PRODUCTION OF COMMINUTED COLLAGEN FOR NOVEL APPLICATIONS

M. KOMANOWSKY, H. I. SINNAMON, S. ELIAS,
W. K. HEILAND, AND N. C. ACETO

U. S. Department of Agriculture
Agricultural Research Service
Eastern Regional Research Center
Philadelphia, Pennsylvania 19118

ABSTRACT

A process for manufacturing five different comminuted products from cowhide trimmings and flesh splits is described. In this process, limed hide is acidified to its isoelectric point and comminuted in successive stages, utilizing a strip cutter, a rotary knife cutter, and an Urschel Comitrol high-speed cutter-grinder. Shearing of hide particles at different stages of comminution is accomplished in a disc mill. Water is added during some operations to minimize denaturation of collagen. The energy consumption and the product rate at the recommended optimum operating conditions for each of the machines are reported. The degree of comminution and shearing accomplished in the manufacture of each of the products is illustrated by means of photomicrographs. Varying in particle size over a wide range, the products are expected to be suitable for many applications.

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INTRODUCTION

New, large-scale applications for cowhide collagen could provide the necessary equilibrium for stabilizing prices of hides during the fluctuations in supply and demand (1). Moreover, such applications would make it profitable to trim hides to a shape that would permit mechanization of the processing steps of tanning.

Fundamental research on collagen and the multiple applications for it which have been reported in recent technical literature (*e.g.,* 2–4) indicate that this raw material has unique chemical and physical properties which could be utilized more profitably in the naturally occurring fibrous state, rather than as the traditional source of gelatin and glue. For each practical application for collagen found in the literature a separate procedure for pretreating, comminuting, and dispersing is given. This precludes the use of a central facility operating on a large, economical scale. The present work reports the development of a comminuting process which yields products that should satisfy the demands of most users of ground collagen. The proposed applications for collagen (as a binder and extender of meat, as a source of animal protein for pet foods, as a texturizing adjunct for vegetable proteins, as a support medium for immobilizing enzymes, and in many other novel applications) require that the comminuted collagen be undenatured. Denaturation can be caused by heat (such as that generated during grinding) or by pH (if far removed from the isoelectric point of collagen for extended periods). Consequently, addition of water to dissipate heat during grinding and pH adjustment to the isoelectric point of limed hide have been incorporated in the process.

The diverse requirements of the different applications have dictated the development of as many as five products of varying particle size and shape. Each of these products has definite and reproducible dimensions. Many uses would not require additional comminution of these products; in other applications, they would be used as intermediates needing some additional treatment.

In developing the process an attempt was made to keep the grinding costs at a minimum. Also, the processing conditions and the equipment used were chosen to yield products that meet chemical and microbiological standards set for human food and animal feed.

EXPERIMENTAL

Processing Equipment and Procedures

Whole cowhides are relatively expensive, but limed flesh splits are quite cheap during years of low demand. For this reason all of our work was carried out with limed flesh splits obtained from tanneries that process fresh, uncured hides.

Our process, as finally developed, consists of three main operations: (1) precutting, (2) acidifying, and (3) grinding. As shown in the flow diagram (Figure 1), limed hides are first sliced in a strip cutter and then cut further into small particles in a rotary knife cutter. These precut hide particles are later acidified with the desired organic acid to the isoelectric point of limed hide (pH 5.3). Finally, they are ground by one of five different procedures. Details of each of the operations are discussed below. All metal parts of the comminuting machines used that come in contact with the rawhide are made of stainless steel, with the exception of the cutting knives of the strip cutter and the rotary knife cutter, which are made from high carbon, high chrome steel alloy, and the microcut head of the Urschel Comitrol* grinder, which contains stellite blades.

Precutting. The first precutting step is carried out in the Taylor-Stiles "Giant" rotary strip cutter (Model 115, with a five HP motor, purchased from Arthur G. McKee and Company, Riegelsville, New Jersey). The limed

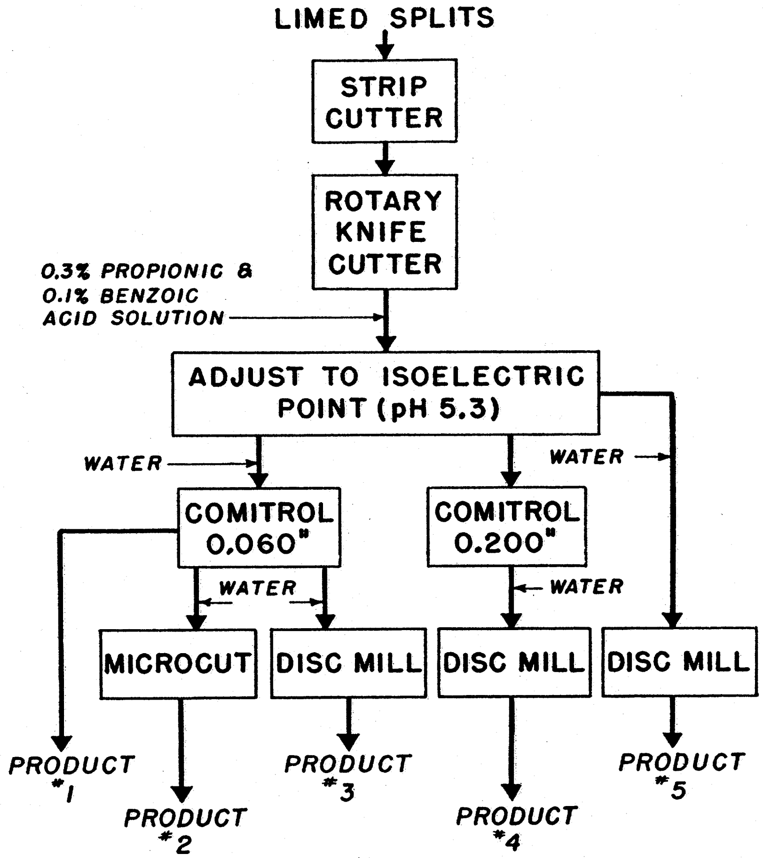


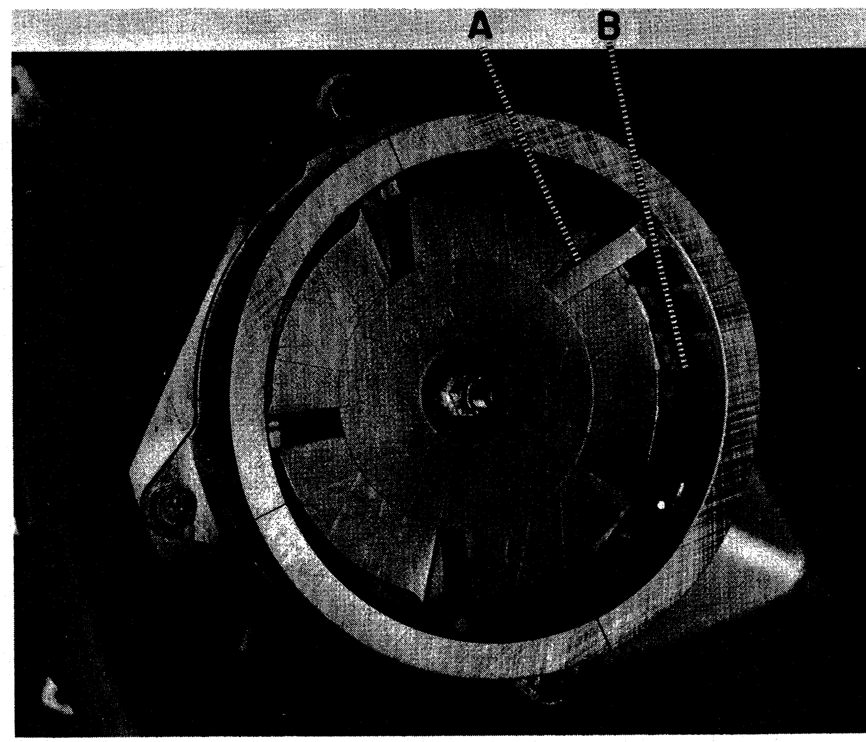
FIGURE 1.—Flow diagram for the comminution of unhaired, fleshed cattlehide.

hides are spread on a moving belt, then picked up by a pair of positive feed rolls which force them in the path of a horizontal cutterhead with four fly knives. These knives cut the hide into strips ⅜ inch wide as they pass with a close clearance down and across a bed knife's opposing cutting edge.

The strips are conveyed to a rotary knife cutter (Model 910, Style No. 5X10 GRAN, ten HP motor, Arthur G. McKee and Company, Riegelsville, New Jersey), which is similar in construction to the strip cutter with respect to the stationary bed knife and the fly knives. The rotor is horizontal and is positioned inside a cylindrical chamber. Hide strips enter this chamber from above and are cut into small thin pieces which emerge at the bottom through a screen having round openings one inch in diameter. The hide pieces are collected in a hopper placed underneath the cutter.

Acidifying. This step is carried out in suitable stainless steel mixing tanks or 55 gallon stainless steel tumbling drums. The hide pieces are contacted with three parts of water containing 0.3 percent propionic acid and 0.10 percent benzoic acid. Equilibrium is established after about four hours, at which time the solution pH approaches 5.3. The water is then separated by pouring the slurry into a three-mesh screen tray and draining for about one half hour.

Grinding. Two types of grinders are used to produce five products differing in particle size and structure. One of the machines is the Urschel "Comitrol," which is manufactured by Urschel Laboratories, Inc., Valparaiso, Indiana, and the other is a disc mill, which is made by the Young Machinery Sales Company, Inc., Muncy, Pennsylvania. The Urschel Comitrol is a centrifugally acting cutter-grinder consisting essentially of a rotating impeller (A) which is positioned inside a stationary cutting head (B) and is driven by a 30 HP, 3550 r.p.m. motor (Figure 2). In addition, it includes a nonremovable cutting chamber, 13 inches in diameter, as well as adapters and piping for force-feeding the hide pieces into the cutting head. In operation the hide pieces are fed into the path of the impeller which rotates at a speed of 5635 r.p.m. and throws the pieces by centrifugal force against the stationary head, where comminution occurs by cutting and impact. When sufficiently comminuted, the hide particles discharge



through small slots in the stationary head. Heads of different design and size that permit different degrees of comminution can be acquired for the Comitrol. In our work we use two inch high cutting heads with 0.2 inch and 0.06 inch particle exit slots, and a microcut head containing 100 closely spaced vertical stellite blades, 0.156 inch thick.

The other machine used is a disc mill (Figure 3) consisting of two abrasive, circular, segmented plates, one of which (E) is mounted on the rotating disc, the other (D) on the stationary disc. The feed material is ground as it is forced

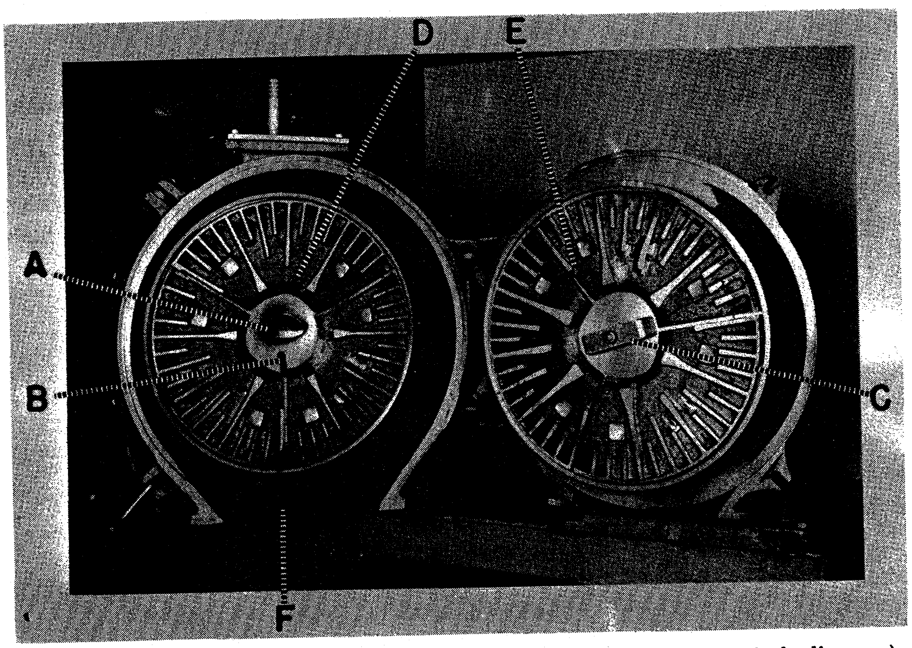
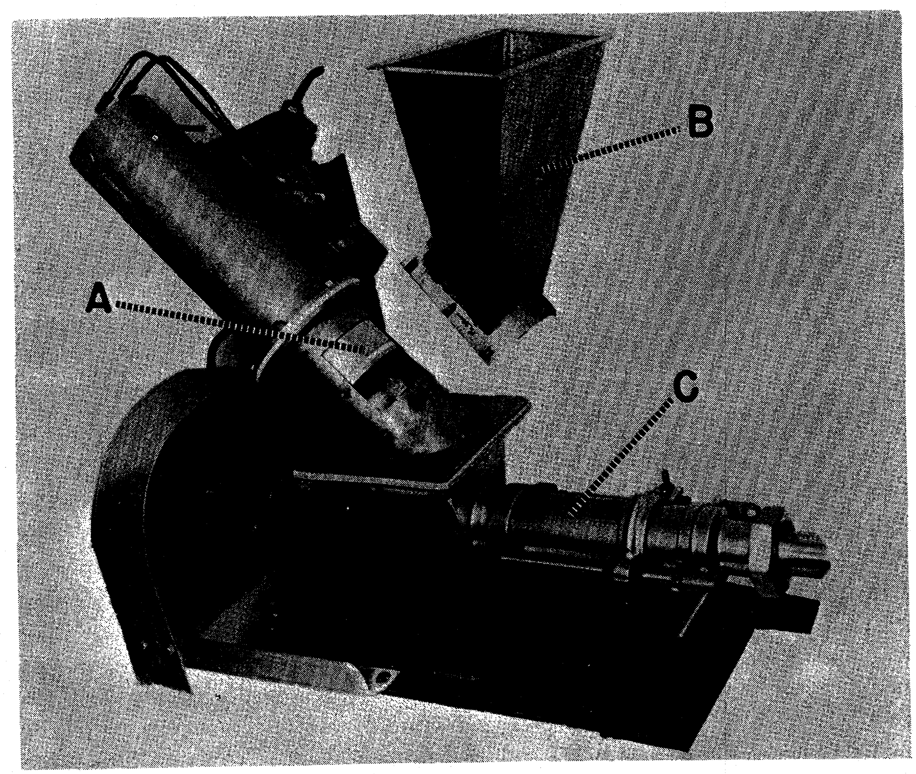


FIGURE 3.—Redesigned Disc Mill: (A) feed pipe for hide pieces (1 inch diameter); (B) water inlet (¼ inch diameter); (C) impeller-scraper; (D) stationary grinding plate; (E) rotating grinding plate; (F) product outlet.

to pass between the plates. The degree of comminution depends primarily on the distance between the plates at the periphery. Figure 3 shows an inner view of the mill with the discs separated. It is a redesigned Robinson 13 inch Junior Disc Grinder, provided with style CC grinding plates and driven at 3525 r.p.m. by a belt from a 7.5 horsepower, 1740 r.p.m. motor. To ensure a steady feeding rate and a uniform power consumption with minimum denaturation, it was necessary to block off the hopper in this mill with a stainless steel partition. This partition has a one inch hole (A) and a ¼ inch hole (B) through which hide pieces and water, respectively, are pumped directly through pipes into the center of the mill. To prevent accumulation of large lumps of hide in the remaining space at the center of the mill, a three inch impeller-scraper (C) is attached at the center of the rotating disc, which throws the hide by centrifugal force outward into the gap between the grinding plates as soon as it leaves the feed pipe.

Moyno pumps are used for force feeding the hide into the grinding machines. To feed the disc mill and the Urschel microcut head, which require lower capacities, a smaller Moyno pump (Robbins and Meyers, Springfield, Ohio, Type SSQ, Frame FJ6) is used. Even though this pump is of the "open throat" type and is provided with a hopper and a screw for conveying the hide pieces to the rotor-stator pumping elements, it does not pick up hide pieces satisfactorily. A smooth continuous operation is obtained with a specially designed plunger which is operated by air at constant pressure and pushes the hide pieces into the pump with a constant force. The plunger (A) and a separate hopper above it (B) are shown mounted on top of the Moyno pump (C) in Figure 4. For the 0.2 inch and 0.06 inch cutting heads of the Urschel Comitrol, a larger Moyno pump (Type SSQ, Frame FJS10H) provides the required pumping capacity. This pump has a bridge breaker instead of a plunger. Lacking the continuous pushing action that a plunger provides, this pump does not yield a metered, uniform flow



and discharges the hide pieces in large slugs. Its operation should be improved by using a plunger-feeder like the one used on the smaller Moyno pump.

Various amounts of water are fed into the Comitrol and the disc mill along with the hide to provide cooling and lubrication in the manufacture of different products. Moyno pumps pick up water preferentially when fed a slurry of hide and water. To ensure a definite water-to-hide weight ratio during grinding, water is, therefore, introduced into the grinding equipment by means of a separate pump. The water is combined with the hide in a T positioned just before both water and hide enter the Comitrol. As described above, mixing in the disc mill occurs at the center between the two discs.

Using different grinding procedures, five different products are obtained. As illustrated in the flow diagram given in Figure 1, Product #1 is made by passing the material, which is precut in the rotary knife cutter, through the 0.06 inch cutting head of the Comitrol. Further grinding of Product #1 in the microcut head of the Comitrol yields Product #2, while shearing of Product #1 in the disc mill gives Product #3. To obtain longer fibers, the rotary knife material is cut in the Comitrol 0.2 inch cutting head before it is sheared in the disc mill. This operation gives Product #4. The fifth product is made by omitting the Urschel Comitrol and feeding the rotary knife product directly into the disc mill. During all operations the gap between the grinding plates at the periphery is 0.012 inch wide.

Optimum Operating Conditions

The optimal conditions for comminuting hide are those that yield products with the lowest gelatin and water content. Such products would have the widest range of application and could be stored and transported most economically.

Experiments were conducted for each of the five products described above in which the water-to-hide weight ratio during comminuting was progressively reduced until a sharp product temperature increase was observed, which was accompanied by visible physical changes in the product and a sudden large increase in power consumption. These experiments helped to determine for each product the lowest water-to-hide weight ratio at which smooth, prolonged operation is possible. These operating conditions are considered to be optimal since little denaturation was observed at higher water-to-hide weight ratios, while excessive denaturation occurred at slightly lower water-to-hide weight ratios.

Table I summarizes the gelatin content, the moisture content, the energy consumed per pound of product (moisture-free basis, MFB), and the product rate for the five products when they were manufactured at the optimum operating conditions.

The energy consumption was determined by means of an alternating current wattmeter (Esterline-Angus Model AW) which automatically plots curves of power output *vs.* time. These curves were integrated with the help of a plani-

TABLE I

RESULTS AT OPTIMUM OPERATING CONDITIONS

Product No.	Type of Operation[a]	Equipment Used	Lb. Water per Lb. Wet Hide[b]	% Gelatin, MFB[c]	Energy Utilized, Kw.-Hr. per Lb. Product (MFB)[d]	Product Rate, Lb. Product (MFB) Per Hr.
	A	Strip Cutter	0:1		0.0005	5268
	A → B	Rotary Knife	0:1	0.72	0.007	1420
1	B → C	Comitrol, 0.06 inch	0.1:1	2.38	0.029	576
2	C → D	Comitrol, Micro cut	0.5:1	3.06	0.044	388
3	C → E	Disc Mill	0.3:1	2.79	.04	118
4	B → F	Comitrol, 0.2 inch	0.0:1	1.17	.011	1005
	F → G	Disc Mill	0.4:1	3.45	.06	69
5	B → H	Disc Mill	0.8:1	5.91	0.09	40

[a]A → B = product from operation A used in operation B.
B → C = product from operation B used in operation C, etc.

[b]The typical moisture content of the raw material was about 76 percent; and 78.2 percent, 85.5 percent, 83.2 percent, 82.9 percent, and 86.7 percent in Products #1 to 5, respectively.

[c]MFB — moisture-free basis.

[d]The power consumption in kilowatts may be readily obtained by multiplying the values of the last two columns.

meter; and the values of the integrals were divided by the total time to obtain the power consumption, and by the average product rate to obtain the energy consumption per pound of product. The experimental data were determined in most cases at or very close to the rated capacity of the motors used on the comminuting equipment, *i.e.,* at conditions of maximum efficiency of the motors.

Chemical Analyses

Moisture Content. Moisture analyses were performed by dehydrating ten g. samples of product under vacuum for approximately 16 hours at 70°C. Samples containing large amounts of water were pre-dried on a steam bath before they were vacuum dried.

Gelatin Content. This method for determining gelatin was recommended by Dr. M. A. Cohly (5).

Preparation of Reagents:

1. Sodium salicylate (3.0 M). Weigh 480.33 g. sodium salicylate, U.S.P. small crystals, Mallinckrodt, into one liter volumetric flask. Make up to mark.

2. Biuret Reagent (3):

   a. Sodium hydroxide (four percent). Dissolve 24 g. reagent grade NaOH in water and bring volume to 40 ml.

   b. Copper sulfate (2.6 percent). Dissolve 2.0 g. $CuSO_4 \cdot 5\ H_2O$ in 50 ml. H_2O.

   c. Ethylene glycol, 100 ml.

Combine reagent (*a*), (*b*) and (*c*). Heat to dissolve salts, cool, and make up to 400 ml. with distilled water.

3. Gelatin, U.S.P. grade.

Procedure: Prepare standard solutions ranging from 1.0 to 12.0 mg. gelatin per ml. Run biuret reactions (6) on these standards and measure absorbance at 550 nm using one cm. cells. Weigh out a collagen sample containing 500 mg. of solids into a 125 ml. glass-stoppered Erlenmeyer flask. Chill the sample immediately in an ice bath. Add 17.0 ml. of 3 M sodium salicylate as well as sufficient water to bring the final water content in the flask to 50 ml. (The water to be added is calculated by considering the moisture content of the collagen sample.) Extract the mixture for two hours while keeping the flask submerged in an ice bath (0–4°C.) and shaking it, using a wrist action shaker. Filter contents of flask through a Whatman filter paper (2V). Finally, determine gelatin content in filtrate by the biuret reaction. Report gelatin content in sample on moisture-free basis.

RESULTS AND DISCUSSION

Limed cattlehide, as received from the tannery, has a high pH (approximately 12.5) and is bacteriologically clean. It has been stored at refrigerator temperature for over a month with little change in percent denaturation and an insignificant increase in bacteria count. It has been also successfully ground through the 0.06 inch head of the Comitrol with little denaturation to yield Product #1. However, manufacture of the other four products using alkaline hide involves a greater danger of denaturation unless excessive amounts of water are used during grinding. Alkaline products would also have disadvantages: in most applications they could not be used directly without acidification because of the high pH and the presence of sulfide. Consequently, an acidification step is included in our work. To limit bacterial growth, acidification is postponed, however, until the hide has been passed through the rotary knife cutter. Since in our work all operations are conducted at room temperature, and since there is an additional increase in temperature during grinding, it has been found necessary to quickly freeze the product.

In commercial practice, however, it is felt that temperatures below 70°F. should be used for acidification, while draining and all subsequent steps should be conducted inside a facility kept at refrigerator temperature. Also, very cold water should be mixed with the hide pieces during grinding, and the product should be cooled down to refrigerator temperature as quickly as possible if it is to be used within a few days, or frozen if it is expected to be stored for an extended period of time.

In this work propionic acid was used for acidifying the $Ca(OH)_2$ of the limed hide. It was chosen because it has a pK_a value of 4.87 and, therefore, acts as a buffer close to the isoelectric point of limed hide (pH — 5.3). However, acetic acid has a pK_a value only slightly lower (4.73) and could have been used with equal success. Both of these acids are also useful in decalcifying hide since their calcium salts are soluble in water. They cost about the same and exert a pronounced preservative action. A small amount of benzoic acid is recommended in conjunction with either of the above acids because it is a better preservative.

Five different processing procedures were studied which yield five different products varying in particle size and fiber length. All these products can actually be divided into two types as a result of the difference in the action, or mechanism of comminution, of the two machines used in the final stage. This difference between the two types of products can readily be demonstrated visually by shaking small amounts of each in large quantities of water. The particles then separate and each one fluffs up, revealing the fact that the Urschel Comitrol products consist mostly of granules whose original fiber structure is still intact, whereas the disc mill products have been shredded and look like fluffy balls of knitting yarn composed of many thin threads which still have retained some points of attachment. The difference in the extent of comminution of the products is shown in the photomicrographs of Figure 5. To obtain these pictures, each product was dispersed in a large amount of water, frozen, and then freeze-dried. An arbitrary, but representative, mass or clump of the dry product was pulled out without disturbing the matrix and evaluated by scanning electron microscopy. Product #1 is shown as a relatively large particle or nodule, composed of densely matted fibers. Product #2 is composed of smaller particles than Product #1, but this is not readily evident from the photomicrograph because Product #2 is somewhat less dense and therefore occupies more area. In contrast, Product #3 consists of fiber bundles that are well separated by the shearing action of the disc mill. And in Products #4 and #5, the fiber bundles, which are much shorter, are quite "airy," having been sheared into individual fibers.

As shown in Table I, no denaturation is observed in the Taylor-Stiles strip cutter. Also, very little gelatin formation occurs in the rotary knife cutter even when no water is added during cutting. Subsequent grinding in the 0.2 inch head of the Urschel Comitrol does not require water addition either, as there is also very little denaturation. In all the other comminution steps some water has to be added to prevent excessive denaturation. Table I gives the recommended water-to-hide weight ratios which are found to be optimal for smooth, prolonged operation. No decrease in denaturation is observed at higher water-to-hide weight

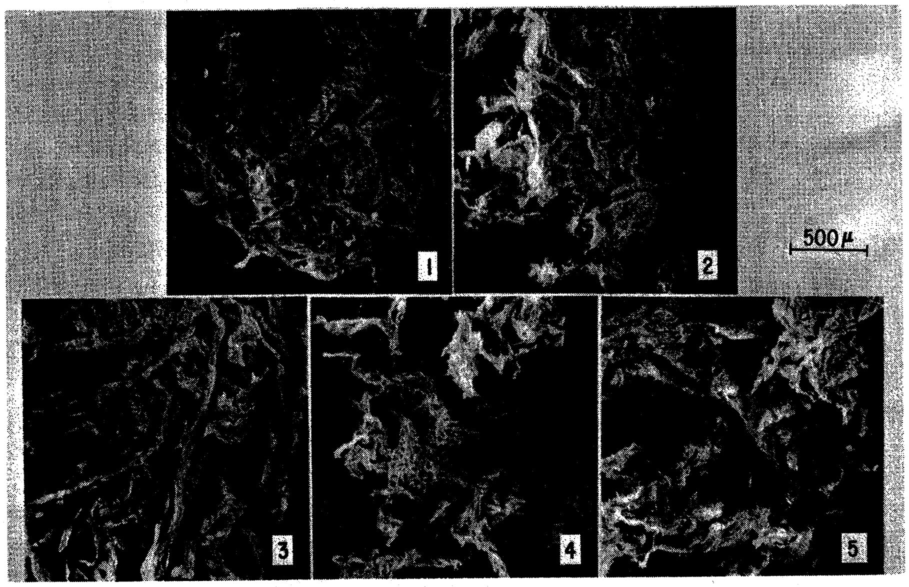


FIGURE 5.—Photomicrographs of Products #1 to 5: Product #1, made by grinding rotary knife product through 0.06 inch head of Urschel Comitrol; Product #2, ground through rotary knife plus 0.06 inch Comitrol plus microcut Comitrol; Product #3, ground through rotary knife plus 0.06 inch Comitrol plus disc mill; Product #4, ground through rotary knife plus 0.20 inch Comitrol plus disc mill; Product #5, ground through rotary knife plus disc mill.

ratios, while lower water-to-hide weight ratios eventually result in a sudden increase in temperature which, in turn, induces denaturation and a concomitant change in color and appearance of the product. This denaturation is accompanied by a drastic increase in power consumption, which overloads the electrical circuits.

As can be seen from Table I, a water-to-hide weight ratio of 0.1:1 is optimal for making Product #1, which involves grinding the rotary knife material through the 0.06 inch cutting head of the Comitrol. This product contains about 2.4 ± 0.8 percent gelatin. Product #2, which is made by passing Product #1 through the microcut head of the Comitrol, requires much more water (a water-to-hide weight ratio of 0.5:1). Its gelatin content is about 3.1 ± 0.9. The amount of water used has to be increased as progressively larger particles are ground in the disc mill. Thus, the optimum water-to-hide weight ratios for the manufacture of Products #3, 4, and 5 are approximtely 0.3:1, 0.4:1, and 0.8:1, respectively. As mentioned above, the mechanism by which size reduction is accomplished with the Urschel Comitrol and the disc mill is different. The Urschel Comitrol, when provided with cutting heads, more or less cuts the feed into small particles, whereas the disc mill shears it. The latter action causes more heat evolution; consequently, the Urschel Comitrol yields products which are lower in gelatin content than those obtained in the disc mill. At a constant gap width, denaturation in the disc mill seems to be a function of the particle size fed to it. Among the disc mill products, the lowest gelatin contents are found in Product #3 (2.8 ± 1.8 percent gelatin) and Product #4 (3.45 ± 0.90 percent gelatin) which are made by passing the 0.06 inch Urschel Comitrol product (Product #1) and the 0.2 inch Urschel Comitrol product, respectively, through the disc mill. The highest gelatin content (5.9 ± 1.9 percent) is found in Product #5, in which the rotary knife material is fed directly to the mill.

From the energy consumption data given in Table I, it is apparent that grinding in the Urschel Comitrol requires less energy than in the disc mill. The energy consumption in the 0.06 inch head of the Urschel Comitrol is 0.029 kw. hour per pound dry solids when rotary knife product is fed to it during the manufacture of Product #1. Passage of this product through the microcut head to obtain Product #2 requires an additional 0.044 kw. hour per pound solids and 0.04 kw. hour per pound solids additional to make Product #3 in the disc mill. The energy requirements increase to 0.06 and 0.09 kw. hour per pound dry hide solids when progressively larger particles are fed to the disc mill in the manufacture of Products #4 and 5, respectively. Including all comminution steps, the total energy consumption for Products #1, 2, 3, 4, and 5 is 0.0365, 0.0805, 0.0765, 0.0785, and 0.0975 kw. hour per pound dry hide, respectively.

Attempts have been made to compare the different products by using their particle size distributions. All methods for measuring particle size have failed, however, because of the fibrous nature and unusual shape of the particles.

The exact cost for making each of the five products has not yet been determined. Cost estimates will be published as soon as they become available. It would seem logical to assume that the product costs would increase proportionately with increase in the energy required. However, this type of reasoning is complicated by the fact that some products are ground in one stage using one machine, while others require a two-stage operation using two different grinders. Preliminary cost calculations show that the grinding costs would be equal to only a fraction of the raw material cost.

The uses of collagen are so diverse and depend on so many factors that it is recommended that each of the products be tested to select the one best suited for any particular application. Considering the fact that Products #1 and 3 have the lowest gelatin content and represent the two main types of product obtained in this work, it is expected that they will find the widest application.

Certain shortcomings in the equipment selection for this process have become apparent during operation. These shortcomings should be corrected in commercial application of the process.

Being one foot wide, the strip cutter used can be fed hide strips only of that width. The data reported in Table I have been obtained using four thicknesses of ten inch wide strips of hide. A wider strip cutter is recommended for commercial practice since folding of whole sides in several layers is time-consuming and tends to damage the drive belts. Bridging in the feed hopper of the rotary knife cutter was encountered during operation. A bridge breaker is, therefore, recommended for feeding this machine. As mentioned previously, the inlet provisions of the Robinson "Junior Disc" attrition mill were not suited for feeding hide pieces. They had to be redesigned to permit pumping the hide through the mill under pressure at a more uniform rate. Also, the five HP motor on the attrition mill proved to be too small. It is constantly being overloaded when large hide particles are fed into it during the manufacture of Product #5. It appears that most of the shortcomings of the "Junior Disc" may be readily overcome by using a mill similar to the Robinson single runner "Attritor," which is pressure fed and furnished with a 30 HP motor. For smoother operation, an impeller-scraper similar to the one used in the "Junior Disc" may have to be attached at the center of the rotating disc of the "Attritor."

Samples of the products described above can be obtained by contacting the authors.

ACKNOWLEDGMENT

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Procedure: Prepare standard solutions ranging from 1.0 to 12.0 mg. gelatin per ml. Run biuret reactions (6) on these standards and measure absorbance at 550 nm using one cm. cells. Weigh out a collagen sample containing 500 mg. of solids into a 125 ml. glass-stoppered Erlenmeyer flask. Chill the sample immediately in an ice bath. Add 17.0 ml. of 3 M sodium salicylate as well as sufficient water to bring the final water content in the flask to 50 ml. (The water to be added is calculated by considering the moisture content of the collagen sample.) Extract the mixture for two hours while keeping the flask submerged in an ice bath (0–4°C.) and shaking it, using a wrist action shaker. Filter contents of flask through a Whatman filter paper (2V). Finally, determine gelatin content in filtrate by the biuret reaction. Report gelatin content in sample on moisture-free basis.

RESULTS AND DISCUSSION

Limed cattlehide, as received from the tannery, has a high pH (approximately 12.5) and is bacteriologically clean. It has been stored at refrigerator temperature for over a month with little change in percent denaturation and an insignificant increase in bacteria count. It has been also successfully ground through the 0.06 inch head of the Comitrol with little denaturation to yield Product #1. However, manufacture of the other four products using alkaline hide involves a greater danger of denaturation unless excessive amounts of water are used during grinding. Alkaline products would also have disadvantages: in most applications they could not be used directly without acidification because of the high pH and the presence of sulfide. Consequently, an acidification step is included in our work. To limit bacterial growth, acidification is postponed, however, until the hide has been passed through the rotary knife cutter. Since in our work all operations are conducted at room temperature, and since there is an additional increase in temperature during grinding, it has been found necessary to quickly freeze the product.

In commercial practice, however, it is felt that temperatures below 70°F. should be used for acidification, while draining and all subsequent steps should be conducted inside a facility kept at refrigerator temperature. Also, very cold water should be mixed with the hide pieces during grinding, and the product should be cooled down to refrigerator temperature as quickly as possible if it is to be used within a few days, or frozen if it is expected to be stored for an extended period of time.

In this work propionic acid was used for acidifying the $Ca(OH)_2$ of the limed hide. It was chosen because it has a pK_a value of 4.87 and, therefore, acts as a buffer close to the isoelectric point of limed hide (pH — 5.3). However, acetic acid has a pK_a value only slightly lower (4.73) and could have been used with equal success. Both of these acids are also useful in decalcifying hide since their calcium salts are soluble in water. They cost about the same and exert a pronounced preservative action. A small amount of benzoic acid is recommended in conjunction with either of the above acids because it is a better preservative.

Five different processing procedures were studied which yield five different products varying in particle size and fiber length. All these products can actually be divided into two types as a result of the difference in the action, or mechanism of comminution, of the two machines used in the final stage. This difference between the two types of products can readily be demonstrated visually by shaking small amounts of each in large quantities of water. The particles then separate and each one fluffs up, revealing the fact that the Urschel Comitrol products consist mostly of granules whose original fiber structure is still intact, whereas the disc mill products have been shredded and look like fluffy balls of knitting yarn composed of many thin threads which still have retained some points of attachment. The difference in the extent of comminution of the products is shown in the photomicrographs of Figure 5. To obtain these pictures, each product was dispersed in a large amount of water, frozen, and then freeze-dried. An arbitrary, but representative, mass or clump of the dry product was pulled out without disturbing the matrix and evaluated by scanning electron microscopy. Product #1 is shown as a relatively large particle or nodule, composed of densely matted fibers. Product #2 is composed of smaller particles than Product #1, but this is not readily evident from the photomicrograph because Product #2 is somewhat less dense and therefore occupies more area. In contrast, Product #3 consists of fiber bundles that are well separated by the shearing action of the disc mill. And in Products #4 and #5, the fiber bundles, which are much shorter, are quite "airy," having been sheared into individual fibers.

As shown in Table I, no denaturation is observed in the Taylor-Stiles strip cutter. Also, very little gelatin formation occurs in the rotary knife cutter even when no water is added during cutting. Subsequent grinding in the 0.2 inch head of the Urschel Comitrol does not require water addition either, as there is also very little denaturation. In all the other comminution steps some water has to be added to prevent excessive denaturation. Table I gives the recommended water-to-hide weight ratios which are found to be optimal for smooth, prolonged operation. No decrease in denaturation is observed at higher water-to-hide weight

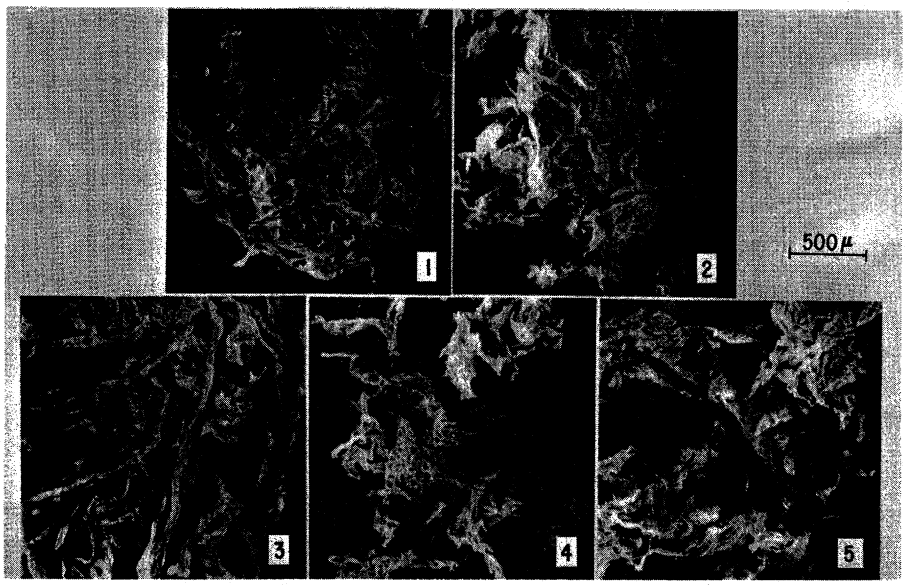

FIGURE 5.—Photomicrographs of Products #1 to 5: Product #1, made by grinding rotary knife product through 0.06 inch head of Urschel Comitrol; Product #2, ground through rotary knife plus 0.06 inch Comitrol plus microcut Comitrol; Product #3, ground through rotary knife plus 0.06 inch Comitrol plus disc mill; Product #4, ground through rotary knife plus 0.20 inch Comitrol plus disc mill; Product #5, ground through rotary knife plus disc mill.

ratios, while lower water-to-hide weight ratios eventually result in a sudden increase in temperature which, in turn, induces denaturation and a concomitant change in color and appearance of the product. This denaturation is accompanied by a drastic increase in power consumption, which overloads the electrical circuits.

As can be seen from Table I, a water-to-hide weight ratio of 0.1:1 is optimal for making Product #1, which involves grinding the rotary knife material through the 0.06 inch cutting head of the Comitrol. This product contains about 2.4 ± 0.8 percent gelatin. Product #2, which is made by passing Product #1 through the microcut head of the Comitrol, requires much more water (a water-to-hide weight ratio of 0.5:1). Its gelatin content is about 3.1 ± 0.9. The amount of water used has to be increased as progressively larger particles are ground in the disc mill. Thus, the optimum water-to-hide weight ratios for the manufacture of Products #3, 4, and 5 are approximtely 0.3:1, 0.4:1, and 0.8:1, respectively. As mentioned above, the mechanism by which size reduction is accomplished with the Urschel Comitrol and the disc mill is different. The Urschel Comitrol, when provided with cutting heads, more or less cuts the feed into small particles, whereas the disc mill shears it. The latter action causes more heat evolution; consequently, the Urschel Comitrol yields products which are lower in gelatin content than those obtained in the disc mill. At a constant gap width, denaturation in the disc mill seems to be a function of the particle size fed to it. Among the disc mill products, the lowest gelatin contents are found in Product #3 (2.8 ± 1.8 percent gelatin) and Product #4 (3.45 ± 0.90 percent gelatin) which are made by passing the 0.06 inch Urschel Comitrol product (Product #1) and the 0.2 inch Urschel Comitrol product, respectively, through the disc mill. The highest gelatin content (5.9 ± 1.9 percent) is found in Product #5, in which the rotary knife material is fed directly to the mill.

From the energy consumption data given in Table I, it is apparent that grinding in the Urschel Comitrol requires less energy than in the disc mill. The energy consumption in the 0.06 inch head of the Urschel Comitrol is 0.029 kw. hour per pound dry solids when rotary knife product is fed to it during the manufacture of Product #1. Passage of this product through the microcut head to obtain Product #2 requires an additional 0.044 kw. hour per pound solids and 0.04 kw. hour per pound solids additional to make Product #3 in the disc mill. The energy requirements increase to 0.06 and 0.09 kw. hour per pound dry hide solids when progressively larger particles are fed to the disc mill in the manufacture of Products #4 and 5, respectively. Including all comminution steps, the total energy consumption for Products #1, 2, 3, 4, and 5 is 0.0365, 0.0805, 0.0765, 0.0785, and 0.0975 kw. hour per pound dry hide, respectively.

Attempts have been made to compare the different products by using their particle size distributions. All methods for measuring particle size have failed, however, because of the fibrous nature and unusual shape of the particles.

The exact cost for making each of the five products has not yet been determined. Cost estimates will be published as soon as they become available. It would seem logical to assume that the product costs would increase proportionately with increase in the energy required. However, this type of reasoning is complicated by the fact that some products are ground in one stage using one machine, while others require a two-stage operation using two different grinders. Preliminary cost calculations show that the grinding costs would be equal to only a fraction of the raw material cost.

The uses of collagen are so diverse and depend on so many factors that it is recommended that each of the products be tested to select the one best suited for any particular application. Considering the fact that Products #1 and 3 have the lowest gelatin content and represent the two main types of product obtained in this work, it is expected that they will find the widest application.

Certain shortcomings in the equipment selection for this process have become apparent during operation. These shortcomings should be corrected in commercial application of the process.

Being one foot wide, the strip cutter used can be fed hide strips only of that width. The data reported in Table I have been obtained using four thicknesses of ten inch wide strips of hide. A wider strip cutter is recommended for commercial practice since folding of whole sides in several layers is time-consuming and tends to damage the drive belts. Bridging in the feed hopper of the rotary knife cutter was encountered during operation. A bridge breaker is, therefore, recommended for feeding this machine. As mentioned previously, the inlet provisions of the Robinson "Junior Disc" attrition mill were not suited for feeding hide pieces. They had to be redesigned to permit pumping the hide through the mill under pressure at a more uniform rate. Also, the five HP motor on the attrition mill proved to be too small. It is constantly being overloaded when large hide particles are fed into it during the manufacture of Product #5. It appears that most of the shortcomings of the "Junior Disc" may be readily overcome by using a mill similar to the Robinson single runner "Attritor," which is pressure fed and furnished with a 30 HP motor. For smoother operation, an impeller-scraper similar to the one used in the "Junior Disc" may have to be attached at the center of the rotating disc of the "Attritor."

Samples of the products described above can be obtained by contacting the authors.

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