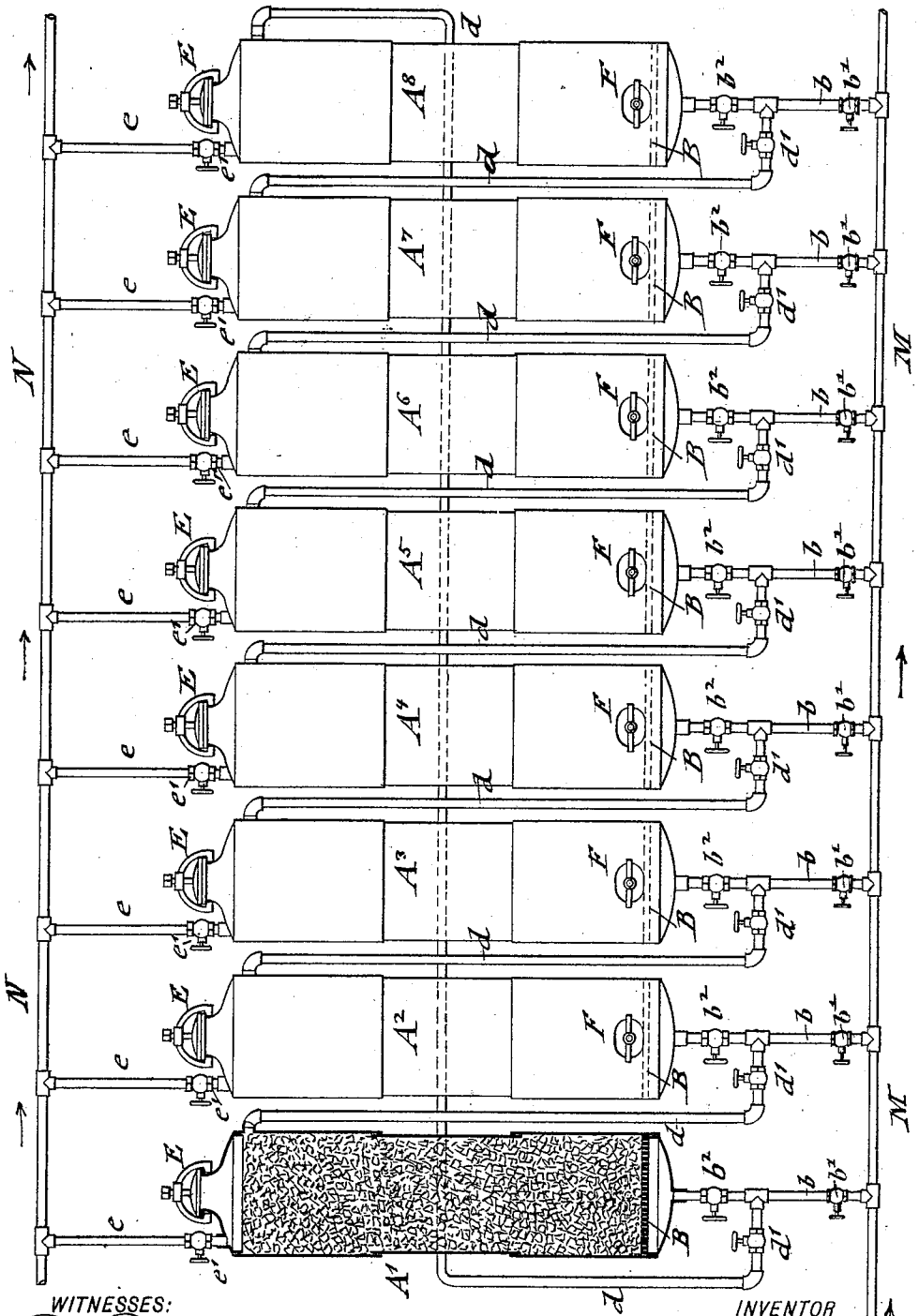
(No Model.)

M. SCHROEDER.

PROCESS OF PRODUCING GLUE AND GELATINE FROM BONES.

No. 518,861. Patented Apr. 24, 1894.



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PROCESS OF PRODUCING GLUE AND GELATINE FROM BONES.

SPECIFICATION forming part of Letters Patent No. 518,861, dated April 24, 1894.

Application filed March 10, 1894. Serial No. 503,127. (No specimens.)

To all whom it may concern:

Be it known that I, MAX SCHROEDER, a subject of the German Emperor, residing in Dusseldorf, Germany, have invented certain new and useful Improvements in Processes of Producing Glue and Gelatine from Bones, of which the following is a specification.

This invention relates to an improved process for the production of glue and gelatine from bones. Hitherto the manufacture of glue from ordinary bone material has been carried out in two different ways. Either the bones were decomposed directly by means of high-pressure steam into a glue-solution and residual phosphate, or the extraction process was employed, according to which the phosphate is first extracted by watery acids, especially muriatic acid and sulphurous acid and then the pure residual cartilage is boiled down to glue. As in the first named process steam-pressures of from two to three atmospheres with the corresponding temperatures of 130° to 140° Celsius are required, which at once bring about a strong decomposition of the glue-substance, there is obtained only a dark brown glue of small commercial value. Much better is the glue produced by the second process because the extracted cartilage may be easily boiled down to a glue-solution at temperatures of 100° Celsius and under, but this process is somewhat costly in consequence of the great expense for the acid and the requisite preparation of the solutions.

The object of this invention is to obtain good serviceable glue and gelatine from bones by producing first the dry disintegration of the same without dissolving the phosphates by means of gaseous sulphurous acid; then decomposing the brittle bones by means of steam or boiling water into an acid glue-solution containing some acid calcium-sulfite and bi-calcium phosphate, and a residuum consisting substantially of mono-calcium phosphate, a neutral sulfite of calcium and some undissolved organic substances.

My invention is based on the fact that bones containing some moisture have a peculiar capacity for absorbing gaseous sulphurous acid. If, at the ordinary temperature, a current of sulphurous acid gas be passed through air-dried or slightly-moistened bones placed in a closed receiver, it will be found that the quantity of sulphurous acid passing out at the top of the receiver does not correspond to that introduced at the bottom-part of the vessel. At the commencement, the sulphurous acid gas is almost wholly absorbed by the bones; later on, the absorption proceeds more slowly so that a portion of the sulphurous acid escapes at the top of the receiver. In the course of twelve hours, the bones, with the exception of those of the very hard tubular kind, will have absorbed sulphurous acid to the extent of from ten to twelve per cent. of their weight. If the current of sulphurous acid be continued, still more and more of the same will be taken up by the bones and it may without difficulty rise to fifteen and even twenty per cent. of the weight of the bones. If the bones be then removed from the closed receiver and exposed for a length of time to the air, they will be found to give off sulphurous acid gas but only until the sulphurous acid contained in the bones is reduced to about eleven to twelve per cent. These contents of sulphurous acid remain constant even when the bones are exposed to the air for months, neither is the sulphurous acid contained in the same expelled by heat, or water, or by a current of steam. From these observations it may be deduced that by the absorption of from eleven to twelve per cent. of sulphurous acid the point of saturation of the bones has been reached, while the quantity of gas which is absorbed above this percentage is held temporarily only either by the capacity for condensation possessed by porous bodies or by a slight chemical binding action.

As the chemical binding of the sulphurous acid is not due to the cartilage-substance of the bones, the absorption of sulphurous acid is due to and attained only by the thorough conversion of the phosphates in the bones. It is known that, on an average, bones consist of one third of organic and two thirds of inorganic substances, the latter irrespective of the small quantity of carbonate, consisting mainly of phosphate of lime. If now the absorption of from eleven to twelve per cent. of sulphurous acid be attributed to the inor-

ganic portion only of the bones, there results an absorption by the same of from sixteen to seventeen per cent. of sulphurous acid. The conversion of the bone-phosphates would therefore proceed substantially in accordance with the following equation, which presupposes an absorption of 16.3 per cent. of sulphurous acid:

$$(PO_4)_2Ca_3+SO_2+H_2O=2PO_4HCa+CaSO_3.$$

With this assumption corresponds the fact that the phosphate has passed over into a water-soluble form. Whether during this conversion an absorption of water of crystallization takes place, is of little importance for the successful carrying out of the process. The ordinary amount of moisture which the bones contain, is as a rule sufficient for the requirements of the conversion, and if this should not be the case, it might easily be increased by a previous addition of some moisture thereto. Bones thoroughly dried at a temperature of 100° Celsius possess only a small capacity for taking up sulphurous acid because they are deficient in the water necessary for the aforesaid conversion.

Instead of the pure gaseous sulphurous acid, mixtures of the same with nitrogen, oxygen, carbonic acid and other indifferent gases may be employed, but with a high degree of dilution the conversion of the phosphates of the bones is retarded. On the other hand, by employing a higher pressure and a corresponding compression of the active gas-molecules, the conversion may be considerably accelerated.

My improved process would have but little value if it were not accompanied by a marked change in the structure of the bones. By the conversion of the phosphates, the thinner and somewhat elastic bones are rendered quite brittle and may be broken into small pieces without much difficulty. In consequence of their loose or spongy structure, they offer but slight resistance to boiling water, and are boiled at 100° Celsius and less into glue nearly as quickly as the pure extracted cartilage. The sulphite and phosphate in the brittle bones are changed into powder-form after only two hours' boiling; stronger and tougher bones are rendered so soft that they may be indented with the fingers; and only the inner portions of hard tubular bones which are not sufficiently acted upon by the sulphurous acid retain their structure. The glue-solution thus obtained is of a bright color but somewhat milky owing to the phosphate distributed therein. It also contains salts in solution and reacts strongly acid. It is therefore not suitable for immediate working up into glue. The salts resulting from the conversion-process, namely the neutral calcium-sulfite and mono-calcium phosphate, are insoluble in water, but as in practice a small excess of sulphurous acid is unavoidable by reason of the condensing action of the bones, there will be found in the solution small quantities of acid calcium-sulfite and bi-calcium-phosphate. These salts are not retained in solution during the concentrating and drying of the glue, but render the same opaque. This objectionable feature may be removed by neutralizing the glue-solution with milk of lime. By this means not only is the acid-reaction suppressed, but nearly all the salts except, a small uninjurious residue, are precipitated in an easily filtered form and carry with them all other impurities so that the result is a perfectly clear neutral glue-solution, mostly of a bright yellow color, which solution may be worked up into glue in the known way.

The accompanying drawing represents a side-elevation, partly in section, of one form of apparatus which can be used for carrying into practice my improved process for treating bones with gaseous sulphurous acid, the drawing representing a battery of eight receivers for the broken bones, in which the bones are successively treated with sulphurous acid gas.

The bones to be treated may have their fat previously removed or not, the previous extraction of the fat, however having the advantage that the badly-smelling substances are removed at the same time and the pores of the bones opened for the reception of the sulphurous acid vapors. The bones are preferably reduced to small pieces by mechanical means, whereby the absorption of the sulphurous acid and the conversion of the bones is accelerated.

The apparatus shown in the drawing consists of a battery of preferably eight air-tight receivers A', A^2, A^3, &c., which are made of wood lined with lead, or of iron or other suitable material. The sulphurous acid gas is supplied to the receivers through a supply-main M which connects the apparatus with the furnace in which the sulphur is burned and from which the sulphurous acid is obtained. The supply-main M is connected with the bottom of each receiver by a pipe b, which is provided with two valves b' b^2, one near the supply-main M and the other near the bottom of the receiver. The vapors pass into the bottom-part of the receiver, which is provided with a perforated false bottom B, a charging man-hole and man-hole cover E at the top, and a discharging man-hole and man-hole cover F at the bottom. The vapors pass from the upper part of one receiver by a downwardly-extending pipe d to the supply-pipe b of the next adjacent receiver, said connecting-pipe being likewise provided with a stop-cock d' at its lower end near its connection with the pipe b. The last receiver of the series is connected by the pipe d with the pipe b of the first receiver so that a closed cycle for the gas is obtained. The sulphurous acid gas passes through the bones charged into the receiver and is conducted through the connecting-pipe d to the lower part of the second receiver, then in upward direction through the bones in the same, then to the

third receiver, and so on. The unabsorbed vapors are passed through the pipe *e* having a stop-cock *e'*, to a conducting-off pipe N, which conducts them back into a furnace or other suitable place. During the flow of the vapors through the first four receivers of the battery, the valve *d'* of the first receiver and the lower valves *b'* of the second, third and fourth receivers, and also the valve *d'* of the fifth receiver, are closed, while the valves *e'* of the outlet-pipes *e e* of the first, second, and third receivers are closed, so that the vapors are compelled to take the course beforementioned. When the bones in the receiver A' are saturated with sulphurous acid, the lower valve *b'* of the first receiver and the valve *d'* of the second receiver are closed, and the lower valve *b'* of the second receiver opened and connected with the supply-main M, so that the vapors pass through the second, third, fourth and fifth receivers, which latter is connected with the fourth receiver by opening the valve *d'* of its connecting-pipe *d*. The saturated bones in the first receiver are permitted to stand in the same for two or three days, so that the perfect conversion of the bones takes place by the action of the acid. When removing the charge from the first receiver, the stop-cock of the pipe *e* is opened, so that the receiver is connected with the discharge-pipe, after which the lower man-hole is opened and the bones removed. The charge of bones in each receiver is supported on the perforated false bottom, which is arranged below the lower man-hole F.

In place of the apparatus described, my improved process for treating bones by means of sulphurous acid vapors can also be carried on in any other apparatus, as, for instance, an apparatus in the nature of a tall cylindrical shaft which is charged at the top and discharged at intervals at the bottom. During the time when the bones are at rest in the receivers, the surplus quantity of sulphurous acid which is retained by condensation, enters into chemical combination with the inner portions of the bones that are not fully saturated. If the battery consists of eight receivers, four are always in use for the absorption of the sulphurous acid, while three are in a state of rest after the absorption is completed, and one is in course of being charged or discharged. After the receiver A' is shut off, the fifth receiver A^5, being charged with fresh bones, is connected with the receivers, A^2, A^3, A^4, while receivers A^7 A^8 and A' are in a state of rest. Receiver A^6 which has been standing longest, is then emptied, charged with fresh bones and connected in place of receiver A^2, which is shut off, with the receivers A^3 A^4 and A^5, and so on in continuous succession. If the size of the several receivers be such that each represents one day's output, the entire cycle would be made in eight days, four of these serving for the absorption, three for rest for the purpose of the chemical combination of the superficially-condensed sulphurous acid and one day for discharging and charging. This battery-apparatus is especially adapted for places where no pure sulphurous acid gases but mixtures of the same with indifferent gases are used, such as are obtained from the combustion of sulphur, the furnace-gases from pyrites, &c. If compressed liquid sulphurous acid be available, the operation may be carried on under pressure in separate iron receivers, in which case for every hundred parts by weight of bones from ten to twelve parts by weight of liquid sulphurous acid is passed into the receiver and the charge allowed to stand until the absorption of the sulphurous acid has taken place, according to rule. The small quantity of carbonic acid which is evolved from the bones, is discharged from time to time by a blow-off valve when the pressure becomes too high. Upon completion of the conversion, the bones are subjected to the action of a vacuum so as to remove the free sulphurous acid still present, which would be found disagreeable if allowed to remain when the receiver is being emptied.

Instead of compressed liquid sulphurous acid, a corresponding quantity of pure sulphurous acid gas may be forced into the receiver by means of a compressor. For every hundred pounds of bones two and a half cubic yards of pure sulphurous acid gas would be required, the quantity being capable of exact measurement by the number of strokes of the compressor. After removal from the receiver the bones are soaked in water for two or three days to remove the soluble salts and especially the smelling and coloring matters made soluble by the sulphurous acid.

The boiling down of the bones to glue is now proceeded with. As iron vessels cannot well be employed owing to the acid properties of the glue-solution, wooden vats or vessels lined with lead are used. They are charged with the converted bones and with sufficient water to cover the same. The heating up to 100° Celsius is effected by means of steam-coils or by the direct introduction of steam at the bottom of the vessel. After two or three hours of boiling, the larger quantity of the glue substance is dissolved and it is best to withdraw the first solution in order that the glue may not be decomposed by boiling too long. Fresh water is then added to the bones to extract the remaining glue-substance and boiled to form a diluted glue-solution, which may be added to the other in special clarifying vats. By a third boiling, a very diluted solution is obtained which is utilized by adding it to the next charge of bone-material.

When bones that have not had their fat extracted, are used for the operation, the separation of the fat from the glue-solution must be effected in the clarifying vats, where it rises to the surface. In the case of bones from which the fat has been previously extracted, this separation of the fat is not nec-

essary. The hot glue-solution is next neutralized with milk of lime to remove the phosphates and sulfites held in solution. The milk of lime used for this purpose is prepared from ten parts of caustic lime and one hundred parts of water. Instead of lime, other alkaline earths may be used, or with a less good result, their carbonates. It is not advisable to use the alkalies proper or ammonia because they form soluble salts in the glue-solution, which salts would in the drying of the glue cakes, separate and cause turbidness. After the neutralization, the glue-solution is allowed to stand for some time whereupon the separated matters are completely precipitated. The clear bright yellow glue-solution is then drawn off or separated from the precipitate by the aid of a filter-press. The further working of the glue-solution into cakes is accomplished in a known way by evaporating it in open or in vacuum-pans, pouring into molds, cooling, cutting and drying. By treating fresh bright bones according to this process, a nearly colorless and odorless gelatine is obtained. The yield of glue is good, amounting to from sixteen to twenty-four per cent., according to the quality of the bone-material used. The sulfite and phosphate residuum of the bones remaining after the boiling process, is dried and ground to powder under a light pressure. The inner unconverted and still hard portions of the tubular bones retain their form and are separated from the powder by sifting. Probably owing to a deficiency of moisture, the innermost portions of the hard bones absorb only from three to four per cent. of sulphurous acid, and they may be again subjected to the action of the same, but as they form only about ten per cent. of the bones used, and do not contain much glue-substance, their further treatment with sulphurous acid may be omitted, more especially as the nitrogen of the same has a certain value as manure.

The ground residuum is not suitable for direct application as manure owing to the sulfite contained in the same. The powder is therefore treated with sulphuric acid in closed cylinders provided with agitators in order that during the formation of superphosphate the sulphurous acid can be drawn off in gas form. This sulphurous acid is again utilized by being introduced into the battery of receivers for the treatment of further quantities of bones.

Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. The process herein-described of treating bones for producing glue and gelatine from the same, which consists in the following steps: first, subjecting the bones to dry disintegration by the action of sulphurous acid gas, second, dissolving the brittle disintegrated bones by boiling water or steam, third, neutralizing the acid glue-solution obtained thereby, and lastly, separating the glue-solution from the precipitates for further treatment, substantially as set forth.

2. The process herein described of producing glue and gelatine from bones, which consists of the following steps, first: subjecting the bones to dry disintegration by the action of sulphurous acid gas, second, subjecting the disintegrated or converted bones to the action of boiling water or steam until an acid glue-solution, containing acid calcium-sulfite and bi-calcium phosphate, and a residue containing neutral calcium-sulfite, mono-calcium phosphate and insoluble organic substances is obtained, third, neutralizing the acid glue-solution, and lastly, separating the clear glue-solution from the precipitate for further treatment, substantially as set forth.

3. In the process of treating bones for producing glue and gelatine from the same, the dry disintegration or conversion of the bones by subjecting them to the action of sulphurous acid gas, substantially as set forth.

4. In the process of treating bones for producing glue and gelatine from the same, subjecting the bones to dry disintegration by the action of sulphurous acid gas up to the point of saturation, and then permitting them to stand for a certain length of time, substantially as set forth.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

MAX SCHROEDER. [L. S.]

Witnesses:
H. F. MERRITT,
WILLIAM OTTO.