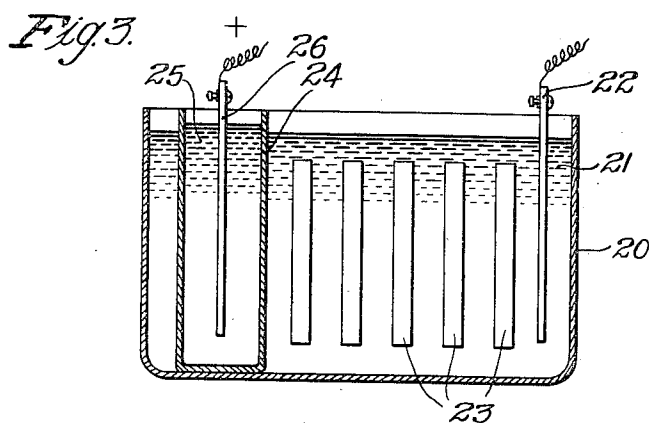
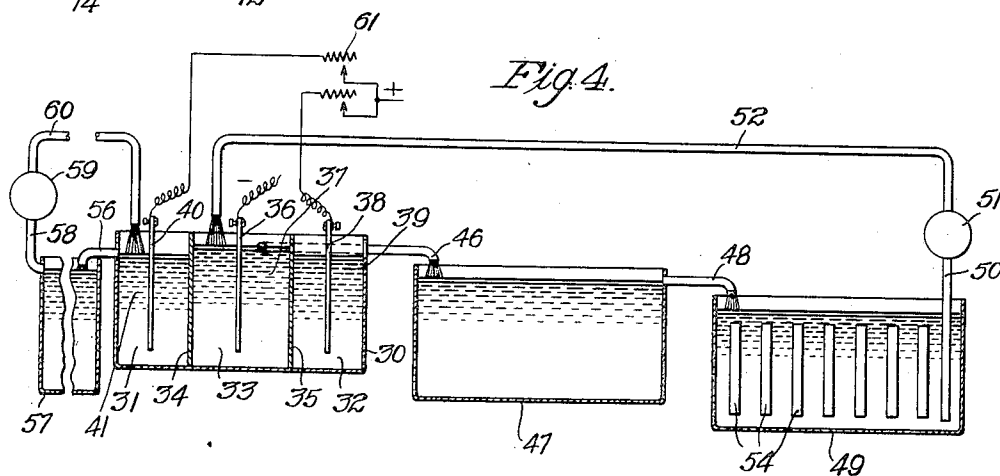
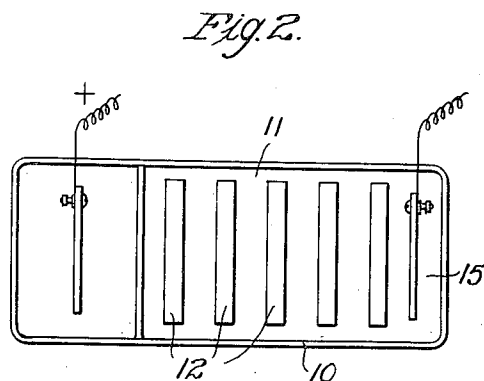
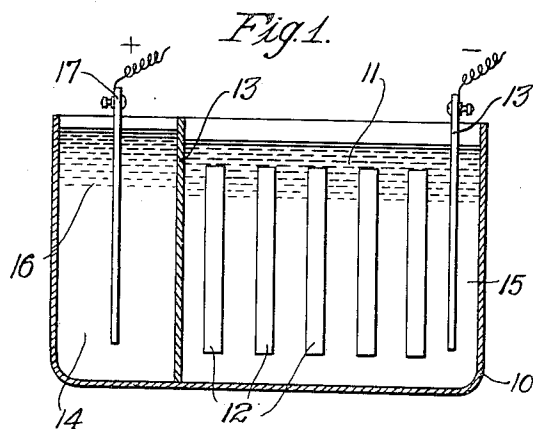


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 PROCESS FOR THE PURIFICATION OF POROUS OR GELATINOUS MATERIALS.
 APPLICATION FILED JAN. 11, 1918.

1,371,699.

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Inventor
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UNITED STATES PATENT OFFICE.

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PROCESS FOR THE PURIFICATION OF POROUS OR GELATINOUS MATERIALS.

1,371,699.

Specification of Letters Patent.

Patented Mar. 15, 1921.

Application filed January 11, 1918. Serial No. 211,383.

To all whom it may concern:

Be it known that I, OSCAR LINDER, a citizen of the Republic of Switzerland, residing at Chicago, in the county of Cook and State of Illinois, United States of America, have invented certain new and useful Improvements in Processes for the Purification of Porous or Gelatinous Materials, of which the following is a full, clear, concise, and exact description.

This invention relates to an improved process for the purification of porous or gelatinous materials, and more particularly to improvements in processes of eliminating and recovering metallic salts, acids, and other chemicals from such porous and gelatinous materials. More specifically the invention is directed to an improved process for eliminating or removing and recovering water soluble salts, acids, alkali, and other ionized chemicals or their solutions from porous or gelatinous materials by subjecting the materials to the washing or dissolving action of an aqueous solution of such chemicals, said solutions being kept lower in concentration than that of the chemicals contained within said material.

The invention is especially adapted for the purpose of removing and recovering metallic salts from certain fibrous materials, and more particularly from the material commonly known as fiber, hard fiber, or vulcanized fiber. The invention is not limited to this specific application, however, but may be used for the purification of any porous or gelatinous material which in itself does not dissolve in cold water and which contains water soluble salts, acids, alkali, or any other ionized chemicals which are to be eliminated therefrom. Albumin, gelatin, glue, and casein may be mentioned as examples of such other materials.

In the manufacture of fiber it is customary to treat paper with a strong and warm solution of zinc chlorid in water and then laminate a number of sheets of this treated paper under pressure, or pile one sheet on another under pressure until the desired thickness is reached. Thereafter the zinc chlorid is removed by washing the fiber in zinc chlorid solutions of diminishing strengths or concentrations until pure

water is reached. This is a long and tedious process and requires, for example, about three to four weeks for fiber $\frac{1}{8}$ inch in thickness and proportionally longer for fiber of greater thickness. Such a lengthy process is necessary for two reasons: First, because it renders possible an economical recovery of the zinc chlorid, and second, in order to avoid the formation of blisters in the fiber, which cause splits and cracks in the finished product and are the causes of great loss. The danger of blistering is minimized by removing the zinc chlorid very slowly, that is, by first placing the fiber in a comparatively strong zinc chlorid solution and then gradually transferring it to zinc chlorid solutions of slowly diminishing strengths and finally washing it in pure water.

This danger of blistering is minimized and the time required for washing considerably reduced by the process of this invention, in which the fiber is immersed in zinc chlorid solutions, the strength of which is decreased gradually and at a uniform rate by eliminating the zinc chlorid from it by electrolysis under such conditions that substantially all of the zinc and chlorin is eliminated.

It has been proposed heretofore in United States Patents No. 923,745, issued June 1, 1909, to Willis R. Whitney, and No. 1,226,279, issued May 15, 1917, to H. E. Tiffany, to eliminate the zinc from the fiber by direct electrolysis, the fiber in the processes of these patents serving apparently either as an anode or being placed between the electrodes of an electrolytic cell. These processes offer difficulties in their practical application which render their use uncommercial. These difficulties are mainly of the following nature:

In the electrolysis of zinc chlorid solutions of such strengths as would be encountered in the practical application of such process (say from 70° Bé. down to 0° Bé.) between a cathode and an insoluble anode immersed directly into the solution, the chlorin radical is liberated at the anode, not only as chlorin gas, but also to a considerable extent as hydrochloric acid. This renders the electrolyte acid and thereby reduces the efficiency of the electrolysis,

because with increasing acidity there is an increasing tendency to liberate hydrogen instead of zinc at the cathode and oxygen instead of chlorin at the anode. It is well known that electro-positive metals like zinc are difficult to deposit electrolytically from acid solutions, and consequently under the very best conditions the efficiency of the processes described in the aforesaid U. S. Patents decreases rapidly with decreasing concentration of the electrolyte. Another difficulty resides in the fact that most of the zinc is deposited in spongy condition and a considerable amount of this deposit generally becomes detached from the cathode. When thus detached the zinc gradually enters into solution again, if the electrolyte is slightly or considerably acid, and obviously will have to be precipitated out again. A third difficulty arises because a considerable part of the chlorin liberated at the anode is dissolved in the electrolyte, and this not only discolors the fiber suspended therein, but also attacks and weakens it.

The processes of the hereinbefore referred to patents are therefore not only very inefficient for the elimination of the zinc chlorid from the fiber, but in addition, at the conclusion of the electrolysis the resulting fiber, instead of being pure and free from zinc chlorid, contains either hydrochloric acid or chlorin or both. These chemicals must be removed by washing the fiber in water and, therefore, cannot be economically recovered.

The hereinbefore enumerated difficulties have rendered the electrolytic process of washing fiber prohibitive commercially and have also made it impossible to remove all the zinc and chlorin from the fiber in this manner. In order to render the process commercial it is necessary, in accordance with the teachings of this invention, that the chlorin liberated at the anode be removed quickly and positively from the electrolyte and that the chlorin and zinc be eliminated from the fiber in substantially equivalent proportions. This is accomplished by placing the anode in a porous cup containing a suitable electrolyte and by carrying on the electrolysis under such conditions that the reaction of the electrolyte in which the anode is immersed is either only very slightly acid, or neutral, or alkaline. The reaction of this electrolyte can be regulated and controlled by employing two or more anodes which may be immersed either in the same or in separate electrolytes of suitable compositions and concentrations and which in turn are inclosed in porous receptacles so that the said electrolytes in which the anodes are immersed are mechanically separated but in electrolytic contact with the electrolyte in which the cathode is immersed and from which the zinc chlorid is to be re-

moved. My co-pending application, Serial No. 211,382, filed of even date herewith entitled an Improved process of and apparatus for electrolysis discloses a process for regulating the reaction of the electrolyte.

For convenience in the following description, the electrolyte in which the anode is immersed will be termed the anode electrolyte, and the electrolyte in which the cathode is immersed, the cathode electrolyte, and the zinc chlorid solution in which the fiber is immersed will be called the washing solution.

The invention is illustrated in the accompanying drawings, in which:

Figure 1 illustrates in diagrammatic form a vertical section of one form of electrolytic cell for use with this process;

Fig. 2 is a plan view thereof;

Fig. 3 illustrates another form of such cell, and

Fig. 4 is a diagrammatic illustration in vertical section of an electrolytic cell and the appurtenances utilized in a commercial system in which fiber is washed according to the process disclosed in this invention.

Referring to Fig. 1, 10 represents any form of electrolytic cell in which is contained the washing solution 11 and the fiber 12 which is to be washed. The cell is fitted with a porous diaphragm 13 which separates the cell into two compartments 14 and 15, the compartment 15 containing the washing solution 11, the fiber 12, and the cathode 13, and the compartment 14 the anode electrolyte 16 and the anode 17. The anode and cathode are connected to any suitable source of electrical energy.

Fig. 3 shows another form of electrolytic cell comprising the inclosing chamber 20 in which is contained the washing solution 21 and cathode 22 and the fiber to be washed 23. Removably placed within the cell is a porous cup 24 containing the anode electrolyte 25 and the anode 26. The cup 24 is completely surrounded by the washing solution 21. The anode 26 and the cathode 22 are connected to some suitable source of electrical energy.

Referring now to Fig. 4, the electrolytic cell comprises the inclosing chamber 30 which is divided into three compartments 31, 32, and 33 by the porous partitions 34 and 35. Contained within the compartment 33 is the cathode 36 and the washing solution 37. The compartment 32 contains an anode 38 and an anode electrolyte 39; while the compartment 31 contains another anode 40 and another anode electrolyte 41. Connected to the compartment 33 is any suitable fluid conveying means such as the pipe 46, the other end of which discharges into either a settling tank or filter press 47. Fitted in the side wall of the settling tank 47 is the diaphragm 48 which discharges into a storage tank

49. Connected to the tank 49 is a pipe 50 which terminates in a pump 51, diagrammatically illustrated in the sketch. To the other side of this pump is connected a pipe 52 which discharges into the compartment 33 of the electrolytic cell. Contained within the storage tank 49 is the fiber 54 which is to be washed.

It will be evident from the drawing that when the pump 51 is in operation the washing solution 37 will be circulated from the chamber 33 through the settling tank 47 and into the washing tank 49, and from there back to the electrolytic cell. The rate at which the washing solution 37 is circulated through this system can be readily controlled by regulating the action of the pump 51.

For the purpose of circulating the anode solution 41, the compartment 31 is fitted with a pipe connection 56 which discharges into a storage tank 57. The storage tank 57 is in turn fitted with a pipe connection which terminates in a pump 59, diagrammatically illustrated, to which pump is also connected the pipe 60 which discharges into the compartment 31 of the electrolytic cell. This pump and the associated pipe connections constitute a means whereby the anode electrolyte 41 may be circulated from the compartment 31 to the storage tank 57 and back again either constantly or intermittently and at any rate desired. The cathode 36 is connected to a negative terminal of any suitable source of electrical energy, and the anodes 38 and 40 are connected through a suitable rheostat 61 to the positive terminals of any suitable source of electrical energy.

Obviously the simplest manner of carrying out this process is to place the anode in a porous cup such as 24, illustrated in Fig. 3, said cup being filled with a suitable electrolyte, as for example, a zinc chlorid solution. The cup 24 is then immersed in the washing solution in which the cathode is also immersed, as shown in said illustration. The fiber to be washed is either suspended or placed in the cathode electrolyte, as illustrated in Figs. 1, 2, and 3, either between the electrodes as there shown or outside of said electrodes, or the fiber is immersed in a separate receptacle or washing tank 49, as illustrated in Fig. 4, and the cathode electrolyte is circulated through this receptacle, as hereinbefore described.

By the use of any of the apparatuses illustrated in Figs. 1 to 4, the zinc is deposited at the cathode which is immersed directly in the solution to be electrolyzed, and the chlorin at the anode inside of either the porous cup 24 or the compartment such as 15 separated from the main cell by the partition such as 13 (see Fig. 1). It will consequently be obvious that the zinc as well as the chlorin is removed from the solu-

tion to be electrolyzed. By properly choosing the anode materials and anode electrolytes, the reaction of the solution to be electrolyzed may be maintained practically neutral and the deposition of zinc and chlorin maintained practically quantitative. To accomplish this purpose, the electrolytic cell illustrated in Fig. 4 is utilized. The method employed for controlling this reaction is illustrated and described in my co-pending application hereinbefore referred to and filed of even date herewith.

In the operation of this process, the concentration of the zinc chlorid or washing solution which constitutes the cathode electrolyte is reduced at a gradual and uniform rate, and consequently this concentration is at all times slightly lower than that of the zinc chlorid solution within the fiber which is to be washed. Under these conditions the zinc chlorid diffuses readily from within the fiber into the washing solution and is thus eliminated from the fiber.

From the foregoing description it will be evident that the improved process herein described differs from known methods and completely from the two patents hereinbefore referred to, in that first, the fiber is not necessarily exposed to the electrolytic action of an electric current and takes no part in the electrolysis, nor does the zinc chlorid which is contained within the fiber while it is in the fiber; second, the removal of the zinc chlorid is due to direct diffusion of these salts or chemicals into the surrounding solvent, and not to any hastening of the migration of the zinc and chlorin ions due to the electric current; and third, substantially all the zinc and chlorin is eliminated, while in the processes described in the herebefore referred to patents only a part of the chlorin can be removed and the balance is left in the electrolyte and in the fiber as chlorin and hydrochloric acid, which must be removed later by washing the fiber in water.

In this process the electric current is not utilized in order to increase the velocity of motion of the ions of the salts or chemicals in the fiber. It is employed solely for the purpose of removing at a uniform and slow rate the zinc and chlorin from the cathode electrolyte or washing solution. This always keeps the concentration of the salts in the washing solution slightly lower than the concentration of the salt in the fiber. It will be apparent, therefore, that the action obtained by this improved process is equivalent to transferring the fiber from zinc chlorid solutions of greater to solutions of lesser strength. Also that the diminution in the strength of the solution is much more gradual in this improved process than that which can be obtained by the customary method of transferring the

fiber from one washing tank to another containing solutions of decreasing concentration. It is apparent, therefore, that this is a process of diffusion, but that it differs from the process commonly practised therein that the degree of diffusion can be closely regulated.

In the operation of this improved process conditions can be produced in the washing solution which facilitate and accelerate the washing process. Thus for example, if an insoluble anode is utilized, the cathode electrolyte will become acid, and if a soluble anode is used, the cathode electrolyte will remain either neutral or will become alkaline, according to the manner in which the process is controlled. In the washing of fiber it is sometimes desirable to maintain the wash water slightly acid at the beginning of the process, which will prevent the precipitation of zinc hydroxid which takes place when solutions of zinc chlorid are diluted. This may be accomplished by using an insoluble anode, such as either lead or carbon, which may be used either alone or in combination with a soluble anode such as zinc. When two anodes are used, part of the current is directed through the insoluble and part of it through the soluble anode, the division of current being so proportioned and regulated that the cathode electrolyte is maintained at the desired reaction. During the final stages of the fiber washing process in the preferred form of the invention, it is advisable to maintain the washing solution in either a neutral or alkaline condition. This condition of the washing is desirable so as to render possible the complete removal of zinc and chlorin, which would be either impossible or prohibitive commercially in an acid solution. The washing solution is maintained in this condition by the use of a soluble anode such as zinc either alone or in combination with an insoluble anode and in which the flow of current is so controlled that the greater part thereof flows through the soluble anode.

In the preferred form of the invention the electrolysis of the washing solution takes place in a receptacle which is separate from that in which the fiber is immersed, as illustrated in Fig. 4. In this case the washing solution is circulated from the electrolytic cell 30 into the washing receptacle 49 which is isolated and disconnected electrically from the electrolytic cell 33. The washing solution may preferably be passed through a settling tank 47 or a filter press for the purpose of settling out or filtering any zinc carried along from the electrolytic cell 30 and any basic zinc chlorid, zinc hydroxid, or zinc oxid which is formed if the reaction is conducted under alkaline conditions. The use of a filter press insures the use of a washing solution which is free from impurities in

the washing tank 49 in which the zinc chlorid is washed from the fiber 54 and the solution recirculated to the electrolytic cell 30.

In the commercial operation of the invention the process is preferably maintained continuous, the current flowing in the electrolytic cell and the rates of fluid circulation being so adjusted that the removal of the zinc chlorid from the fiber 54 is very uniform and gradual. Obviously a continuous operation of the process is not essential, the washing of fiber being also performed by an intermittent operation of the process. The rate of diminution of the concentration of the zinc chlorid solution is controlled by the amount of current which flows through said solution, the rate of its circulation, and its total quantity. These rates for any particular washing operation are dependent mainly upon the thickness of the fiber which is to be washed.

When the electrolytic action is regulated so as to produce an alkaline cathode electrolyte, there will be a precipitation of zinc hydroxid from the cathode electrolyte. This zinc oxid or hydroxid may be utilized by placing it in the anode compartment, preferably in the compartment inclosing the insoluble anode, where it will be dissolved to zinc chlorid. When a zinc anode is used, a solution of zinc chlorid is obtained in the anode receptacle. This zinc chlorid is useful and may be utilized in the manufacture of fiber. In the preferred form of the invention the zinc anode is obtained and constructed from the zinc which is deposited at the cathode. In the operation of the process it is best to prevent an excessive accumulation of zinc chlorid in the anode receptacle. This is accomplished, as illustrated in Fig. 4, by an overflow and circulating system involving the chamber 57, the chamber 59, and the pipe connections 58 and 60. With this system the anode electrolyte may be either continuously or intermittently circulated. In this manner all of the zinc chlorid removed from the fiber is recovered and reutilized.

Any suitable means may be used for the purpose of mechanically separating the electrolytes. Thus for example, the anode electrolyte may be separated from the cathode electrolyte by means of a porous diaphragm of clay, parchment, fiber, felt, fabric, or any other similar substance in any desired form, the only requirement being that the substance is porous, will readily become saturated with the electrolyte on either side thereof, and will readily conduct the current utilized in the electrolytic action. To obtain these results it may be advisable to use a composite diaphragm, using a combination of materials whereby the electrolytes will be separated by a diaphragm having considerable porosity and which, therefore, do not

offer great electrical resistance and which at the same time do not allow excessive diffusion of the electrolytes through their walls.

Obviously the washing process may be accelerated by heating the washing solution by any ordinary means. This heating process may be performed by so arranging the apparatus that the heating is done by the electric current which is used for the electrolysis.

In washing the fiber according to the process herein disclosed, it sometimes occurs that a very small amount of chlorin cannot be readily eliminated by the electrolysis. The chlorin which thus remains is that which is combined with metal radicals which were originally contained in the paper, fiber, zinc chlorid, and wash water as impurities and which are so electropositive that they cannot be precipitated at the cathode by electrolysis. The amount of chlorin thus retained in the fiber and in the wash water depends entirely on the amount and character of the impurities in the paper, zinc chlorid, and water. The main impurities found in these materials are metals such as sodium, potassium, magnesium, calcium, and manganese. For most practical and commercial purposes the amount of chlorids thus retained in the fiber is negligible and may be disregarded. In cases where especially impure materials are employed, it may be desirable to remove these chlorids by additional washing in pure water for a very short interval after the removal of the zinc chlorid by the process disclosed herein.

In order to accelerate the process of deposition such expedients as rotating electrodes, mechanical stirring of the electrolyte by means of stirring devices or compressed air may be used.

In the commercial application of this invention for the washing of fiber it may be advisable in some cases to remove part of the zinc chlorid initially by the customary method of placing the fiber in zinc chlorid solutions of diminishing strengths and then

completing the washing operation by the electrolytic process of this invention. This modification would be desirable for economic reasons.

Obviously this invention is not limited to the specific embodiment thereof herein described, namely, the process of removing zinc chlorid from fiber, but may be used for removing any salt, acid, or alkali which is capable of being separated out by electrolysis from any porous or gelatinous material, the scope of the invention being set forth in the following claims.

What is claimed is:

1. The process of removing salts and other chemicals from porous materials by electrolysis of the wash water between electrodes separated by a porous diaphragm.
2. The process of washing fiber in an acid zinc chlorid solution, the acidity of which is regulated by electrolysis.
3. The process of washing fiber initially in an acid zinc chlorid solution, and then in a neutral zinc chlorid solution the reaction being regulated by electrolysis.
4. The method of washing fiber, which consists in completely removing from the washing solution by electrolytic elimination the zinc and chlorin in substantially equivalent proportions.
5. The method of washing fiber, which consists in immersing the fiber in a heated zinc chlorid solution the concentration of which is diminished at a uniform rate by electrolysis.
6. The process of washing fiber, which consists first in washing the fiber in zinc chlorid solutions of diminishing concentration, and then washing said fiber in a zinc chlorid solution the concentration of which is diminished at a uniform rate by electrolysis.

In witness whereof, I hereunto subscribe my name this 28th day of December, A. D. 1917.

OSCAR LINDER.