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METHOD OF EXTRACTING ANIMAL GLUE

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This invention relates to a method of extracting animal glue, which can be employed most advantageously for extracting hide glue from cattle hide glue stock.

It is the practice to extract animal glue with hot water from conditioned and swollen collagen-bearing tissue, such as hide trimmings, etc. The conditioning and swelling of the glue stock in conventional operations is produced by first soaking the hide trimmings in saturated lime solutions and then washing out the excess lime. The hide trimmings are then neutralized with acid and the hot aqueous extraction is carried out at approximately a neutral pH, that is, both the solid pieces of tissue and the water bath are maintained at a pH of around 7.0. Usually, the conditioned and swollen hide trimmings are subjected to a series of extractions, often referred to as "cooks," to obtain glues of decreasing quality in regard to yell strength and viscosity.

The above procedure is followed because of the difficulty of extracting glue while maintaining a sufficiently high pH strength and correspondingly high viscosity in the product. The extraction under neutral pH conditions has been believed essential to accomplish the desired result, although it was known that a more rapid and complete extraction could be obtained under acid conditions. However, under acid conditions, say for example at pHs below 6.5, the extracted glue rapidly decreases in viscosity and becomes more and more unsuitable as a glue. In other words, it becomes more like gelatin which, although almost chemically identical to glue, has such a low viscosity compared to its yield strength that it is regarded by the trade to be undesirable for adhesive purposes.

Another difficulty arises if it is desired to subject the glue stock to an acid-treating step to condition or swell the glue stock, or for other purposes. Acid-treating of glue stock such as hide trimmings is highly desirable to produce maximum swelling of the glue stock. Also, an acid treatment of lime-swelled hide trimmings is virtually mandatory to remove insoluble calcium salts from the tissues. In either case, the glue stock may be at an acid pH after the acid treatment which would not be thought to be extractable for the extraction of the glue. Therefore, it would usually be felt desirable to neutralize the glue stock by washing the stock for a considerable length of time to bring it back to a neutral pH. However, if the glue could be satisfactorily extracted from the stock at an acidic pH, such long and costly washing steps could be eliminated.

It is a general object of this invention to provide a method for extracting animal glue from collagen-bearing material under acid conditions without at the same time impairing the viscosity of the extracted glue. A further specific object of this invention is to provide a method for extracting animal glue which permits the manufacturer to go directly from an acid swelling step to an extraction step without the intervening steps of neutralizing the tissue solids. Further objects and advantages will appear as the specification proceeds.

This invention is based in part on the discovery that porous pieces of collagen-bearing material, such as hide trimmings, can be maintained at an acidic pH interiorly during the extraction of glue therefrom, while at the same time maintaining the surrounding water at an approximately neutral pH, and that in this way the objects set out above can be substantially accomplished. The preferred practical embodiment of this discovery will now be discussed in detail.

The starting material for use in the process of this invention can be any collagen-bearing animal tissue, although the process is best adapted for use with hide glue stock, and especially cattle hide glue stock. The two main types of cattle hide glue stock are (a) trimmings from salt-cured cattle hides and (b) fresh cattle hide glue stock, such as the "ears" and "lips."

The collagen-bearing tissue can be conditioned according to standard practice by soaking in a saturated lime solution for 60 to 120 days, depending on the temperature conditions. Alternatively, it can be conditioned by the enzymatic action of yeast, particularly Mycoderma and Torulopsis, as described in detail in our co-pending application, United States Serial No. 339,165, filed February 26, 1953, for Method of Preparing Animal Glue.

The completely or partially conditioned glue stock can then be treated in an acid bath, for example, in water at a pH below 6.5, and preferably at a pH from 1.5 to 6.0. In the commercial practice, the limed hides are generally treated with water at a pH of around 5.0 to 6.0, although in connection with the extraction method of this invention it probably would be desirable to employ somewhat lower pHs in this step. In applicants' co-pending application, cited above, the microorganism-conditioned hides are soaked in water at a pH from 1.5 to 3.5 to swell the hides. As indicated therein, pHs of from 2 to 2.5 are preferred, since the swelling has been found to be at a maximum of around 2.3. In the acid-treating or swelling step, various acids can be employed, but hydrochloric acid is preferred. Instead of hydrochloric acid other acids can be employed, such as nitric acid, sulfuric acid, acetic acid, phosphoric acid, etc.

The acidulated glue stock can then be directly extracted without neutralization by the method of this invention. However, it is desirable to separate the tissue from the acid-treating liquid. This can readily be done by draining off the liquid. The tissue thus obtained will be at the acid pH employed in the swelling treatment. These solid pieces of tissue are then ground with water containing an insoluble base such as calcium carbonate. Any insoluble base which will react with the acid contained within the tissue solids can be employed. However, the alkaline earth metal carbonates, and particularly calcium carbonate, have been found to give best results. Insoluble basic metallic oxides, such as alumina, can also be used advantageously. In addition, acid binding materials commonly known as "ion exchangers" may also be useful for acid removal.

It is preferred to employ the insoluble base in a pulverized or finely-divided condition so that it can be distributed throughout the extraction bath. It is also desirable to employ an excess of the insoluble base, that is, it is desired to use more base than is required to neutralize the acid which is extracted with the glue. If the glue stock is to be subjected to a series of cooks, it will usually be necessary to employ an excess insoluble base in the first cook than in the succeeding cooks, since more acid will be extracted in the first cook. There is no particular disadvantage to using a considerable excess of the insoluble base, since it has been found that it can readily be separated from the glue liquor by decantation after settling or by centrifugation or filtration.

During the extraction, the glue is extracted under the
acid conditions within the solid pieces of tissue, but as soon as the acid diffuses out of the tissue it is neutralized by reacting with the insoluble base, thus maintaining non-acidic pH conditions for the extracted glue and thereby preventing its viscosity from being impaired. In the process, the extracted glue acts as a dispersant for the particles of insoluble base, and therefore these particles will be well distributed throughout the bath and readily available for neutralization of the extracted acid. When an insoluble carbonate is used, as preferred, the carbon dioxide evolved in the neutralization serves the further purpose of agitating the mixture. Apparently the insoluble base particles do not appreciably enter the tissue, since the interior of the pieces of glue stock can be maintained at acid pH’s for a series of cooks in the presence of an insoluble base.

In the glue extraction step, conventional temperatures can be employed, that is, temperatures ranging from 65 to 100°C. By way of specific example, the glue stock might be extracted for four times by covering it with water having the insoluble base therein, and subjecting it to a series of 3-hour cooking periods at 65°, 75°, 85°, and 100°C. The glue liquor obtained in this manner can then be separated from any excess of insoluble base by centrifugation or filtration. As an alternative to the above procedure, the insoluble base can be maintained in a separate chamber from the glue stock solids, and the water continually circulated from the extraction chamber through a neutralizing chamber and back to the extraction chamber. In other words, in its broader aspect, this invention contemplates the use of an insoluble base to keep the extracting water at a neutral pH while the collagen-bearing solids are maintained internally at an acidic pH. For example, the glue can be extracted by pumping hot water over hide trimmings in an extraction chamber, and continually circulating water from the extraction chamber through a neutralizing chamber packed with calcium carbonate. In this way, substantially the same result can be obtained, although the first described procedure will be best adapted to the present methods of preparing animal glue. This invention is illustrated by the following specific examples.

EXAMPLE I

Salt-cured cattle hide trimmings were conditioned with yeasts as described in Example IV of copending application United States Serial No. 339,166, cited above. The yeast-conditioned trimmings were then soaked in hydrochloric acid solution at pH 2.0 for 4 days. The trimmings apparently reached the point of maximum swelling at the end of the 4-day period. The trimmings were then washed to remove loose hair. The washed hides were stored in hydrochloric acid solution at pH 2.0.

In the extraction, a schedule of four 3-hour cooks was employed and calcium carbonate in decreasing quantities was added to each of the first three cooks. Cooking temperatures were 65°, 75°, 85°, and boiling. For a 10# batch of hide pieces, 45 g. of calcium carbonate was added in the first cook, 30 g. in the second cook, and 15 g. in the third cook. Hide pieces and calcium carbonate were placed in a pot and the temperature was quickly elevated by addition of sufficient water at the desired cooking temperature to cover the hide pieces. The cooking pot was maintained at cook temperature by external heating for a 3-hour period. At the completion of the cook, glue liquors were drained, preservative (Dowicide G) was added, the solution was centrifuged to remove excess calcium carbonate, concentrated under vacuum, jelled, and dried either in a wind or vacuum oven. A light-colored and pleasantly transparent dried glue was obtained. At the end of the fourth cook, the residue, which still appeared to contain some potential glue-forming material, was dried for weighing in the wind oven. In a series of replicate runs following the specific procedure set out above, the average yield of glue was around 20% on an as-received basis. The average jel strength of the glue was around 440 grams, and the average viscosity was 150 millidynes.

EXAMPLE II

The process was carried out as described in Example I, except that no insoluble base was directly introduced into the cooking vat. Instead, the glue liquor from the cooking vat was continuously pumped through a compressible loose-wool filter to remove fat and suspended particles. It was next passed through a column bath with alumina and returned to the cooking vat. This method was found to be satisfactory for the extraction of glue from acid glue stock without an impairment of the viscosity of extracted glue. The water within the cooking vat was maintained at a substantially non-acidic pH.

EXAMPLE III

A lot of fresh cow shanks was microorganism conditioned in the presence of sodiumsilicofluoride at pH 4.8-5.1 for 3 days at 35°C, followed by a hydrochloric acid treatment of 6 days at pH 2.0-2.5 and 20°C. The lot was equally divided into two parts and each portion tested with a different carbonate. The carbonates were added to each cook at a 5% level based on the weight of the stock.

In all of the experiments described in this example the stock was at pH 2.0 when cooking was started. Each individual cook was of three hours duration and the glue liquors were clarified by filtering. The liquors were dried in a wind oven at 160°F. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Carbonsate</th>
<th>Temp. in °C.</th>
<th>pH of Glue liquor</th>
<th>pH of glue</th>
<th>Viscosity</th>
<th>Jelly</th>
<th>Percent Yield on a dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2CO3...</td>
<td>85</td>
<td>6.9</td>
<td>8.4</td>
<td>184</td>
<td>657</td>
<td>70</td>
</tr>
<tr>
<td>BaCO3...</td>
<td>75</td>
<td>7.3</td>
<td>8.0</td>
<td>124</td>
<td>986</td>
<td>70</td>
</tr>
<tr>
<td>CaCO3...</td>
<td>100</td>
<td>7.2</td>
<td>7.1</td>
<td>78</td>
<td>275</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 1

EXAMPLE IV

Another run of fresh shanks was conditioned in the same manner as in Example III with one exception. The pH in the 35°C step was held at 4.0-4.5 by the periodic addition of small amounts of hydrochloric acid. In this experiment crushed limestone was employed as a source of calcium carbonate. Results are shown in Table 2.

<table>
<thead>
<tr>
<th>Temp. in °C.</th>
<th>pH of Glue liquor</th>
<th>pH of glue</th>
<th>Viscosity</th>
<th>Jelly</th>
<th>Percent Yield on a dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>4.4</td>
<td>6.3</td>
<td>265</td>
<td>332</td>
<td>80</td>
</tr>
<tr>
<td>75</td>
<td>5.1</td>
<td>6.5</td>
<td>66</td>
<td>86</td>
<td>70</td>
</tr>
<tr>
<td>100</td>
<td>7.5</td>
<td>6.5</td>
<td>85</td>
<td>235</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 2

EXAMPLE V

Fresh cattle hide trimmings without previous conditioning were acid treated in water at a pH of between 2.0 to 2.5 and at a temperature of 20°C. In a series of runs, glue was extracted after 3 days of acid treatment and in another series of runs, after 9 days of acid treatment. The stock was separated from the acid-treating bath and drained, and then cooked out in the presence of calcium carbonate. The results of these experiments are summarized below in Table 3.
Table 3

<table>
<thead>
<tr>
<th>Days in Acid at 20° C.</th>
<th>Temp. in ° C.</th>
<th>pH of Glue</th>
<th>Viscosity</th>
<th>Jelly</th>
<th>Percent Yield on a dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>65</td>
<td>7.4</td>
<td>64</td>
<td>501</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>7.9</td>
<td>107</td>
<td>469</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>7.1</td>
<td>68</td>
<td>125</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>7.2</td>
<td>141</td>
<td>404</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.4</td>
<td>110</td>
<td>260</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7.3</td>
<td>90</td>
<td>220</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE VI

Salted cattle hide scrap was washed until free of salt and then covered with water to which was added 5% of calcium hydroxide. When the stock had stood in the lime solution for about 30 days it was removed, rinsed and covered with fresh water. Sulfurous acid was added to neutralize the lime and to bring the hide up to a pH of 3.0. Two percent of calcium carbonate was added and the glue was extracted in the manner described in Example I.

While in the foregoing specification a number of specific embodiments of this invention have been set forth and various specific details have been given, it will be apparent to those skilled in the art that many of the specific embodiments and details can be varied widely without departing from the broad idea of the invention.

We claim:

1. The method of extracting animal glue from collagen-bearing animal tissues, characterized by the step of carrying out the extraction by contacting acidulated collagen-bearing animal tissues with hot water to extract the glue and also contacting said hot water with an insoluble base to maintain said water at a substantially non-acidic pH during said extraction, whereby the extraction is facilitated by the acidity of the tissues while the extracted glue is protected from acidic conditions which would impair its viscosity.

2. In a method for making glue from collagen-bearing animal tissues wherein said tissues are first conditioned to prepare them for the extraction of the glue, the step of extracting glue from said conditioned tissues with hot water containing a water-insoluble base while the interior portions of said tissues are at a substantially acidic pH whereby the extraction is facilitated by the acidity of the tissues while the extracted glue is protected from acidic conditions which would impair its viscosity.

3. In a method for making glue from solid pieces of hide glue stock wherein said glue stock is first conditioned to prepare it for the extraction of the glue, the step of extracting glue from said conditioned solid pieces of hide glue stock with hot water containing a water-insoluble base dispersed therein while said solid pieces are maintained interiorly at a pH below 6.5.

4. The method step of claim 3 in which said insoluble base is an alkaline earth metal carbonate.

5. The method step of claim 4 in which said alkaline earth metal carbonate is calcium carbonate.

6. In a method for making glue from collagen-bearing animal tissues wherein said tissues are conditioned to prepare them for the extraction of glue, the steps of acidifying said tissues by soaking them in water at a pH below 6.5, separating the acidulated tissue solids, and extracting glue from said acidulated solids with hot water containing a water-insoluble base dispersed therein while the interior portions of said tissues are at a substantially acidic pH, whereby the extraction is facilitated by the acidity of the tissues while the extracted glue is protected from acidic conditions which would impair its viscosity.

7. In a method for making glue from hide trimmings wherein said trimmings are conditioned to prepare them for extraction of the glue, the steps of acidifying said trimmings by soaking them in water at a pH from 1.5 to 6.0, separating the acidulated trimmings, and thereafter extracting glue from the acidulated trimmings by contacting them with hot water and also contacting said hot water with a water-insoluble base, during said extraction, whereby the extraction is facilitated by the acidity of the tissues while the extracted glue is protected from acidic conditions which would impair its viscosity.

8. The method steps of claim 7 in which said water-insoluble base is an alkaline earth metal carbonate.

9. The method steps of claim 8 in which said alkaline earth metal carbonate is calcium carbonate.

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