder to effect the maximum homogeneity of fibril distribution so as to impart substantial burst strength and transverse tear strength to the tube and ultimae casing while also effecting orientation or alignment of fibrils or masses of fibrils in the direction of extrusion, particularly those adjacent the tube walls, thereby to achieve substantial longitudinal or tensile strength as well.

A preferred form of extruder utilizing the action of counter-rotating discs which facilitate a homogeneous and non-oriented distribution of fibrils, especially within the interior of the casing walls, is shown and described in United States Patent No. 3,122,788.

In accordance with the invention the extruded fluid mass of swollen collagen fibrils leaves the orifice of the extruder in the form of a tubular body of watery fluid travelling preferably upwardly into a dehydrating or coagulating bath which surrounds the orifice of the extruder and extends upwardly therefrom. The initial coagulating bath into which the extruded tubular body immediately passes is preferably in the form of a vertical column of liquid constituting a housing surrounding and extending upwardly from the extruder orifice. A portion of this liquid flows upwardly within the extruded tubular body, passing between the extruded body and an internally disposed over-flow or return tube. The flow rate within the extruded body is quite slow, to avoid pressures and velocities harmful to the delicate extruded body, and may be, e.g., about 1 gallon per hour. Another portion of the coagulating liquid flows upwardly in the housing outside the extruded tubular body and returns through an external overflow drain for recirculation. The flow rate of said outside column of liquid may be relatively rapid, e.g., about 2 gallons per minute. Thus the inside and outside of the tubular body are initially bathed in upwardly flowing columns of a coagulating liquid.

It should be noted that the density of the extruded tubular body as it comes from the extruder orifice is substantially less than that of the coagulating salt solution into which it passes. Accordingly the tendency of the extruded tubular body is to rise and travel naturally upwardly in the coagulating liquid. This phenomenon facilitates the starting up of the extruder and the maintenance of the desired upward travel of the tubular body with the exertion of a minimum of external forces thereupon. This action occurs at that stage in the treatment of the tubular body when it is weakest and most fragile and possesses virtually no integrity of its own.

After reaching the top of the liquid housing, the tubular body is passed into and through an extended bath of the coagulating liquid for a total coagulating exposure of about 6 minutes, although this time may be as short as about 3 minutes. The means and apparatus for accomplishing this transfer and subsequent conditioning operations will be hereinafter described in detail. This coagulating treatment is the first conditioning step applied after extrusion of the tubular body. The extended coagulating bath itself is preferably an aqueous ammonium sulfate solution containing about 40% ammonium sulfate adjusted to a pH substantially higher than that of the acid-swollen collagen material, e.g., a pH of about 7.0, with some suitable alkaline material such as sodium or ammonium hydroxide. The coagulating liquids in the vertical housing above the extruder and in said extended bath are of the same aforesaid composition. The purpose served by these coagulating baths is primarily to replace the water in the extruded tubular body by ammonium sulfate solution, thereby coagulating and giving temporary form and integrity to the tubular body so that it may be handled in the subsequent conditioning operations.

The tubular body, when it passes from the extrusion nozzle or orifice, has a wall thickness determined by the annular space between the internal and external extruder tubes forming the orifice. In a preferred embodiment of the invention the external diameter of the inner extrusion tube is preferably about .75" while the radial distance between the exterior of said inner tube and the interior wall of the external tube is about .014". Thus the tubular body referred to will have an initial wall thickness of about .014" (14 mils) and this thickness will be substantially maintained throughout most of the liquid conditioning treatments as hereinafter described. Ultimately, in accordance with the invention, the dried tubular body will be reduced to a wall thickness of the order of .001" (1 mil), but the initial inner diameter of about .75" will be preserved. These dimensions are given by way of example and are not limiting, but to illustrate the relatively great reduction in wall thickness required and achieved by practice of the invention. The casing diameter of about .75" is typical of casings used for fresh pork sausages.

As a second conditioning step the concentration of coagulating salt in the coagulated tubular body is substantially reduced, thereby to facilitate the hardening action hereinafter described. In the preferred embodiment of the invention, hardening is effected by treatment with alum and it has been found that such treatment is effective only when the concentration of ammonium sulfate in the tubular body has been substantially reduced, yet a sufficient amount thereof retained pro tem to avoid undue softening and weakening of the coagulated tubular body. Accordingly the tubular body is pre-washed for a period of about six minutes in a much diluted water solution of ammonium sulfate (e.g., about 4% to 18%) similarly adjusted to pH of about 6.5.

In accordance with the invention, a third conditioning step constitutes a hardening of the coagulated casings by reaction of the collagen therein to alum. For this purpose the pre-washed coagulated tubular body is immersed in and treated with a solution containing, e.g., about 6% alum [$NH_4Al(SO_4)_2 \cdot 24H_2O$], 1% citric acid and 4% ammonium sulfate. The contact time is about six minutes and this alum hardening solution is maintained at pH 4.3.

This hardening treatment is sometimes called "tanning," but the primary purpose is to effect a hardening of the casing so as to make it resistant to water, which is not the case with collagen coagulated with ammonium sulfate. Without such hardening action the application of water to the tubular body coagulated with ammonium sulfate would reduce it to a formless gel. In other words the coagulation with ammonium sulfate is essentially a temporary step after which a more permanent hardening action is effected by treatment with alum. More detailed descriptions of the alum treatment with various examples thereof are given in United States Patent No. 3,123,481.

The fourth conditioning step, in accordance with the invention, involves removal of the ammonium sulfate salt which has remained in the tubular body after the pre-wash and alum hardening steps. This excess ammonium sulfate as well as any excess alum in the tubular body are removed by a prolonged washing of the tubular body in tap water, e.g., for about twenty minutes, preferably using two or more changes of water.

The fifth step in the conditioning of the tubular body is called a plasticizing operation. This procedure involves essentially two steps, one of which is the application of a humectant such as glycerine which preserves the softness of the material after drying and helps in rehumidifying it. This plasticizing material also prevents cracking and other effects consequent upon undue drying. As an example, the plasticizing bath may contain 3.6% glycerol, 20 parts per million formaldehyde and 0.1% sodium bicarbonate. The dwell time in this bath is about five minutes.

Concomitantly with the plasticizing step, carboxymethyl-cellulose (CMC) is preferably included in the plasticizing bath and applied thereby to the tubular body. For this purpose, about 0.33% CMC is added to the bath and the glycerol concentration is preferably increased to about 4.8%. A more detailed description of the composition of this combined plasticizing and CMC bath and variations thereof are given in United States Patent No. 3,123,483. The application of CMC has the effect of partially drawing out water from the tubular body and thereby reducing its thickness. In the example here given, the thickness reduction is from the original 14 mils to about 10 mils. Moreover, as described in United States Patent No. 3,123,483, the application of CMC improves the wet-strength of the casing before drying because of the proportionate increase in solid content. Moreover, it increases the burst-strength of the ultimate casing, thereby improving its properties during stuffing and cooking.

As the next or sixth conditioning step in the method, the hardened, plasticized and partially solidified tubular body is dried by hot air currents. For this purpose the casing is inflated by blowing air into and through the length thereof as it passes into a drying chamber while at the same time warm air is blown over and around the exterior. This drying air is at approximately 80° C. and 8% relative humidity and the casing is subjected to such treatment until the wall thickness of the tubular body has been reduced to about 1 mil in the example under discussion. In accordance with the invention, great care is taken during this step to prevent expansion or stretching of the air-inflated casing beyond the internal diameter imparted to it by the extrusion, e.g., 75 inch in the example given. The achievement of suitable drying can be determined by visual inspection, the dried casing tube being translucent, while the presence of moisture is indicated by a whitish, opaque color.

During the drying operation or immediately thereafter, an albumin powder may be blown into and through the inflated casing or otherwise applied, as more particularly described in United States Patent No. 3,123,480. Also after drying the dried tube may be partially re-humidified, by application of moist air, to avoid brittleness or cracking.

The dried casing tube may then be subjected to automatic shirring and shirred lengths severed to form casings adapted to be stuffed on automatic stuffing machines. As a final step, prior to stuffing but after shirring, the casing is preferably subjected to a heat-curing treatment. This treatment comprises storage for about eight hours at a rising temperature bringing the casing material from room temperature to about 80° C. It is then maintained at 80° C. for some sixteen hours more, which completes the heat curing thereof.

Other weak water soluble organic acids such as formic acid, citric acid, butyric acid, and lactic acid may be substituted for the acetic acid in the specific example described above.

What is claimed is:

1. In a process for making a mass of swollen collagen fibrils suitable for extrusion from fresh undehaired animal hide the improvement which comprises:

immersing fresh undehaired animal hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3}.

soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

removing the hide from the acid solution and scraping the hide on both sides to remove from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consists of the sebaceous glands and sudorific glands;

treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

washing the cleaned hide corium with water;

comminuting the cleaned hide corium; and,

reswelling the comminuted corium in acid solution to form a homogeneous mass of swollen collagen fibrils, all of the above steps being carried out at temperatures below 25° C.

2. The process of claim 1 in which the aqueous acid solution is an acetic acid solution.

3. The process of claim 1 in which the aqueous alkaline solution is a solution of the salt of a strong base and a weak acid.

4. The process of claim 1 in which the aqueous acid solution is a lactic acid solution.

5. The process of claim 1 which the aqueous acid solution is a butyric acid solution.

6. The process of claim 1 in which the aqueous acid solution is a citric acid solution.

7. The process of claim 1 in which the aqueous acid solution has a pH greater than 2.3 and less than 3.7.

8. A process of producing swollen collagen fibrils for extrusion into edible sausage casings comprising the steps of:

Immersing fresh undehaired hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3};

Soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

Removing the hide from the acid solution and removing from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands;

Treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

Comminuting the neutralized and deswelled corium, and

Subjecting the comminuted corium to the swelling action of an aqueous solution of an acid having a dissociation constant between 1.0×10^{-5} and 1.0×10^{-3}, whereby a mass of swollen collagen fibrils is obtained;

all of the above steps being carried out at temperatures below 25° C.

9. In the method of producing a tubular collagen casing, the steps of:

immersing fresh undehaired animal hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3};

soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

removing the hide from the acid solution and scraping the hide on both sides to remove from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands,

treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

washing the cleaned hide corium with water;

comminuting the cleaned hide corium and reswelling the comminuted corium in acid solution to form a homogeneous mass of swollen collagen fibrils;

extruding the homogeneous mass of swollen collagen fibrils to form a continuous, fragile tubular body;

applying a coagulant to said tubular body;

hardening the coagulated body;

washing coagulant from the hardened body;

maintaining substantially the same wall thickness in said tubular body throughout the aforesaid steps of coagulating, hardening and washing said body; and,

drying said body.

10. In a method of producing collagen casings, the steps of:

immersing fresh undehaired animal hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3};

soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

removing the hide from the acid solution and scraping the hide on both sides to remove from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands;

treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

washing the cleaned hide corium with water;

comminuting the cleaned hide corium and reswelling the comminuted corium in acid solution to form a homogeneous mass of swollen collagen fibrils;

extruding the homogeneous mass of swollen collagen fibrils to form a continuous, fragile, tubular body;

applying a coagulant to said tubular body;

hardening said body in the wet state; and,

drying said hardened body by passing it through a drying chamber and subjecting it therein to heated currents of air while maintaining the drying body in the form of a tube by inflation with air under pressure and controlling the pressure of said inflating air so as to maintain the inner diameter of the tube substantially the same as that at which it was extruded in the wet state.

11. In the method of producing a tubular collagen casing, the steps of:

immersing fresh undehaired animal hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3};

soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

removing the hide from the acid solution and scraping the hide on both sides to remove from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands;

treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

washing the cleaned hide corium with water;

comminuting the cleaned hide corium and reswelling the comminuted corium in acid solution to form a homogeneous mass of swollen collagen fibrils having a collagen solids content in the range of more than 2.5% and less than 6% by weight;

extruding the homogeneous mass of swollen collagen fibrils to form a continuous, fragile, tubular body;

applying a coagulant to said tubular body;

hardening the coagulated body;

washing coagulant from the hardened body;

maintaining substantially the same wall thickness in said tubular body throughout the aforesaid steps of coagulating, hardening and washing said body; and,

drying said body,

while maintaining the internal diameter of said body substantially equal to that at which it is extruded.

12. In the method of producing a tubular collagen casing, the steps of:

immersing fresh undehaired animal hide in a dilute aqueous solution of an acid having a dissociation constant in aqueous solution between 1.0×10^{-5} and 1.0×10^{-3};

soaking the hide in said acid solution until the epidermal layer and thermostat layer of said hide are swollen and softened;

removing the hide from the acid solution and scraping the hide on both sides to remove from the hide corium all hair and flesh, the hair follicles, epidermal layer, dermis and adnexial glands which consist of the sebaceous glands and the sudorific glands;

treating the dehaired and defleshed hide corium so obtained with a dilute aqueous alkaline solution to neutralize residual acid present and deswell the corium;

washing the cleaned hide corium with water;

comminuting the cleaned hide corium and reswelling the comminuted corium in acid solution to form a homogeneous mass of swollen collagen fibrils having a collagen solids content in the range of more than 2.5% and less than 6% by weight;

extruding the homogeneous mass of swollen collagen fibrils to form a continuous, fragile, tubular body;

immersing said body in a solution of ammonium sulfate to coagulate the collagen therein;

immersing the coagulated body in an alum solution to harden the body and render it resistant to softening by water;

water washing the hardened body;

immersing the washed, hardened body in a plasticizing solution; and,

drying said body.

References Cited by the Examiner

UNITED STATES PATENTS

2,101,877	12/37	Sheppard	8—94.16 X
2,105,036	1/38	Freudenberg	8—94.14 X
2,485,957	10/49	Cresswell.	
3,123,482	3/64	Lieberman	95—176
3,123,653	3/64	Lieberman	264—99

OTHER REFERENCES

Marriott: J. Soc. Lea. Trades Chemists, 1921, pp. 2–9.

Wilson: Chemistry of Leather Manufacture, 2nd ed., pp. 311–312, Vol. 1, 1928, pub. by The Chemical Catalog Co., Inc., N.Y.C.

NORMAN G. TORCHIN, *Primary Examiner.*

ABRAHAM H. WINKELSTEIN, *Examiner.*