Patented Feb. 8, 1949 2,460,809

UNITED STATES PATENT OFFICE

2,460,809

METHOD OF PREPARING GELATIN

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No Drawing. Application February 7, 1946, Serial No. 646,211

6 Claims. (Cl. 260—118)

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This invention relates to a method of preparing gelatin from gelatin-containing material by dissolving the organic constituents of the material in an aqueous solution of ammonia or a lower aliphatic amine and recovering the gelatin from that solution.

Ordinarily gelatin is obtained from animal products, particularly hides or acidulated bones, by a method involving first liming the hides or bone stock to plump the gelatin-forming material. This is a long slow process and to shorten the time of treatment sharpeners have been added to the liming suspension employed for that purpose. After treatment with the lime, the hide or bone stock may then be treated with acid to remove the lime, followed by extraction of gelatin therefrom with hot water. In addition to its being a long drawn-out process, also in the previous operations, there was often danger of loss of gelatin in the acid treatment which tends to hydrolyze the collagen present, thus forming material which may be washed out in the washing operations.

One object of our invention is to provide an improved method of preparing gelatin from gelatin-containing material. Another object of our invention is to eliminate the liming step in preparing gelatin from hides or bones. A further object of our invention is to provide a method of preparing gelatin in which the organic material from which the gelatin is to be obtained is dissolved and the gelatin is separated therefrom. Other objects of our invention will appear herein.

We have found that the organic constituents of gelatin-containing materials can be dissolved in a water solution of ammonia or a lower aliphatic amine, such as methyl amine, dimethyl amine, or ethyl amine, in which dissolving-operation collagen is converted to gelatin and the gelatin thus obtained can be separated from the solution and employed as desired.

In proceeding in accordance with our invention, it is desirable that the gelatin-containing materials be first divided into small units so that the dissolving action may readily take place. For instance if the particles to be treated are 50 mesh or finer, the dissolving action may take place in a few minutes. If the particles are as much as 20 mesh, the dissolving action is slower and with still larger units, a still slower dissolving action occurs. For instance, if a material such as hides be in the form of pieces as much as ¼ inch in diameter, it may take as much as an hour to dissolve that material. The disadvantage of a long time of dissolution is that the material which dissolves first is being subjected to hydrolysis during the dissolving of the remainder of the material and, therefore, that gelatin is hydrolyzed more than is desired for a uniform

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product. If the presence of some excessively hydrolyzed gelatin is not objectionable in the final product, the use of small particles of hide or bone as the starting material is not so important.

Our invention is applicable to obtaining gelatin from gelatin-containing materials generally, whether wet, dried, or salted, but particularly from bones. The hides employed may be on the one hand green calfskins or on the other hand old, dried hides, such as dried buffalo skins. In the case of calfskins or the like which are more susceptible to the dissolving of organic matter dissolution will take place in a short time, whereas with hides which are dry, horny, and thick, the dissolving action may be slow, although a fine particle size of this material will speed up the action. Other gelatin-containing materials, such as raw bones or sinews, feet, tails, or other parts of cattle, sheep, or other animals may be treated by our process, although with many of these the gelatin obtained will not be in nearly as high a degree of refinement as that obtained from for instance, hides.

The agent which is employed to promote the dissolving operation may be ammonia or an aliphatic amino compound of not more than three carbon atoms or a mixture of these agents. Some of the amino compounds which have been found to be particularly useful for this purpose are the following: ammonia, methylamine, dimethylamine, ethylamine, ethylene diamine, ethanolamine, propanolamine, propylene diamine.

It is desirable to have a concentration of at least 10% of the amine or ammonia in water in order to promote the dissolving of the organic matter of the gelatin-containing material. As a rule, it will be preferable to operate the process with concentrations of less than 30% of ammonia or amine. We have found, however, that concentrations less than 10% are operative and their use is within the scope of our invention. For instance, a 3% solution may be employed for the dissolving operation although a time of two hours may be necessary with a readily treatable material as compared with 10 or 20 minutes with concentrations of amine or ammonia within the preferred range. The lower limit of concentration which will dissolve the gelatin-forming material as specified above appears to be about 1% of amine or ammonia.

Although we have found that the dissolving of that organic matter of gelatin-containing material in accordance with our invention takes place satisfactorily at temperatures in the vicinity of 130° F., such as 120–140° F., other temperatures may also be employed, the time of dissolving the material depending not only on the temperature but also upon the condition of the material, its particular size, and the concentration of amine

or ammonia used. For instance, if a temperature of 140° F. is employed and organic material of hide or bone stock is dissolved out in ten minutes, a temperature of 85° F. would result in dissolving of the organic material of the hide or bone in probably 50 minutes or one hour. In the process in accordance with our invention the temperature employed and the concentration of the dissolving liquid used may be adjusted, depending upon the purpose for which the gelatin is to be employed. The use of a low temperature of solution and not too high a concentration of amine consumes a relatively longer time in dissolving organic constituents of the hide or bone than with higher temperatures and concentrations, but at the same time the rate of hydrolysis of the gelatin is kept to a minimum. With the use of a high temperature such as approximately 150° F. and a higher concentration of amine, the solution of the gelatin-forming material is hastened, but also the hydrolysis of the gelatin proceeds at a greater rate.

In some cases the presence of over-hydrolyzed gelatin is somewhat objectionable and in those cases it is necessary to select the temperature and concentration which will give the quickest dissolving time without any substantial amount of hydrolysis taking place. In this case, as soon as dissolving has occurred it is desirable to remove a substantial proportion of the amine or ammonia from the solution as rapidly as possible. Where the object is to prepare a gelatin which is to be employed for some purpose in which the presence of over-hydrolyzed gelatin is not objectionable, at least in some measure greater latitude is allowable for the preparation of the gelatin from the hide or bone stock. With the ordinary methods of dissolving the organic constituents of hide or bone, if an extremely high quality is desired, such as would be employed in preparing photographic emulsions, it is desirable to employ a temperature of less than 160° F. in the operation.

One of the best materials for mixing with water to form a liquid which will dissolve the organic matter of gelatin-containing materials is methylamine. This amine may be used in a concentration of 10% or 12% and will dissolve the organic matter from hide or bone stock, especially if in finely divided condition, in but a short time. However, the other amines mentioned are also of value in such a process.

In its broader aspects our invention is carried out by treating comminuted gelatin-containing materials with a water solution of the amine for a time sufficient to dissolve a substantial proportion of the organic matter therein at the temperature used and with the particle size employed. In many cases it has been found preferable to carry out the process at a controlled pH obtained by buffering the alkaline solution with the use of a buffering salt. The ammonium salts, such as ammonium carbonate, acetate, chloride, sulfate, acid phosphate, citrate, or tartrate have been found to be useful for this purpose, especially for adjusting the pH to 9–10.

The gelatin may be removed from the solution in any desired manner. The three following methods have been found to be particularly useful, however, for this purpose:

1. *The evacuation method*

After the dissolving operation has been completed, the solution is subjected (preferably almost immediately) to evaporation of the amine or ammonia to reduce its concentration to the minimum necessary to retain the gelatin in solution. This evaporation is conveniently aided by reducing the pressure in the system. After the amine or ammonia content has been reduced, the pH is preferably adjusted to 7 so as to retard the hydrolyzing effect of the amine or ammonia present. The solution may then be filtered to remove any solid material and the gelatin may then be recovered from the solution. This evacuation method is not adapted to cases where high boiling amines are employed (such as the last four mentioned in the list given) due to the difficulty of evaporating off.

2. *The salting out method*

This is accomplished by adding salt to the gelatin solution and is effective within a wide pH range, such as 1 to 10. This salting out requires less salt in the lower part of the pH range and, therefore, when salting out is used, it is preferred to operate at a pH of 1–4.

In processes where a buffering salt is used, it is only necessary to cause salting out of the gelatin from its solution that the pH of the solution be dropped, such as by the addition of acid thereto. Salting out would also result by the neutralization of the ammonia or amine used in the preparation of the gelatin solution such as by adding acid so as to lower the pH of the solution to the iso-electric point of the gelatin or below, whether or not a buffering agent had been employed. Thus, salting out of the gelatin from solution may be attained by the addition of either acid or a water-soluble salt to the solution.

3. *Solvent method*

The gelatin may be precipitated from the solution resulting from treating gelatin-containing material as described herein, by adding to the solution an organic solvent in which the gelatin is insoluble, such as acetone or ethyl alcohol in sufficient amount to precipitate the gelatin from the solution.

The gelatin obtained where calf skin is used is ordinarily of good quality and substantially colorless. If, on the other hand, some other type of gelatin-containing material is employed, the gelatin may have some impurities therein and, therefore, unless the impurities are removed, might be employed for some less particular purpose. For instance, a colored gelatin might be employed for glue or it might be purified by filtering through the adsorption material to remove any impurities which would be objectionable as to taste or odor in the gelatin. Also, the use to which the gelatin is to be put will determine to some extent the care which is necessary in obtaining the gelatin from raw material. If the gelatin is to be employed for photographic purposes, it is desirable to carry out the operation with care so that the hydrolysis or degradation of the gelatin in the recovery process is kept at a minimum. For other purposes the same degree of care need not be employed and because of this a gelatin of fair quality and eminently suited for various purposes would be obtained. For instance, the resulting product might have all the attributes which are necessarily employed in the making of glue or sizing therefrom.

The following examples illustrate our invention:

Example 1.—Dry, acidulated bones, such as obtained by the degreasing of bones and treatment with hydrochloric acid as described in the

prior art, were ground so that they would pass a mesh finer than 50. This ground, acidulated bone was agitated in a water solution of methyl amine of 12% concentration for ten minutes at 130° F., whereupon the acidulated bone was dissolved. The thus-formed solution was evacuated by means of an aspirator pump to a vacuum of 30–40 mm. of mercury for twenty-five minutes at 130–140° F. This treatment reduced the methylamine content to about 1% of the original content of methylamine. The pH of the solution was adjusted to 6.0 by the addition of a small proportion of sulfuric acid, and the solution obtained was filtered. This solution was then set by cooling and the resulting gelatin obtained was washed and dried.

Example 2.—Ground, acidulated bone was agitated in a 28% solution of ethylamine for ten minutes at 130° F. whereupon a considerable fraction of the bones dissolved. This solution was evacuated by means of an aspirator pump for twenty-five minutes at 130–140° F. This reduced the ethylamine content to about 1–2% of the original. The pH of the solution was adjusted to 6.0 by addition of sulfuric acid and this solution filtered. The chilled set gelatin solution was then dried.

Example 3.—Dry bones as obtained by degreasing bones as described in the prior art were ground so that they would pass a mesh finer than 50. This ground non-acidulated bone was treated the same as in Example 1, and by such treatment, gelatin was obtained albeit poor quality.

Example 4.—Dry, acidulated bones were dissolved in 100% ethylenediamine in 48 hours at 25° C. This solution was filtered and then diluted with 4–6 volumes of ethyl alcohol. The precipitated gelatin was dissolved in water, set by chilling, washed and dried.

Example 5.—Finely divided water buffalo hide was treated with 12% methylamine solution for sixty minutes at 135° F., whereupon the hide dissolved. This solution was evacuated twenty-five minutes at a pressure of 30–40 mm. of mercury at a temperature of 135° F. This treatment reduced the amine content to about 1% of the original. The pH of the solution was adjusted to 6.0 by the addition of a small amount of sulfuric acid. The solution was then gelled by chilling and dried.

Example 6.—Finely divided acidulated bones were agitated in a 12% ammonia solution for twenty minutes at 135° F. whereupon the acidulated bones dissolved. Evacuation of this solution for fifteen minutes at 135° F. at a pressure of 30 mm. of mercury reduced the ammonia content to less than 1% of the original. This solution gelled on cooling and was then dried.

Example 7.—The same procedure as described in Example 6 can be used substituting a solution made 6% with respect to ammonia and 6% with respect to methylamine.

Example 8.—Acidulated bones were agitated in a 12% solution of ammonia, buffered to a pH of 9.5 to 10.0 by appropriate amounts of an ammonium salt, such as ammonium carbonate, ammonium sulfate, ammonium acetate, or ammonium chloride, for thirty minutes at 140° F. whereupon a considerable portion of the bones dissolved. Several techniques were used to recover the gelatin.

(*a*) Additional salt, i. e., $(NH_4)_2SO_4$ was added, sufficient to precipitate the gelatin at the above-mentioned pH values. This coagulated gelatin was washed free from salts, dissolved in water, set and dried.

(*b*) The pH of the salt gelatin solution was lowered to the point where the gelatin separated from solution. This coagulated gelatin was treated as in (*a*).

(*c*) The gelatin salt solution was chilled at the pH of the reaction and the set gelatin washed free of salt before drying.

We claim:

1. A method of obtaining gelatin from collagen-containing parts of the animal body which comprises subjecting such parts to the dissolving action of an aqueous solution of 1–30% concentration of an aliphatic amine selected from the group consisting of methylamine, dimethylamine, ethylamine, ethylene diamine, ethanolamine, propanolamine, and propylene diamine, whereby the collagen is dissolved and converted into gelatin.

2. A method of obtaining gelatin from collagen-containing parts of the animal body which comprises subjecting such parts to the dissolving action of an aqueous solution of 1–30% concentration of methylamine whereby the collagen is dissolved and converted into gelatin.

3. A method of obtaining gelatin from collagen-containing acidulated bone which comprises subjecting the acidulated bone to the dissolving action of an aqueous solution of 1–30% concentration of methylamine whereby the collagen is dissolved and converted into gelatin.

4. A method of obtaining gelatin from collagen-containing animal hide which comprises subjecting the hide to the dissolving action of an aqueous solution of 1–30% concentration of methylamine whereby the collagen is dissolved and converted into gelatin.

5. A method of obtaining gelatin from collagen-containing parts of the animal body which comprises subjecting such parts to the dissolving action of an aqueous solution of methylamine of 1–30% concentration and a buffering agent selected from the group consisting of ammonium and amine salts whereby the collagen is dissolved and converted into gelatin, separating the resulting solution from any insoluble material therein followed by insolubilizing the gelatin and washing free of the salts therein.

6. A method of obtaining gelatin from collagen-containing parts of the animal body which comprises subjecting such parts to the dissolving action of an aqueous solution of 1–30% concentration of a mixture of methylamine and ammonia, the amount of methylamine being at least equal to the amount of ammonia, whereby the collagen is dissolved and converted into gelatin.

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