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METHOD OF PREPARING OXIDIZED CELLULOSE GAUZE

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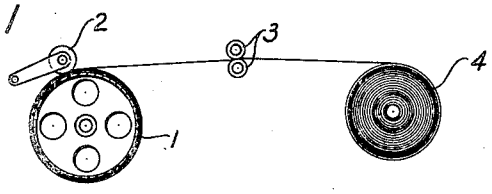
Fig. 1



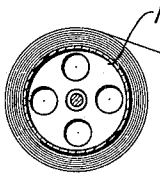


Fig. 2

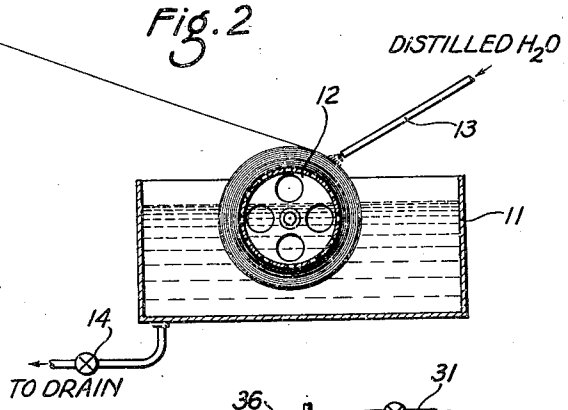


Fig. 3

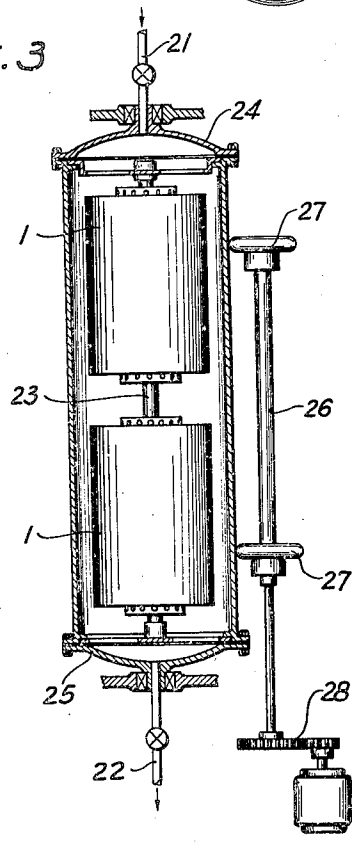
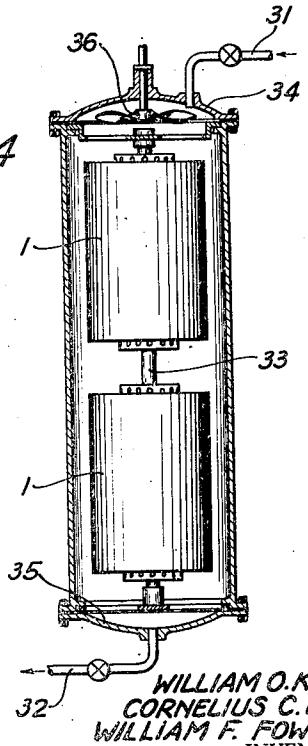


Fig. 4



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METHOD OF PREPARING OXIDIZED CELLULOSE GAUZE

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1 Claim. (Cl. 8—149.2)

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This invention relates to a method of preparing a polyanhydrouronic acid from cellulose gauze in pad form and to polyanhydrouronic acid surgical pads.

Previously cotton as such has been treated with gaseous NO_2 to form an alkali-soluble polyanhydroglucuronic acid. This material has been found to be useful for surgical purposes and in order to adapt the material for those purposes, it has been necessary to spin the oxidized cellulose and form gauze therefrom. We have found, however, that material for surgical purposes is much more conveniently prepared by taking ordinary surgical gauze, forming a pad therefrom, and treating the so-formed gauze pad with gaseous NO_2, thereby forming a pad having a substantial polyanhydrouronic acid content. We have found that this material is conveniently cut up into pads of a size useful for surgical purposes with a minimum of handling. We have found that by this method the gauze is uniformly oxidized providing dripping of any liquid NO_2 or HNO_3 upon the gauze pad is prevented. We have also found that the gauze may be freed of nitrogen compounds without any deterioration thereof if the gauze is quickly contacted with a large excess of water in the washing operation. We have also found that by using oxidized cellulose, such as scraps thereof, for treating water which is to be employed for the washing of oxidized gauze cations may be removed from the water and the gauze which results from the washing operation with water so-treated is substantially free from any mineral matter which might otherwise be added in the washing operation.

One object of our invention is to prepare oxidized cellulose gauze in which the gauze is present in small volume as compared with the cellulose in ordinary oxidation operations but yet a homogeneous product is obtained by oxidizing the gauze in pad form. Another object of our invention is to provide a process for oxidizing cellulose gauze with NO_2 in which a product of uniform shrinkage and carboxyl is obtained by avoiding any dripping of liquid oxidizing or nitrating material upon the cellulose gauze while in pad form. Another object of our invention is to provide a method of washing the cellulose gauze in which no deterioration of the gauze occurs. A still further object of our invention is to remove the cations from water having a mineral content by treating the water with oxidized cellulose, thereby obtaining a water free of cations, which water is useful for washing the gauze prepared in accordance with our process or for any other purpose in which water free of cations is desired.

Our invention involves the forming of cellulose into a pad by laying down layers of cellulose gauze, one upon the other and subjecting that cellulose gauze in pad form to the action of NO_2

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in gaseous form in a closed system for a time sufficient to impart the desired carboxyl content to the cellulose gauze. In this way a pad of polyanhydroglucuronic acid is prepared.

Our invention may best be explained by reference to the drawings illustrating apparatus in which that process may be embodied. Figure 1 is a vertical section of a device by which cellulose gauze may be formed into a pad for treatment by oxidizing gas. Figure 2 is a washing apparatus in vertical section, adapted for the rapid washing of the oxidized cellulose gauze contaminated with nitric acid and adsorbed oxides of nitrogen so as to prevent heat formation. Figure 3 is a plan view of apparatus employed to oxidize cellulose gauze while in pad form by treating the gauze with gaseous NO_2, the apparatus being so arranged that liquid NO_2 or another nitrating or oxidizing liquid does not contact the gauze. Figure 4 is a plan view of a modified apparatus for oxidizing cellulose gauze pads in accordance with our invention. The apparatus of Figure 4 provides a method of oxidizing cellulose gauze in which the oxidizing chamber is held stationary and the oxidizing gas is circulated through and among the layers of cellulose by means of a fan.

In preparing a polyanhydrouronic acid in accordance with our invention cellulose gauze is first formed into a pad. Figure 1 illustrates a mechanism by which a pad of the gauze may be formed. That apparatus consists of a perforated drum 1 having open spaces at the ends whereby gases may circulate through and permeate the gauze pad which is prepared thereon. This drum is contacted with an idle roll 2 so that when the gauze is wound upon the drum, it is smoothed down into uniform layers. Guide rolls 3 are provided to prevent uneven feed of the gauze from the roll of gauze 4 from which it is supplied to the revolving drum. After the gauze is loosely wound upon the perforated roll to form a pad of any desired thickness, the roll 1 is inserted in a tank or chamber where it is centered by means of a stainless steel rod 23 terminating in centering arms at each end. Although the invention is illustrated using two rolls of medium width, it is to be understood that a wide drum and a pad of corresponding width may be used to occupy the length of the oxidizing chamber. Instead, if desired, a plurality of narrow units may be used, the best conditions for operation in any one case being adjusted to the width of gauze which is available. The oxidizing chamber is provided with covers 24 and 25 whereby the rolls are inserted and the chamber is then enclosed so as to be substantially gas tight. In putting the covers 24 and 25 on the chamber, it is desirable that a gasket or some other means be employed to seal the chamber. The chamber is also provided with an inlet 21 and an outlet 22, each of which is

provided with valves so that after the desired conditions are obtained within the chamber, it may be closed off. The oxidizing apparatus may also be provided with rolls **27** rotating upon axis **26** by a rotating mechanism, such as **28** to slowly rotate the tank while in a horizontal position. If desired, the gauze may be oxidized in a stationary oxidizing chamber in which a fan is depended upon for circulating the gaseous NO_2 through the gauze. This chamber may be provided with a stainless steel rod **33** for centering the rolls therein, rod **33** terminating in centering arms at each end, covers **34** and **35** for access to the chamber, inlet **32** and outlet **31** and a fan **36** for circulating the gaseous NO_2 therein. Also, the inside walls of the tank should be smooth so that there are no points therein which would serve as a nucleus for dripping of liquid. If anyone desired to employ a tank of larger diameter, the rate of rotation thereof would necessarily be such that the rate of speed of revolution of the tank would not be too rapid.

We have found that it is important that the cellulose gauze (once washing is commenced) after oxidation, be rapidly treated with an excess of water so as to remove the nitric acid adsorbed by the gauze quickly and to dissipate any heat attendant upon solution of the nitric acid by the water and the reaction of the oxides of nitrogen therewith. A convenient washing apparatus for accomplishing this purpose is illustrated in Figure 2 where the perforated drum containing a layer of gauze which has been oxidized is slowly unwound, the gauze being unwound by means of a partially submerged perforated drum **12** directed towards which is a spray pipe **13** which constantly sprays water onto the gauze as it is wound by the drum **12**, which drum rotates in water within wash tank **11**. Wash tank **11** is also provided with a drain containing a valve **14** whereby used water may be drained from the tank and fresh supplies of water may be added. Also, it is desirable during the washing operation that the influx of water through pipe **13** should be compensated for by draining off of water at a corresponding rate from the tank **11**. It is desirable in the washing operation that either distilled water or water which has been rendered free of cations, such as by treatment with scrap oxidized cellulose, be used.

The preparation of pads of oxidized cellulose gauze may be prepared by winding the gauze upon a perforated drum or some other open structure core so as to form a pad of sufficient thickness to give a homogeneous product and a worthwhile amount of oxidized gauze but not so thick that the penetration of the gauze by the gaseous NO_2 is difficult. After the gauze pad has been formed, the roll or other unit is placed in a chamber and centered so that it is out of contact with the sides of the vessels. It is then desirable to evacuate the tank and draw liquid NO_2 therein so that the liquid NO_2 remains at the bottom of the tank and out of contact with the gauze. The vessel is then sealed shut. The clearance between the gauze pad and the liquid NO_2 should be sufficient that there will be no danger of contact of liquid NO_2 with the gauze at the speeds at which the oxidizing chamber is rotated. The cylindrical tank in which the gauze pad was placed in horizontal position is then rotated for a sufficient time to obtain the desired carboxyl content on the gauze. In the oxidizing procedure the tank should be rotated very slowly, such as 5 to 10 R. P. M. for a tank having a diameter of 15 to 20 inches. Ordinarily the oxidized gauze is soluble in dilute alkali when it has a carboxyl content imparted thereto of 12% or more. This carboxyl content is imparted by running the oxidizing apparatus for 7–16 hours or more. It is to be understood that variation occurs depending upon the amounts of liquid NO_2 which are used. Also, temperature variation may change the time required although it is desirable to carry out the oxidation at or close to room temperature, 20° C., although a few degrees variation in temperature is to be tolerated. If a lower carboxyl content is desired, such as 5, 8, or 10%, the oxidizing time is reduced to give the desired carboxyl under the conditions employed. When the oxidizing process is run for several hours, such as 7 or more (varying somewhat with conditions), a positive pressure builds up within the tank, apparently due to the formation of NO therein which increases the pressure. After the oxidation has been completed, the rotation of the tank may be stopped and the pressure may be released by opening the valve (valve **21** or **22**). After the pressure is released by opening the valve, the chamber may be opened and the drums containing the gauze pad may be removed therefrom. It is preferred upon removal of the oxidized cellulose roll from the oxidizing chamber to allow the roll to stand or to subject it to an air blast, either of which removes a substantial proportion of the NO_2 from the roll. This procedure makes the roll easier to handle and contributes to the convenience of operation. The gauze is then run into a large excess of mineral-free water rapidly to remove the bulk of the HNO_3 therefrom without any heating occurring using the apparatus of Figure 2, described above. After this initial washing, the cellulose gauze is preferably given a number of washes with mineral-free water. By passing the gauze into the presence of a large excess of water as accomplished by the current of water flowing upon the new layer of gauze and immediately immersing the same, any deterioration of the cellulose gauze is avoided.

Instead of carrying out the oxidation in a rotating chamber a stationary chamber may be employed, the liquid NO_2 may be introduced therein, the chamber preferably being in vertical position and a fan may be positioned therein to circulate the gaseous NO_2 in the chamber. In this way circulation of the gaseous NO_2 through the cellulose gauze may be readily obtained. It is desirable that the clearance between the liquid NO_2 and the gauze in a 15-inch diameter tank when run as a closed system be at least 2 inches and preferably about 3 inches. For practical convenience it is desirable that this clearance be no more than 5 inches as otherwise the capacity of the tank is seriously restricted.

The following examples illustrate our invention, but it is to be understood that various conditions described in those examples may be varied according to the desires of the individual operator, without distinguishing from the scope of our invention:

Example 1.—150 feet of 15-inch width cellulose gauze were loosely wound on a 4-inch perforated roll and the ends of the gauze were sewed on so that they remained fixed. The gauze formed a pad upon the roll about 1½ inches thick and had a weight of ¾ of a pound. A second roll of this same type was prepared. These two rolls which had a diameter at this point of about 7 inches were placed in a tank of 15-inch diameter and centered upon a stainless steel rod therein. The tank was evacuated to about 20 mm. of mercury

and 1500 g. (3.3 pounds) of liquid NO_2 were drawn into the tank. Care was exercised throughout that none of the liquid NO_2 or any liquid HNO_3 which may be present touched the gauze. The tank was then sealed and carefully laid horizontally on rollers which rotated at a speed of 8 R. P. M. and the tank was rotated for 16 hours at room temperature. It was found that a positive pressure of about 10 pounds had built up within the tank. This pressure was released by opening the valve with suitable ventilation in the inlet of the tank. The rolls were removed and allowed to stand briefly in the air so as to evaporate off some of the nitrogen oxides present. The gauze was then unwound from the roll upon which it had been padded and was run in single layers onto a water immersed drum during which operation a spray of mineral-free water played upon the gauze. After the gauze had been wound upon a second drum, it was washed by three washes of water in a period of about 10 minutes. The gauze was then washed in thirty changes of de-mineralized water. A current of warm air (40–50° C.) was used for drying the gauze, the latter being passed as a single layer over wooden rolls in contact with the current of warm air which was circulated around the gauze. An oxidized cellulose gauze was obtained which was completely soluble in 1% sodium hydroxide solution.

Example 2.—Two rolls of cellulose gauze were formed consisting of 50 laps each. The gauze was introduced and centered in the oxidizing chamber which was then evacuated to 15 mm. and 1250 g. of NO_2 were added. The tank was then sealed. The fan within the chamber was rotated. The oxidation process was run eighteen hours at room temperature. Pressure was released from inside the vessel and the rolls were then removed, aerated, and the gauze washed and dried as described in the preceding example. To obtain a pad having a substantial content of anhydro-D-glucuronic acid units, the gauze may be fed directly from a roll upon which it is found, or it may be rolled upon a fresh roll as it comes from the drier. For surgical purposes the large pads may be cut into smaller size.

The water which is employed for the washing operation may be distilled water. However, the use of distilled water is unnecessary if the water has been treated so as to remove cations therefrom. For instance, the water employed may be obtained by passing ordinary water through a permutite treatment so that it first has approximately 2–7 P. P. M. of sodium chloride therein. This water is then passed through scrap pieces of oxidized cellulose thereby removing sodium ion from the water. In this form the water is useful for washing the oxidized cellulose gauze. This water may also be employed for any purpose where the absence of cations is desirable and where the presence of a very minute amount of acid is not objectionable. Not only is this treatment valuable for removing alkali metal ions but also water which has been rendered hard due to solution of calcium or magnesium salts may be treated directly with oxidized cellulose or other polyanhydrouronic acids to remove the calcium or magnesium ions therefrom. This is illustrated by preparing a solution of calcium carbonate in

distilling water, such as by forming an aqueous solution of calcium carbonate having a concentration of 0.0622 g. per liter of calcium carbonate. By filtering this solution slowly through a pad of oxidized cellulose which had been washed thoroughly with distilled water, which oxidized cellulose had a carboxyl content of 17–18%, a water is obtained which is completely colorless and has an acid reaction toward methyl orange. A solution of magnesium carbonate in water was formed and upon using the same procedure a colorless, clear filtrate is obtained, acidic in its action toward methyl orange indicator. This property of removing cations from water is characteristic of oxidized cellulose or polyanhydrouronic acids generally, those having a higher carboxyl content being the more effective, per unit weight.

Pads of polyanhydrouronic acid have been found to be eminently suitable for surgical purposes, particularly for the prevention of internal hemorrhage. For instance, in a case of a flow of blood internally the pad, preferably in sterilized condition, is placed against the bleeding surface with the use of enough pressure to prevent the further bleeding at that particular point. The polyanhydrouronic acid pads have the property of dissolving or disintegrating within the body within a short time, which is a matter of days, so that there is no need for removal of the pad which has been used for hemostatic purposes internally, even though the incision of the patient has been closed. It is desirable that these pads have a carboxyl content of at least 12% for the most effective use for hemostatic purposes. Nevertheless, our invention includes pads of polyanhydrouronic acids generally. For instance, pads of NO_2-oxidized starch or alginic acid may be used for hemostatic purposes, it being desirable that the materials employed be highly refined for surgical uses.

We claim:

A method for preparing oxidized cellulose gauze which comprises forming a pad of the cellulose gauze on a perforated drum, centering the drum containing the gauze pad in a cylindrical chamber, introducing liquid NO_2 into the chamber so as to not contact the cellulose gauze pad, sealing the chamber and circulating vapors of the NO_2 therein, whereby only the vapors of the NO_2 contact the gauze until the cellulose has been oxidized to a substantial degree, sousing the oxidized gauze in water free of cations and after thorough washing, drying the gauze while wound several layers deep upon the drum.

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