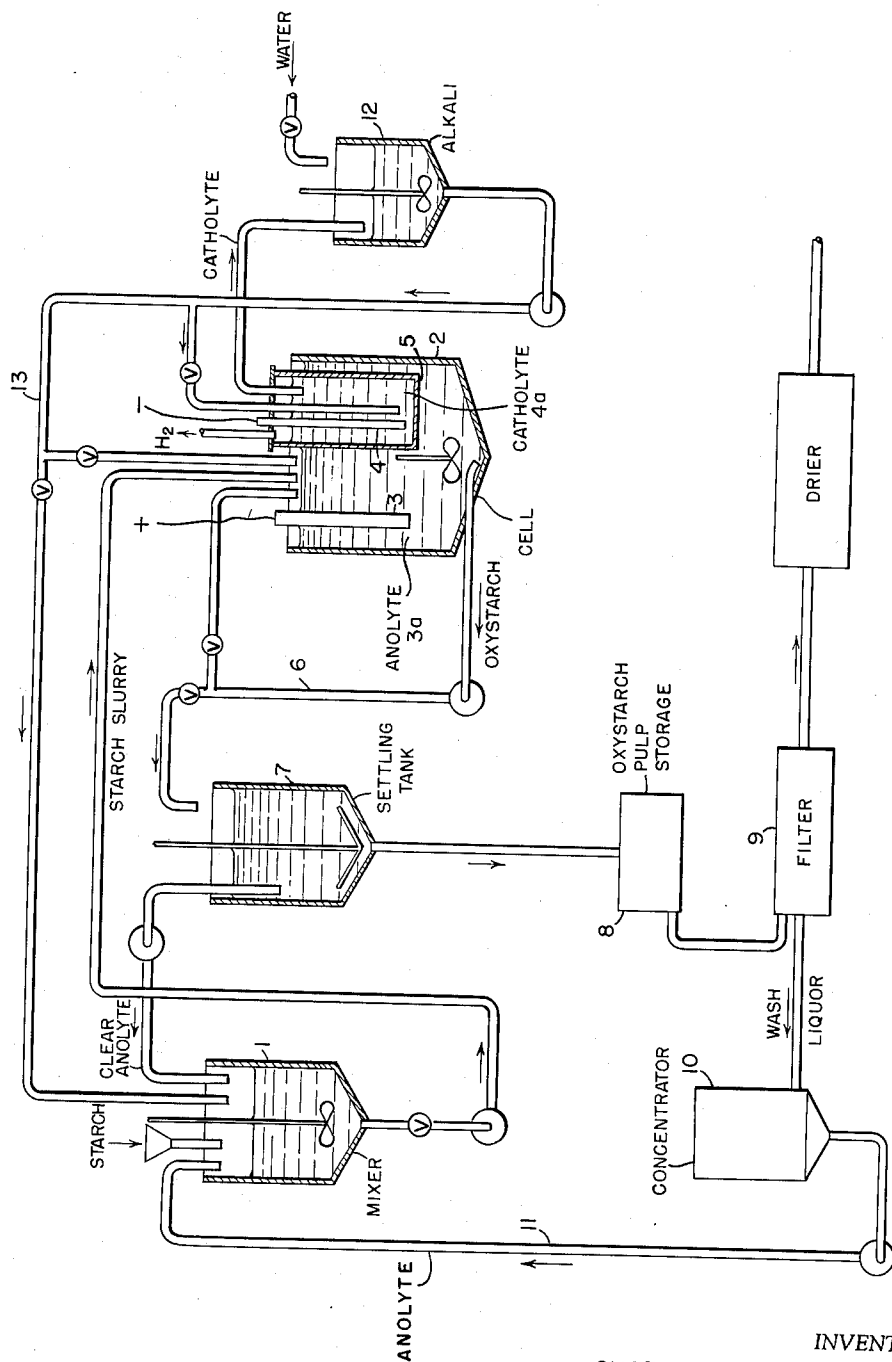


July 19, 1955

C. L. MEHLTRETTER
ELECTROCHEMICAL PRODUCTION OF
PERIODATE OXYPOLYSACCHARIDES
Filed July 23, 1954

2,713,553



INVENTOR
CHARLES L. MEHLTRETTER

BY

2a Seegrist
R. Hoffman
ATTORNEYS

1

2,713,553

ELECTROCHEMICAL PRODUCTION OF PERIODATE OXYPOLYSACCHARIDES

Charles L. Mehlretter, Peoria, Ill., assignor to the United States of America as represented by the Secretary of Agriculture

Application July 23, 1954, Serial No. 445,489

3 Claims. (Cl. 204—79)

(Granted under Title 35, U. S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to a method for producing oxypolysaccharides such as oxystarch, oxycellulose and the like, and is a modification of the electrolytic process described and claimed in the Dvonch and Mehlretter Patent No. 2,648,629. It relates to a method involving the use of an alkaline catholyte, and attendant technological advantages over the prior use of an acidic catholyte.

According to the invention disclosed and claimed in the patent previously mentioned, a polysaccharide material such as starch is treated in an electrolytic cell containing small amounts of periodic acid. An electric current is passed through the system to regenerate periodic acid as it is consumed by reaction with the starch. Thus, the periodic acid, upon reaction with the starch, oxidizes it and is itself transformed to iodic acid. This iodic acid is then regenerated to periodic acid, and the reaction cycle recurs.

In the prior method a compartmented cell is employed using a lead dioxide anode in an anolyte compartment separated by a porous partition from the cathode in an acidic catholyte. At the end of each reaction period the anolyte is separated and the oxidized material recovered therefrom. As disclosed in the patent, it has the technological advantage of requiring only very small amounts of expensive periodic acid.

In the prior invention using a 2 percent sulfuric acid catholyte, sulfate ions enter the anolyte by electrolysis to produce sulfuric acid which builds up on recycling or reuse of the anolyte, and eventually a deleterious excess is created which must be removed. This is technologically difficult because it must be done without loss of iodic or periodic acid. The common precipitants for sulfuric acid also tend to precipitate iodic and periodic acids. Also the accumulated high acidity of the anolyte is a source of possible damage by hydrolysis to the polysaccharide being treated as well as the oxidized polysaccharide.

The present invention is an improvement over this prior patented process, the major feature being the use of an alkaline catholyte. In the present invention the anolyte contains the iodate (or periodate) in salt form or as the free acid, as for example sodium iodate or iodic acid. It also contains an electrolyte salt such as sodium sulfate for the purpose of achieving good conductivity of the solution and thus saving electric current. In the system of the present invention the passage of electric current causes sodium ions to transfer to the catholyte and hence build up its alkalinity. The negative ions of the electrolyte additive transfer to the anode to make the anolyte acid. This acidifying effect of the anolyte is supplemented by the transfer of iodate and periodate ions taking part in the chemical reaction. This acidity which builds up in the anolyte, however, is considerably less than that

2

produced with the sulfuric acid catholyte and is a constant amount for a definite period of oxidation. It may be partially or completely neutralized during the oxidation process or after removal of the oxidation product at the completion of the oxidation. A suitable source of alkali for this purpose is that which is formed in the catholyte chamber or sodium bicarbonate formed by reaction of the alkali from the catholyte with carbon dioxide.

Neutralization of the acidity which is continuously generated in the anolyte occurs during the oxidation by passage of alkali into the anolyte from the catholyte chamber, through the porous partition separating the two. In order for this passage of alkali to be appreciable, it is desirable that a hydrostatic head of pressure be maintained so that flow occurs from the catholyte to the anolyte, i. e. the surface of the catholyte is hence kept higher than the surface of the anolyte. This feature of operation has an additional major purpose in preventing migration of iodate and periodate ion to the catholyte chamber. This latter function is important in preventing loss of the expensive iodate reagent.

The rate of passage of alkali is governed by the hydrostatic pressure and also by the porosity of the partition. By using a partition of proper porosity and maintaining proper hydrostatic pressure from the catholyte to the anolyte it is feasible to induce sufficient transfer of alkali to maintain the pH of the anolyte at the desired value. I prefer, however, to supplement this by recirculation of excess alkali as shown in the flow sheet drawing by recycling to the anolyte a portion of the withdrawn and diluted catholyte. This offers positive control over the hydrogen ion concentration in the anolyte. The latter should be kept below pH 8, preferably pH 2 to pH 5, in order to suppress hydrolysis of the polysaccharide.

The novel system of this invention, when practiced as disclosed herein, is inherently self-sustaining except for the polysaccharide being oxidized. Since the quantity of negative electrolyte ions, for example, sulfate and iodate ions, present in the anolyte will always be the same during the operation of the cell, it follows that the total quantity of electrolyte salt and sodium iodate will remain constant in the recycled liquors except for small additions of these salts to make up for slight losses during processing. Hence, no other chemicals are required by the system, and no build-up of acid in the anolyte can occur because of recycling.

The invention has a further technological advantage, in that high yields of oxidized polysaccharide are obtained because of low hydrolysis loss. Moreover, the recycled anolyte contains fewer impurities because addition of foreign substances to remove accumulated acid as in the prior patent process is not required.

Although it is preferred to carry out the process as discussed above maintaining the pH of the anolyte within the range of pH 2 to pH 8, it has nevertheless been found that the process can be carried out without neutralizing the acidity of the anolyte. It has been found for example that the process can be carried out at a hydrogen ion concentration considerably below pH 2, if desired.

The anolyte of sodium iodate and sodium sulfate solution may also be electrolyzed for several hours to build up the periodate concentration and the solution neutralized with alkali preliminary to the addition of the polysaccharide to the cell. This reduces the time of exposure of the polysaccharide to the acid anolyte and consequently reduces any losses due to hydrolysis.

The accompanying drawing illustrates an embodiment of the process. It shows the flow of materials in a complete process wherein starch is oxidized electrochemically to oxystarch. Starch is fed into mixer 1 where it is slurried with anolyte recycled from the process. From

mixer 1 the starch is fed to the oxidizing cell 2. The cell is provided with anode 3, immersed in anolyte 3a and cathode 4 situated inside porous compartment 5 containing catholyte 4a.

While in the anolyte part of the cell, the starch is oxidized chemically by contact with periodate ions formed by oxidation of iodate ions at the lead dioxide electrodes (anodes), and after oxidation, is removed from the bottom of the cell while suspended in the anolyte and pumped through line 6 to settling tank 7. From the settling tank the settled oxidized starch is removed as a pulp where it may be recovered by any suitable system of recovery. In the drawing it is shown passing to storage tank 8 from which it is led to a filter installation 9 where it is filtered and washed countercurrently to displace the associated anolyte. The recovered anolyte is then sent to a concentrator 10 for evaporating the wash water used and re-establishing the required concentration of anolyte for recycling to mixer 1 through line 11. The anolyte from the settling tank 7 is decanted and used for mixing with the feed starch as previously noted.

The steel cathode 4 is situated in porous compartment 5 as previously noted, and in this compartment the sodium ions which migrate under influence of the electric current are converted to sodium hydroxide. Some of this sodium hydroxide passes to the anolyte through the porous partition and partially neutralizes the acids formed during the electrolysis. Further neutralization to the desired pH is accomplished by the direct addition of alkali to the anolyte, either before or after removal of the oxypolysaccharide by filtration. The alkali used for this purpose may be taken from the excess alkali removed from the catholyte as shown in the flow chart. The alkalinity in the catholyte may be reduced by withdrawing catholyte to vessel 12 where it is adjusted to the required concentration by dilution with water for eventual recycling through line 13 to neutralize anolyte acidity.

The process may be carried out either batch wise or by continuous or semi-continuous operation. As shown in the drawing the recovery of the product may be accomplished by any suitable recovery system, which may involve the use of a drum type filter or centrifuge for the recovery of substantially pure oxystarch.

The conditions of electrolysis used in this invention are substantially those required in the previously patented process. For example, the anolyte is preferably well stirred to maintain homogeneity and a temperature maintained within the range of 5° C. to 50° C. The amount of current required may vary over a rather wide range. It has been found that a current density of from 0.5 to 5 amperes per square decimeter of anode surface gives good results.

The present invention affords a wide range of degree of oxidation of polysaccharides, the degree substantially ranging from 0 to 100 percent. One factor which controls the degree of oxidation is the concentration of iodic acid and sodium iodate. When relatively low concentrations of sodium iodate are employed, longer times are required to obtain a given degree of oxidation. However, the time may be shortened by increasing the current. Furthermore, if relatively large concentrations of sodium sulfate are employed, the oxidation can go longer before it is necessary to neutralize to maintain effective conductivity of the cell.

The following examples illustrate the invention. In each, an electrolytic cell was employed consisting of two cathode compartments of Coors No. 730 size 1 porous clay cups. Other acid and alkali resistant materials, such as asbestos, may also be used to separate the anode and cathode compartments. The cathodes were of steel of about 10 sq. cm. surface area, immersed in the sodium hydroxide solution placed inside the clay compartments. The concentration of alkali in the catholyte was maintained at 2-5 percent throughout the oxidation by dilution

with water. The catholyte surface was higher than the anolyte surface to prevent loss of anions by migration through the diaphragms into the catholyte.

The anode was a lead dioxide battery plate or lead coated with lead dioxide by electrolysis for 8 hours in 6 N sulfuric acid at 3 amperes and was from 60-80 sq. cm. in effective surface area.

Example 1

The two cathode compartments of a three compartment cell were each charged with 20 ml. of 5 percent sodium hydroxide solution. To the anode compartment was added 300 ml. of 2 percent sodium iodate-8 percent sodium sulfate solution and 50 grams of defatted corn starch on a dry basis.

A few drops of octyl alcohol were added to control foaming. After 19 hours of electrolysis at 2 amp. and 5 volts at a temperature of 20° C. the anolyte was filtered and washed free of iodate with water. The white product was then stirred in acetone and filtered. After equilibration at 65 percent r. h. and 20° C. for several days the product weighed 58.5 g. (Moisture 18.47 percent, yield 95 percent.) It analyzed 77 percent dialdehyde starch.

The filtrate was clear and colorless and after neutralization and concentration to the appropriate volume could be recycled in the process.

Example 2

Using the same set-up as in Example 1 and an anolyte consisting of 300 ml. of an aqueous solution of 3 percent sodium iodate and 8 percent sodium sulfate and 50 g. (0.3) defatted corn starch, electrolysis at 2 amp. was carried out for 24 hours at 20° C. Gradual neutralization of the anolyte with 40 percent sodium hydroxide was performed to maintain a pH of 2 to 5 in the anolyte. The oxystarch was isolated as in Example 1, and a product was obtained in a yield of 92 percent which gave an analysis of 97 percent oxystarch on a dry basis. Recovery of iodate and periodate in the filtrate and washings was 98 percent. The catholyte contained no iodate or periodate.

Example 3

Using the same set-up as in the previous examples and an anolyte consisting of 300 ml. of a solution containing 26.5 g. iodic acid, 45 g. sodium sulfate and 162 g. (D. B.) defatted corn starch, electrolysis was carried out at 2 amperes for 23 hours. The oxystarch was isolated as in the previous examples. The product was obtained in a yield of 98 percent, and analyzed 62 percent oxystarch on a dry basis.

I claim:

1. Method for the preparation of oxypolysaccharides comprising subjecting a polysaccharide material to the effect of substantially catalytic amounts of periodic acid in the presence of a cathode and a lead dioxide anode at a temperature of about from 5° C. to 50° C., passing electric current through the system, said periodic acid being continuously transformed to iodic acid by chemical reaction with the polysaccharide material and said iodic acid being continuously regenerated to periodic acid at the anode, and continuing said electric current until substantial amounts of the polysaccharide are oxidized, said cathode being immersed in an alkaline catholyte confined in a catholyte compartment and said anode being immersed in an anolyte, and counteracting the acidity which tends to build up in said anolyte by recycling to said anolyte a portion of withdrawn and diluted catholyte.

2. The method of claim 1 in which the pH of the anolyte is maintained within the range of 2 to 5.

3. The method of claim 1 in which the polysaccharide is starch.

References Cited in the file of this patent

UNITED STATES PATENTS

2,648,629 Dvornich et al. Aug. 11, 1953