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PROCESS FOR ELECTROLYTIC REDUCTION

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11 Claims. (Cl. 204—77)

This invention relates to improvements in processes for the electrolytic reduction of monosaccharide solutions. More particularly, it relates to improvements in processes such as those set forth in United States Letters Patent to H. J. Creighton, Numbers 1,612,361 and 1,990,582.

The electrolytic reduction described in the above-identified patents is carried out in a cell having a catholyte comprising an aqueous solution of one or more monosaccharides and sodium sulphate, or other suitable compounds of the alkali or alkaline earth metals. The catholyte is in contact with a mercury or amalgamated metal cathode, and is separated from the anolyte, comprising an aqueous solution of sulphuric acid, sodium sulphate or other suitable electrolyte, by a porous diaphragm. The anode in contact with the anolyte, may consist of chemical lead or lead coated with lead dioxide. When electric current is passed through the cell, sulphate ions are discharged at the anode and subsequently react with the water forming oxygen and sulphuric acid adjacent the anode. In the catholytic section of the cell, sodium atoms migrate to the cathode and unite with the mercury, forming sodium amalgam, which subsequently decomposes the water, forming nascent hydrogen and sodium hydroxide. The nascent hydrogen formed in this way reduces the monosaccharide.

The reduction of solutions of sugars or composite sugar-bearing mixtures which have been rendered capable of conducting electric current in accordance with the foregoing, has been attended with low rates of reduction, varying unaccountably at times to extremely low rates of reduction.

An object of the invention is to provide an improved process for the electrolytic reduction of monosaccharides.

Another object of the invention is to provide greater efficiency and higher and more uniform rates of reduction in the electrolytic reduction of monosaccharides. Other objects will hereinafter more fully appear.

In practising the process of reducing monosaccharides certain variations of the process described in the said Creighton Patents have been introduced. It has been customary to use a catholyte comprising an aqueous solution of one or more monosaccharides containing as an electrolyte an alkali metal salt, usually sodium sulphate. From the standpoint of availability as well as satisfactory performance, sodium sulphate is preferred although other alkali metal salts which do not contain objectionable anions can be used. The alkaline earth metal salts have not been as readily available and have other objectionable features, e. g. the insolubility of some of their salts. For an alkaline reduction the catholyte has usually added to it also a small amount of alkali such as sodium hydroxide. It is also possible to reduce monosaccharides while maintaining the catholyte in an acid condition instead of in alkaline condition. As a cathode there is used either an amalgamated metal plate, such as amalgamated lead or amalgamated zinc, or an unamalgamated zinc plate.

According to the present invention it has been discovered that the presence of magnesium, even in very small amounts, exerts a surprising hindering effect on the reducing process. Particularly the presence of more than about 7.0 parts per million magnesium based on the total solids in the catholyte causes a very sharp drop in the efficiency of the reducing process. This hindering effect has been noted particularly in the case of the reduction of glucose and inverted cane sugar. The hindering effect is independent of the nature of the cathode and has been observed both with amalgamated and unamalgamated cathodes. Furthermore, the deleterious action is not limited to alkaline catholytes but is also noted in the case where the catholyte is maintained in an acid condition.

In the case of glucose reduction where magnesium is present as about 7.0 parts per million of total solids, for example, the reduction is approximately 50% more efficient than in the case where 13 parts per million magnesium are present. A further improvement in the rate of reduction is noted where the amount of magnesium is not more than about 4.0 parts per million and in this case it has been found that the efficiency is approximately double that found in a reduction where the catholyte contains about 13.0 parts per million magnesium. Again, where the magnesium content is further cut down to not more than about 1.6 parts per million a further improvement in the rate of reduction is noted. Below this concentration of magnesium the rate of reduction is approximately constant.

In the case of the reduction of inverted cane sugar and the other monosaccharides, the same general phenomenon appears.

Although magnesium as such is not added to the catholyte before or during the reduction, it was discovered that such small amounts as those found harmful were frequently introduced as impurities in either the original ingredients of the catholyte or materials added from time to

time during the reduction. For example, the sodium sulphate or other alkali metal salt used as the electrolyte in the catholyte frequently contains small amounts of magnesium salts as impurities. The sugars themselves may be contaminated with small quantities of magnesium. The water used in making up the catholyte frequently contains magnesium, particularly where it has not been purified by distillation prior to its use. It is the usual practice during the course of the reduction to control the pH of the catholyte by the addition of alkali or acid and the magnesium content was found to be increased frequently due to the presence of this element as an impurity in the base or acid employed. A further source of magnesium was found to be the porous diaphragm or other parts of the cell in which the reduction was conducted.

It is necessary therefore that the materials making up the catholyte and anolyte as well as all parts of the electrolytic cell which may come in contact with the catholyte during the reduction process, be sufficiently free of magnesium so that the catholyte does not become contaminated to the extent which has been found harmful.

In the table, examples are given showing the increase in time required for reduction of 90% of the sugar at amalgamated lead cathodes with increased contamination of the catholyte with magnesium. In the examples of the table, the initial composition of the aqueous catholyte in grams per liter was:

Glucose	325
Na_2SO_4	75
NaOH	10

The glucose was reduced to a mixture of sorbitol and mannitol. In each run the current density was reduced from 1.07 to 0.54 amp./dm.^{2} at the time approximately 65% of the sugar was reduced. The catholyte temperature was maintained throughout the reduction at about 68° F.

Table

Examples	Mg. present in catholyte, ppm. of total solids	Time of reduct. at 1.07 amp. per dm.^{2}, hrs.	Hrs. reduct. to 90% sug. red.	Alcohol, yield, per-cent of theory	Current efficiency (corr. for yield) at 90% sug. red
1	0.81	37	74.4	91.3	53.7
2	0.91	39	71	90.2	53.4
3	1.00	38	76	91.6	52.2
4	1.19	36	76	88.8	51.5
5	1.56	39	77	94.9	53.1
6	2.31	38	86	92.8	49.1
7	4.00	37	88	93.5	49.6
8	7.19	42	117	90.6	37.0
9	13.56	70	157	89.1	25.5

It can be seen from the foregoing table that when the catholyte contains more than about 7.0 parts per million magnesium on the basis of total solids, a decided slowing up of the rate of reduction results. Thus, in Example 8 a magnesium content of 7.19 parts per million allowed a current efficiency of 37.0% to be obtained in the reduction, whereas in Example 9, 13.56 parts per million magnesium lowered the current efficiency to 25.5%. Example 8 was therefore nearly 50% better than Example 9 as to current efficiency. In Example 7 4.0 parts per million magnesium allowed a current efficiency of 49.6% to be obtained, which is nearly double the efficiency of Example 9. A further improvement in current efficiency is noted in Example 5 wherein the magnesium content was 1.56 parts per million. Below this value of 1.56 parts per million there was no substantial improvement in current efficiency.

According to the invention, therefore, the magnesium content is limited to not more than about 7.0 parts per million. More specifically, 4.0 parts per million shows very high efficiency and for the best current efficiency not more than about 1.6 parts per million magnesium should be placed as the tolerance.

By placing a tolerance of 1 part per million maximum magnesium content on the ingredients such as sugar, caustic soda, sodium sulphate, and 0.3 part per million maximum magnesium content on sulphuric acid employed in the control of the pH of the catholyte and in making up the anolyte, and further by selecting material for cell construction which does not contaminate the catholyte with magnesium whereby the catholyte is maintained throughout the reduction free from magnesium in an amount greater than 1.6 parts per million of total solids, excellent rates of reduction have been obtained.

Although in the table the advantages of the present invention have been pointed out particularly with respect to the reduction of glucose, it is to be understood that it applies also to the reduction of monosaccharides generally, such as invert sugar, fructose, mannose, galactose, sorbose, xylose, etc.

The present application is a continuation in part of my application Ser. No. 180,533.

In the following claims where I have used the term "alkali metal salt" I mean to include all of the alkali metal salts which do not have objectionable anions. For example, the sulphates are satisfactory while, for example, chlorides and nitrates have too corrosive an effect on the anodes for practical use and may be considered objectionable. "Objectionable anions" therefore refers to any anion which interferes with the reduction of the sugar or which attacks the anode to an undesirable extent.

The invention has been described with reference to the examples but the invention is to be taken as limited only by the scope of the following claims.

I claim:

1. The process for the preparation of polyhydric alcohols which comprises electrolytically reducing an aqueous monosaccharide solution containing an alkali metal salt as the catholyte in a diaphragm cell, and maintaining said catholyte free from magnesium in amount greater than about 7.0 parts per million based on the total solids during the reduction.

2. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqeous glucose solution containing an alkali metal salt as the catholyte in a diaphragm cell, and maintaining said catholyte free from magnesium in amount greater than about 7.0 parts per million based on total solids during the reduction.

3. The process for the preparation of polyhydric alcohols which comprises electrolytically reducing an aqueous monosaccharide solution containing an alkali metal sulfate as a catholyte in a diaphragm cell, and maintaining said catholyte free from magnesium in amount greater than about 7.0 parts per million based on total solids during the reduction.

4. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqueous glucose solution containing an alkali metal sulfate as the catholyte in a dia-

phragm cell, and maintaining said catholyte free from magnesium in amount greater than about 7.0 parts per million based on total solids during the reduction.

5. The process for the preparation of polyhydric alcohols which comprises electrolytically reducing an aqueous monosaccharide solution contaning an alkali metal sulfate as the catholyte in a diaphragm cell having an amalgamated metal cathode, and maintaining said solution free from magnesium in amount greater than about 7.0 parts per million based on total solids during the reduction.

6. The process for the preparation of polyhydric alcohols which comprises electrolytically reducing an aqueous monosaccharide solution containing an alkali metal salt as the catholyte in the diaphragm cell, and maintaining said catholyte free from magnesium in amount greater than about 4.0 parts per million based on total solids during the reduction.

7. The process for the preparation of polyhydric alcohols which comprises electrolytically reducing an aqueous monosaccharide solution containing an alkali metal salt as the catholyte in the diaphragm cell, and maintaining said catholyte free from magnesium in amount greater than about 1.6 parts per million based on total solids during the reduction.

8. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqueous glucose solution containing sodium sulfate as the catholyte in a diaphragm cell, and maintaining said solution free from magnesium in amount greater than about 4.0 parts per million based on total solids during the reduction.

9. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqueous glucose solution containing sodium sulfate as the catholyte in a diaphragm cell, and maintaining said solution free from magnesium in amount greater than about 1.6 parts per million based on total solids during the reduction.

10. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqueous glucose solution containing sodium sulfate as the catholyte in a diaphragm cell having an amalgamated lead cathode, and maintaining said solution free from magnesium in amount greater than about 4.0 parts per million based on total solids during the reduction.

11. The process for the preparation of hexahydric alcohols which comprises electrolytically reducing an aqueous glucose solution containing sodium sulfate as the catholyte in a diaphragm cell having an amalgamated lead cathode, and maintaining said solution free from magnesium in amount greater than about 1.6 parts per million based on total solids during the reduction.

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