

UNITED STATES PATENT OFFICE

2,303,210

ELECTROLYSIS OF SUGARS

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No Drawing. Application October 20, 1939,
Serial No. 300,375

10 Claims. (Cl. 204—77)

The present invention relates to improvements in a process for the electrolysis of sugars.

The invention is broadly concerned with an improvement in the electrolytic process for reducing reducible sugars such as glucose and the like in accordance with the teachings of the patent to Creighton No. 1,990,582. In this process an electrolytic diaphragm cell is employed in which the cathode compartment is separated by a permeable diaphragm from the anode compartment. This patent teaches the use of an amalgamated lead cathode for use in the cell. The catholyte which is in contact with the cathode is an aqueous solution of the sugar to be reduced and a suitable electrolyte. The electrolyte is preferably an alkali metal salt such as sodium sulfate although other alkali metal salts can be used provided that the anions are not injurious to the reduction or to the cell equipment. The anolyte comprises an aqueous solution of an acid or other suitable electrolyte and is in contact with an anode which is formed of chemical lead or other suitable material.

It has been noted that with amalgamated lead cathodes in the case of reductions in which the catholyte is maintained in a condition of low alkalinity, for example under 10 g. NaOH per liter of catholyte or its equivalent, very poor rates of reduction and poor current efficiency are obtained as compared with reduction at a similar cathode at high alkalinity. Similarly poor rates of reduction are noted with amalgamated lead cathodes where the catholyte is maintained in a weakly acid condition, such as 0.5 to 1.5 g. H_2SO_4 per liter of catholyte. The explanation of this phenomenon is unknown at the present time but amalgamated lead cathodes has entailed considerable loss of time and current efficiency in low alkalinity reductions. For many purposes low alkalinity reductions are desirable and this disadvantage just described makes this type of reduction needlessly expensive as compared to the high alkalinity reductions. When the rate of reduction and the current efficiency thereof fall there is not only the factor of loss of electric power but also the output of a given group of cell equipment is curtailed.

The present invention has therefore for its object the improvement of the process for the electrolysis of sugars at low catholyte alkalinity or low acidity and with amalgamated lead cathodes.

It has been discovered that the addition of small amounts, for example 0.1 to 10.0 or preferably 2.0 to 4.0 g. per liter of catholyte, of zinc sulfate, speeds up the reduction at low alkalinity

or low acidity with a lead cathode and cuts the reduction time substantially in half. The current efficiency is correspondingly improved.

The addition of zinc sulfate to a catholyte appears to be of value principally at low alkalinity, that is, not substantially more than the equivalent of 10 g. NaOH per liter of catholyte and preferably from 0.1 to 2.0 g. NaOH per liter of catholyte, and with amalgamated lead cathodes. At higher alkalinities the lead cathodes have the property of reducing with good efficiency without the aid of the zinc sulfate and therefore little advantage is gained by using it. It has been noted that an amalgamated lead cathode which has been used in a reduction in which zinc sulfate was incorporated into the catholyte retains a higher efficiency for reduction at low alkalinity in the next succeeding several runs even though no further zinc sulfate is added in the subsequent runs. The invention also contemplates employing this effect and adding zinc sulfate to the catholytes, for example in alternate runs, or the addition of very small quantities of zinc sulfate in each run.

The invention will be better understood from the following examples which compare with the results obtained in practising the invention with results obtained otherwise. The invention is not limited to the details of the examples nor is it restricted to the electrolysis of glucose but is also applicable to the electrolysis of other reducible sugars such as inverted cane sugar, fructose, mannose, lactose and the like.

In the tables which follow, the data are listed under abbreviated headings which refer to the following:

"Con." is the initial concentration of sugar in the catholyte in grams per liter and unless otherwise noted will refer to the concentration of glucose.

"Alk." is the alkalinity of the catholyte in grams NaOH per liter.

"Ratio" is the quotient of the area of the cathode in square decimeters divided by the number of liters of catholyte.

"C. D." is the current density in amperes per square decimeter of cathode area.

"T." is the temperature of the catholyte in degrees Fahrenheit.

"90% S. R." is the time in hours after the start of the reduction at which 90% of the sugar is reduced.

"99% S. R." is the time in hours after the start of the reduction at which 99% of the sugar is reduced.

"ZnSO₄" represents the quantity of ZnSO₄·7H₂O added to the catholyte.

By "P. N." as used herein is meant an index of sorbitol content of sorbitol-containing material. This index is determined by crystallizing sorbitol from sorbitol-containing products in the form of a sorbitol-pyridine complex, filtering the crystalline complex, adding water to it to decompose the complex into pyridine and sorbitol, driving off the pyridine by vacuum distillation with water, dehydrating the sorbitol residue and weighing it as sorbitol. The procedure is specific for sorbitol since no other polyhydric material, such as sugar,

served in two reductions more than the cathode in Example 1 and the reduction time and current efficiency of Example 2 are therefore better than those of Example 1.

A very good rate of reduction and current efficiency are found in Example 3 where zinc sulfate was added in the proportion of 4 g./l. of catholyte instead of 2 g./l. as in the other three examples.

For the sake of comparison the following examples illustrate reductions comparable in all respects to the reductions of Examples 1 to 4 except that no zinc sulfate was included in the catholyte.

Table 2

Ex.	Conc.	Alk.	Ratio	C. D.	T.	90% S. R.	99% S. R.	ZnSO ₄	P. N.	C. E.
5	325	0.5-1.5	2.0	1.0	68	132	258	0	70.5	17.8
6	325	0.5-1.5	2.0	1.0	69	105	182	0	71.5	24.3

mannitol, etc., exhibits the same behavior with pyridine. The pyridine number is the weight of sorbitol crystallized from anhydrous pyridine as above multiplied by 100, and divided by the weight of the sample, (ash, moisture and sugar free). The pyridine number for pure sorbitol is about 95. The preparation of the sorbitol pyridine complex and its treatment to free sorbitol therefrom is described by Strain in J. Am. Chem. Soc., vol. 56, page 1757/(1934). The pyridine number of a sorbitol-containing product is an index of its crystallizing tendency from relatively highly concentrated aqueous solutions. The higher the pyridine number the greater the crystallizing tendency. The greater the complexity of the sorbitol-containing product the less its crystallizing tendency and vice versa.

"C. E." is the current efficiency up to 99% sugar reduced corrected for the yield of polyhydric alcohol.

In each of the following examples the catholyte was an aqueous solution containing 325 g. of glucose per liter and 75 g. of sodium sulfate per liter. The anolyte at the start was an aqueous solution of 300 g. per liter of sulfuric acid. The anode was 10 lb. chemical lead plates and anode area was 8.1 square decimeters. The cathode area was 9.0 square decimeters. The diaphragm was of porous alundum. The alkalinity indicated in the examples was maintained by the addition of suitable quantities of alkali or acid from time to time during the reduction.

Table 1

Ex.	Conc.	Alk.	Ratio	C. D.	T.	90% S. R.	99% S. R.	ZnSO ₄	P. N.	C. E.
1	325	0.5-1.5	2.0	1.0	68	96	165	2 g./l.	72.5	27.5
2	325	0.5-1.5	2.0	1.0	68	80	133	2 g./l.	70.5	34.6
3	325	0.5-1.5	2.0	1.0	68	77	124	4 g./l.	70.0	36.5
4	325	0.5-1.5	2.0	1.0	69	73	113	2 g./l.	70.0	39.9

The above examples illustrate typical reductions at low alkalinity and with amalgamated lead cathodes. The variations in the time of reduction, current efficiency and P. N. are traceable to a considerable extent to individual differences in the cathodes. For instance, Example 4 used a much older cathode than any of the other examples and the efficiency was higher in this run than in any of the others. Runs 1 and 2 further serve to show the effect of different cathodes since Example 2 used the same cathode as Example 1 but represents its performance two runs later. In other words, the cathode of Example 2 had

The effect of the zinc sulfate addition is clearly brought out by a comparison of these two tables. Example 5 is a normal low alkalinity reduction at a fairly new amalgamated lead cathode. It took 258 hours to reduce 99% of the sugar and a current efficiency of only 17.8% was obtained. Compare Example 1 in which a similar cathode was used but 2 g./l. of zinc sulfate were added. In Example 1 only 165 hours were required to reduce 99% of the sugar and the current efficiency was 27.5%. Thus, the addition of zinc sulfate gave a high rate of reduction even in a run employing a fairly new, hence relatively inefficient, cathode. Example 2 shows an even better run in which 133 hours were required to reduce 99% of the sugar and the current efficiency was 34.6%. In Example 3 where 4 g./l. of zinc sulfate were added a further improvement was noted in that only 124 hours were required to reduce 99% of the sugar and a current efficiency of 36.5% was had. Example 6 used an old amalgamated lead cathode and relatively better results were had than with Example 5. Example 4 used an old cathode comparable to that of Example 6 and the current efficiency was 39.9% as against 24.3% where no zinc sulfate was employed.

The quantity of zinc sulfate that will be used in a given reduction is subject to considerable variation. Usually it will be desired to use the least possible amount which will give efficient improvement in rate of reduction and current efficiency. Therefore, certain of the following

claims refer to "a small but efficient quantity of zinc sulfate" by which is meant a quantity sufficient to produce a substantial improvement in the rate of reduction as compared to the rate in an otherwise similar reduction from which the zinc sulfate is omitted. In general, however, it can be said that preferably zinc sulfate is added to the catholyte as from 0.1 g./l. to 10.0 g./l. to obtain the desired improvement. While the examples show the use of the hydrate ZnSO₄·7H₂O it will be understood that this is only a convenient form in which to use the salt and that any

other means for introducing a zinc sulfate into the catholyte is to be considered the equivalent.

The invention is not limited to the details of the examples but is limited only by the scope of the following claims.

I claim:

1. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, and a small but sufficient quantity of zinc sulfate to increase substantially the rate of reduction of the sugar; and passing an electric current between said anode and cathode and through said sugar solution to reduce said sugar to polyhydric alcohol.

2. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, a quantity of an alkali equivalent to not more than 10 grams sodium hydroxide per liter of solution, and from 0.1 to 10 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said sugar solution to reduce said sugar to polyhydric alcohol.

3. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of glucose, an alkali metal salt as electrolyte, from 0.1 to 2.0 grams of alkali per liter of solution, and from about 2 to 4 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said glucose solution to reduce said glucose to polyhydric alcohol.

4. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of glucose, an alkali metal sulfate as electrolyte, from 0.1 to 2.0 grams of alkali per liter of solution, and from about 2 to 4 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said glucose solution to reduce said glucose to polyhydric alcohol.

5. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, from 0.1 to 2.0 grams of alkali per liter of solution, and from 0.1 to 10 grams of zinc sulfate per liter of solution; and passing an electric current between said anode

and cathode and through said sugar solution to reduce said sugar to polyhydric alcohol.

6. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of glucose, an alkali metal salt as electrolyte, from 0.1 to 2.0 grams of alkali per liter of solution, and from 0.1 to 10 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said glucose solution to reduce said glucose to polyhydric alcohol.

7. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, a small quantity of an acid, and from about 2 to 4 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said sugar solution to reduce said sugar to polyhydric alcohol.

8. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of glucose, an alkali metal salt as electrolyte, a small quantity of an acid, and from 0.1 to 10 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said glucose solution to reduce said glucose to polyhydric alcohol.

9. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, and from 0.1 to 10 grams of zinc sulfate per liter of solution; passing an electric current between said cathode and anode and through said sugar solution to reduce said sugar to polyhydric alcohol; and thereafter employing said cathode in a subsequent reduction of a reducible sugar in an aqueous solution with an alkali metal salt as electrolyte but without the addition of zinc sulfate.

10. A process for the production of polyhydric alcohols in an electrolytic cell having an anode and a cathode respectively in anode and cathode compartments separated by a permeable diaphragm, said cathode comprising amalgamated lead; which comprises maintaining in the cathode compartment and in contact with said cathode an aqueous solution of a reducible sugar, an alkali metal salt as electrolyte, and from about 2 to 4 grams of zinc sulfate per liter of solution; and passing an electric current between said anode and cathode and through said sugar solution to reduce said sugar to polyhydric alcohol.

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CERTIFICATE OF CORRECTION.

Patent No. 2,303,210.

November 24, 1942.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 36, after "but" insert --the fact has been observed and the use of--; and second column, line 26, after "compare" strike out "with"; line 37, for "Con." read --Conc.--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of February, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.