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ELECTROLYTIC PRODUCTION OF FATTY ACIDS

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1

This invention relates to industrial recovery processes and is more particularly concerned with the recovery of the acid and base from sodium acetate and other salts of lower fatty acids.

In a number of industrial processes considerable quantities of sodium acetate are made available often in the form of aqueous solutions. For example, in the saponification of cellulose acetate, caustic soda is commonly employed and results in the production of a solution of sodium acetate and the industrial value of this process is affected very considerably by the cost of the necessary recovery of the caustic soda and the acetic acid for further use.

According to the present invention caustic soda and acetic acid are recovered from aqueous solutions of sodium acetate by electrolysis such a solution to produce hydrogen and oxygen, the electrolysis being carried out under conditions which prevent admixture of the electrolytic surrounding the anode with that surrounding the cathode and which avoid the destruction of the acetic acid formed by the electrolysis.

From the very considerable amount of published data on the electrolysis of sodium acetate it would appear that except in very dilute solutions it is usually impossible to obtain liberation in recoverable form of acetic acid equivalent to the amount of electricity expended, this result being due to the fact that there is danger of ethane and carbon dioxide formation as a result of the decomposition of acetate ions liberated at the anode. This difficulty can be minimised by working at elevated temperatures and using low current densities. In general, it has been found desirable to use a temperature of at least 80° C. but temperatures much above 95° C., also lead to the destruction of acetic acid probably by the reaction between the acetic acid and oxygen produced in the electrolysis. Certainly at such high temperatures carbon dioxide begins to appear in increasing amounts in the gas recovered from the anode compartment and accordingly the preferred range of temperature is from 80–95° C. As previously indicated a low current density is to be preferred and excellent results have been obtained using from 1.5–2.5 amps. per square decimetre of anode surface although somewhat higher current densities can be employed if desired.

Of paramount importance from the point of view of an efficient recovery of acetic acid is the nature of the anode material. While platinum electrodes can be used, commercial operation demands the use of a somewhat cheaper material

2

if an expensive installation is to be avoided and the normally used carbon electrodes are quite unsuitable since it is usually found that a considerable quantity of carbon dioxide appears in the anode gas when for example, a graphite anode is used. Usually it is considered that the metals of the iron group are on a par as regards their suitability as electrodes. In contradistinction to this our experience has been that nickel is far superior to iron since the latter tends to go into solution with a considerable formation of basic ferric acetate. With nickel this can be avoided although here again care must be taken to avoid conditions likely to lead to attack of the anode and in particular it is best to avoid using a potential difference across the cell substantially above that of the over-voltage of the cell. In practice it has been found possible to operate satisfactorily from a low voltage supply of say 6 volts, the current through the cell being controlled by means of a suitable rheostat. On the other hand, the cathode may be of almost any material which is not attacked by the electrolyte and satisfactory results have been obtained with both iron and zinc.

As previously indicated, steps are taken to ensure that the electrolyte in the neighbourhood of the anode does not mix with that in the neighbourhood of the cathode. This result can be achieved by the use of a suitable electrolyte bridge, for example a bank of capillary tubes connecting separate vessels or compartments containing the anode and cathode electrolytes, but in practice it is simplest to use a suitable porous diaphragm. Thus, the anode may be immersed in electrolyte contained in a vessel constructed of a porous material, such as unglazed porcelain or earthen-ware, this vessel itself being immersed in an outer vessel containing the cathode electrolyte and it is convenient to use a metallic outer vessel, for instance of iron or zinc, and to make this vessel the cathode. Such an arrangement can be provided with a cover which will seal the spaces above the two portions of electrolyte from each other and from the atmosphere. By means of suitable unions on such a cover the hydrogen and oxygen produced can be separately removed to storage. On the other hand, a diaphragm of any other suitable material, for instance an asbestos diaphragm, may be used if desired. With a suitable diaphragm and the provision of heating means and outlet and supply pipes for withdrawing and replacing electrolyte, a plant generally similar to those commonly used for the electrolytic manufacture of hydrogen and oxygen

3

may be employed in carrying out the process of the invention.

The invention is of great value in the recovery of the acid and base from solutions of sodium acetate of substantial concentration, for instance 20 to 30% or even more, e. g. 40%–50%, but the invention is not limited in this respect and may be applied to the treatment of weaker solutions, e. g. 5 or 10% solutions. In practice it has been found that it is uneconomic to attempt to affect complete separation of the acidic and basic radicals by electrolysis. Electrolysis may be carried out until the anode electrolyte reached a composition corresponding to a solution of acid sodium acetate, i. e. until for each initial two molecules of sodium acetate the electrolyte contains one molecule of titratable acetic acid, with a high degree of efficiency both as regards the recovery of acid and base and as regards the gases produced. If the electrolysis be continued beyond this stage the current efficiency, in so far as separation of acid and base is concerned, falls off rather rapidly. Accordingly the anode electrolyte at least should be replaced immediately or soon after this stage is attained but the cathode electrolyte may, if desired, be retained in the cell until it consists of a solution of caustic soda only. The removal of the electrolytes after electrolysis can, if desired, be carried out without interrupting the process, fresh electrolyte being added to replace that removed. This operation may be performed continuously by arranging for continuous flow of fresh electrolyte into the anode and cathode compartments of the cell with a continuous removal of electrolytes from the compartments at points remote from the entry of fresh electrolyte. Acetic acid can be recovered from withdrawn anode electrolyte by distillation, water first coming over and then, at a higher temperature, acetic acid resulting from the decomposition of the acid sodium acetate, a residue of normal sodium acetate remaining which can be returned to the process. If desired the electrolyte may be concentrated only sufficiently for acid sodium acetate to crystallize on cooling the mother liquor being returned to the process with sodium acetate left after decomposition of the acid salt recovered by crystallization.

While the invention has been described more particularly in connection with the recovery of caustic soda and acetic acid from solutions of sodium acetate with simultaneous production of hydrogen and oxygen the invention is not limited in this respect and may be applied similarly to the treatment of solutions of other salts of lower fatty acids for instance, propionates and butyrates not only of sodium but also of other metals, more particularly metals forming strongly basic oxides, including the other alkali metals, e. g. potassium and lithium and the earth alkali metals, e. g. calcium, and also magnesium. Where, as in the case of calcium and magnesium the liberated base is not of high solubility a precipitation of this base will occur and it is most convenient in such circumstances to arrange for a draw-off at the bottom of the cell for the removal of the sludge of base produced. An important point in connection with the electrolysis of solutions of salts of bases of low solubility is the nature of the cathode employed. It has been found in practice that unless suitable precautions are taken the cathode becomes coated with the base so that the internal resistance of the cell rises but that this disadvantage can be avoided by interposing between the cathode and electrolyte a porous screen, for example, of the same nature as that used for separ-

4

ating the anode and cathode electrolytes and filling the space between the cathode and the screen with an electrolyte free from the insoluble base.

The following example illustrates the invention as applied to the production of acetic acid and caustic soda from aqueous sodium acetate:

Example

Aqueous sodium acetate of about 20% concentration is subjected to electrolysis in a battery of cells having iron cathodes and nickel anodes contained in compartments separated from each other by porous unglazed porcelain diaphragms. The cells are so constructed that the free spaces above the electrolytes in the anode and cathode compartments are sealed from each other and from the atmosphere and are connected to separate oxygen and hydrogen mains respectively. Means are provided for withdrawing electrolyte from the top of the anode compartments and for withdrawing separately electrolyte from the top of the cathode compartments. Means are also provided for supplying fresh electrolyte to the bottoms of both anode and cathode compartments separately. Heating means are provided arranged so as to maintain the temperature of the cells at about 87–90° C.

The electrolysis is conducted using a current density of 1.75–2.5 amperes per square decimetre of anode surface area, and the electrolysis is continued for a period of about an hour with the electrolyte initially charged to the cells. Thereafter a slow feed of fresh electrolyte is supplied to the anode compartments while a corresponding amount of liquid is removed. The withdrawn anode electrolyte contains a substantial proportion of sodium acetate in the form of acid sodium acetate, for example as much as 90% or even more of the sodium acetate may be in the acid form. This anode electrolyte is concentrated by evaporation until the acid sodium acetate crystallises on cooling, and can be separated and subjected to distillation for the recovery of acetic acid. The residual sodium acetate from this operation and also the mother liquor from the crystallisation are returned to the process in the form of aqueous sodium acetate of about 20% concentration.

The cathode electrolyte is allowed to remain in the cell until the concentration of caustic soda has risen substantially, e. g. until 75% or more, for example 80 or 90% of the sodium acetate initially charged, is in the form of caustic soda. Thereafter the cathode electrolyte is replaced by running off the electrolyte while simultaneously feeding in fresh sodium acetate solution. This operation may conveniently be conducted at intervals of 2–3 hours or more according to the concentration of alkali which it is desired to obtain in the withdrawn liquor.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the production of a free fatty acid of formula $R.COOH$, where R is an alkyl group containing from 1 to 3 carbon atoms, from an alkali metal salt thereof, which comprises electrolyzing an aqueous solution of the salt of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of fatty acid for each initial two molecules of fatty acid

5

alkali metal salt in the form of the acid alkali metal salt, removing anolyte and recovering fatty acid by decomposition of the acid alkali metal salt.

2. Process for the production of a free fatty acid of formula $R.COOH$, where R is an alkyl group containing from 1 to 3 carbon atoms, from an alkali metal salt thereof, which comprises electrolyzing an aqueous solution of the salt of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted with a nickel anode at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of fatty acid for each initial two molecules of fatty acid alkali metal salt in the form of the acid alkali metal salt, removing anolyte and recovering fatty acid by decomposition of the acid alkali metal salt.

3. Process for the production of acetic acid from an alkali metal acetate, which comprises electrolyzing an aqueous solution of the alkali metal acetate of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of acetic acid for each initial two molecules of alkali metal acetate in the form of the acid alkali metal acetate, removing anolyte and recovering acetic acid by decomposition of the acid alkali metal acetate.

4. Process for the production of acetic acid from an alkali metal acetate, which comprises electrolyzing an aqueous solution of the alkali metal acetate of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted with a nickel anode at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of acetic acid for each initial two molecules of alkali metal acetate in the form of the acid alkali metal acetate, removing anolyte and recovering acetic acid by decomposition of the acid alkali metal acetate.

5. Process for the production of acetic acid from sodium acetate, which comprises electrolyzing an aqueous solution of the sodium acetate of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and

6

2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of acetic acid for each initial two molecules of sodium acetate in the form of the acid sodium acetate, removing anolyte and recovering acetic acid by decomposition of the sodium acetate.

6. Process for the production of acetic acid from sodium acetate, which comprises electrolyzing an aqueous solution of the sodium acetate of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted with a nickel anode at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of acetic acid for each initial two molecules of sodium acetate in the form of the acid sodium acetate, removing anolyte and recovering acetic acid by decomposition of the sodium acetate.

7. Process for the production of acetic acid from sodium acetate, which comprises electrolyzing an aqueous solution of the sodium acetate of 5% to 50% concentration while preventing admixture of the anolyte and catholyte, the electrolysis being conducted at a temperature between about 80° C. and about 95° C., while maintaining the anode current density between about 1.5 and 2.5 amps. per square decimeter and, before electrolysis has proceeded substantially beyond the stage where the anolyte contains one molecule of acetic acid for each initial two molecules of sodium acetate in the form of the acid sodium acetate, removing anolyte and recovering acetic acid by decomposition of the sodium acetate, continuously removing anolyte and catholyte and continuously replacing the same with fresh electrolyte, and recovering acetic acid by decomposition of the acid sodium acetate in the anolyte.

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