

UNITED STATES PATENT OFFICE

2,224,814

ELECTROLYTIC PRODUCTION OF METALS

Harvey N. Gilbert, Niagara Falls, N. Y., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application August 25, 1938,
Serial No. 226,747

4 Claims. (Cl. 204—105)

This invention relates to the production of metals from metal salts and more particularly to a method of producing substantially pure metals by methods which involve electrolysis of aqueous salt solutions using mercury as a cathode and recovering metals from the resulting amalgams.

This is a continuation in part of my copending application Serial No. 109,129, filed November 4, 1936.

The art of electrolyzing alkali metal salt solutions, using mercury as a cathode to obtain alkali metal amalgam is a comparatively old one. Heretofore this method of electrolysis has been used only in the production of caustic alkalies and similar processes, wherein the amalgam is reacted to produce alkali metal compounds. Various methods have been proposed whereby alkali metal amalgams thus obtained may be treated to recover uncombined alkali metals therefrom but heretofore none of these have attained commercial importance.

The dilute alkali metal amalgams obtained by using mercury as a cathode for electrolysis of alkali metal salt solutions usually contain not more than about 0.2% of alkali metal, since at higher concentrations the amalgam is not easily maintained in a flowable state at temperatures at which it is convenient to operate the electrolysis cell. Various methods have been proposed for recovering alkali metal from these dilute amalgams, some of which comprise heating to distill off the mercury and others of which comprise utilizing the amalgam as an anode in a second cell with a suitable electrolyte, for example, fused alkali metal hydroxide. In such methods it is difficult to obtain alkali metal which does not contain appreciable amounts of mercury. In order satisfactorily to recover the alkali metal from the amalgam in a substantially pure state by distillation methods it is necessary to use some method of fractional distillation, which entails the employment of large and costly equipment. In electrolytic methods for recovering alkali metal, the vapor pressure of mercury is such that some mercury tends to pass through the electrolyte and contaminate the cathodic deposit of alkali metal.

Likewise, it has long been known that dilute amalgams of various other metals can be made by aqueous electrolysis with mercury cathode but heretofore, so far as I am aware, no satisfactory process for recovering metals from such amalgams has been proposed.

An object of the present invention is to provide an improved method for the production of

substantially pure metals, including the alkali metals, by a process which involves the electrolysis of aqueous solutions with a mercury cathode. A further object is to provide an improved method for recovering substantially pure alkali metal from dilute alkali metal amalgams obtained by electrolysis. Another object is to provide an improved method for separating mercury from a dilute alkali metal amalgam to obtain a concentrated amalgam. Other objects will be apparent from the following description of my invention.

The above objects are obtained in accordance with the present invention by providing a dilute liquid alkali metal amalgam, containing less than about 1% of the amalgamated metal, cooling the dilute amalgam to a temperature sufficiently low to cause precipitation of a solid, concentrated amalgam in liquid mercury and separating the precipitated solid concentrated amalgam from the liquid mercury. The dilute amalgam may be obtained by electrolysis of an aqueous metal salt solution, using mercury or liquid amalgam as the cathode.

The concentrated amalgam separated from the liquid amalgam by the cooling step may be treated in various ways. I prefer to treat the concentrated amalgam to recover the metal therefrom in substantially pure state. One method of recovering metal from the concentrated amalgam in my process consists in heating the amalgam to decompose it and vaporize off the mercury. Such distillation or vaporization operation may be carried out to any extent desired, depending upon whether pure metal or metal containing mercury is desired. The distillation may be carried out in a single stage or in a plurality of stages or some method of rectification may be employed. I prefer to distill the amalgam with a rectification column at such temperature that substantially pure metal or metal containing only traces of mercury is produced as residue which may be drawn off from the base of the still. Under such conditions, the vapors from the still may be pure mercury or may be mercury contaminated with more or less of the amalgamated metal, depending upon the design and efficiency of the distilling column and the volatility of the metal.

In practicing my invention for the production of alkali metals, e. g. sodium, lithium or potassium, I may carry out the electrolysis of an aqueous solution of an alkali metal salt, e. g. a halide or carbonate, with a mercury cathode under such conditions that a liquid amalgam is obtained.

Preferably the electrolysis is carried out at an elevated temperature, e. g. 60 to 80° C., so that an amalgam liquid at such temperature may be obtained, containing the maximum amount of amalgam which will not be too viscous to flow from the cell. The dilute liquid amalgam flowing from the cell is cooled sufficiently to precipitate a concentrated, solid alkali metal amalgam. If the amalgam at 60 to 80° C. has a sufficiently high alkali metal content, usually it is not necessary to cool below 10 to 30° C. to obtain the desired precipitate. For more dilute amalgam, it may be necessary to cool to still lower temperatures, which are above the freezing point of the mercury, e. g., to 0 to -10° C. The precipitated amalgam then may be separated by mechanical operations, such as filtering or pressing.

It has been found that alkali metal amalgam produced by electrolysis with mercury cathode is not in a homogeneous condition as it comes from the electrolytic cell. During the electrolysis, a layer of more concentrated amalgam tends to form at the surface of the mercury, this layer having a lower specific gravity than that of mercury. This more concentrated amalgam tends to dissolve in the more dilute amalgam only very slowly. As a result, the material issuing from the cell usually consists of a dilute liquid amalgam having a floating upper layer of particles of more concentrated solid amalgam. The proportionate concentrations of alkali metal in the two layers will vary, depending on the conditions of the electrolysis operation. For example, the main portion of the amalgam, may contain around 0.2 to 0.5% by weight of alkali metal, the floating material containing 0.7 to 1.0% by weight of alkali metal, while the ratio of the two may be such that the mean alkali metal concentration in the total amalgam is 0.3 to 0.7% by weight. I have discovered that such non-homogeneous alkali metal amalgams may be circulated through pipes or allowed to stand for considerable periods of time, e. g., for several hours, without becoming homogeneous. In order to quickly obtain a homogeneous amalgam I have found that it is necessary to stir the material vigorously and preferably at elevated temperatures.

In the preferred embodiment of my invention, I utilize the above-described non-homogeneous character of liquid amalgams obtained by electrolysis. I have discovered that by cooling the non-homogeneous amalgam, the tendency for the solid amalgam present to go into solution is markedly decreased. Hence, by cooling the amalgam, I may place it in a condition for further mechanical handling for separation of the solid phase from the liquid phase, for example, by such methods as filtration, centrifuging, pressing or skimming. The cooling operation thus insures the recovery of substantially all of the solid material initially floating on the amalgam flowing from the electrolytic cell.

In conducting the amalgam from the place of electrolysis to the cooling point, I avoid stirring or otherwise agitating the amalgam coming from the electrolytic cell, insofar as possible, prior to cooling the amalgam. Preferably, the amalgam is directly flowed from the electrolyte cell into a cooling zone. I may cool the amalgam by flowing it through a pipe surrounded by a refrigerating medium and continuously pass the cooled amalgam to a filtering device or I may cool it in a reservoir. The best results are obtained by cooling the amalgam immediately after it leaves the electrolytic cell. However, satisfactory separation

also may be obtained if the amalgam is cooled several hours later, provided it is not subjected to excessive agitation in the interim.

The degree of cooling required will vary considerably, depending, for example, on the alkali metal content of the amalgam, the method of separation to be employed, and the extent of separation desired. In general, it is preferable to cool the amalgam to a temperature at least 20° C. lower than the temperature at which it is formed in the electrolytic cell. For example, an amalgam coming from the cell at a temperature of 60 to 80° C. and containing 0.2 to 0.5% by weight of sodium may be cooled to 10 to 30° C., while an amalgam of the same sodium concentration initially at a temperature of 20-30° C. may advantageously be cooled to -10 to 0° C. The invention, however, is not restricted to a particular cooling range, as the effect of decreasing the solubility of the solid phase in the liquid portion is relative and directly proportional to the extent to which the temperature is lowered.

The liquid mercury separated from the concentrated amalgam may be returned to the electrolysis cell to be reused as cathode. The separated solid amalgam may be treated to recover alkali metal either by distilling off the mercury or by a chemical method of separating mercury as more fully explained below. In separating the mercury from the concentrated amalgam by distilling off the mercury, I prefer to employ a distillation method which will leave a residue of substantially pure alkali metal or alkali metal containing not more than about 5% by weight of mercury.

If the distillation step is carried out under such conditions that an alkali metal product is obtained which contains relatively small amounts of mercury; e. g. 1-5% or less, I may remove substantially all of the residual mercury by treating the alkali metal in substantially liquid state with a substance which reacts with the mercury to form a solid substance but which does not react with the alkali metal to any appreciable extent. This chemical method of purifying alkali metal to separate mercury therefrom is described and claimed in U. S. Patent 2,124,564, entitled "Metal purification." As reagent for this chemical method of removing mercury from an alkali metal, I prefer to use calcium or other alkaline earth metal. In place of distillation to remove the mercury from a concentrated alkali metal amalgam obtained by cooling the dilute amalgam from the electrolysis cell, I may treat the concentrated amalgam by the above mentioned chemical method to remove part or substantially all of the mercury therefrom.

For the purpose of illustrating my invention I shall describe one method of utilizing it to produce substantially pure sodium. An alkali metal salt, e. g., sodium chloride or sodium carbonate, is dissolved in water and the aqueous solution is electrolyzed by known means with a mercury cathode. The electrolysis preferably is carried out at a temperature of 60-80° C. and I prefer to use the method and apparatus described and claimed in my copending application Serial No. 68,274. Preferably, the mercury or dilute amalgam cathode is continuously circulated through the cell, the rate of circulation being adjusted so as to produce an amalgam of maximum concentration which still will be sufficiently liquid to flow from the cell. The dilute amalgam leaving the cell is cooled to a temperature of 10-30° C. and then filtered. The filtrate, which is sub-

stantially liquid mercury, is recirculated through the cell. The filter residue consists of the concentrated solid amalgam, wet with more or less liquid mercury. If desired, this residue may be

5 subjected to a pressing operation, e. g. by means of a suitable hydraulic press in order to remove further amounts of liquid mercury and leave a more concentrated press cake.

The concentrated sodium amalgam thus obtained then may be heated in a still preferably provided with a fractionating column, to decompose the amalgam and distill off mercury. Molten sodium is withdrawn from the lower portion of the still, the purity of the sodium withdrawn from the still depending on the efficiency of the distillation process. By utilizing a properly designed distilling column or by carrying out successive distillations (in other words, by utilizing the well-known principles of fractional distillation), it is possible to obtain substantially pure sodium. If the distillation conditions are such that the resulting sodium contains a small amount of mercury, I then may purify the sodium by treatment with calcium in the following manner. Finely divided calcium first is prepared by dissolving metal calcium in liquid sodium at a temperature of 500 to 700° C. and cooling the melt to precipitate metal calcium, e. g. to about 100 to 120° C. The cooled melt then is filtered to obtain a filter residue consisting of calcium crystals mixed with molten sodium, which filter residue I term "calcium sludge." The sodium to be purified is melted and heated to 200 to 300° C. and an amount of the calcium sludge containing calcium equal to 3 to 5 times the weight of the mercury present is added to the molten sodium and mixed thoroughly therewith. After the melt has been maintained at a temperature of 200 to 300° C. for a period of 1 to 10 minutes, the melt is cooled to about 100 to 120° C. and filtered. The resulting filtrate will consist of sodium substantially free from mercury.

In an alternative method of thus producing pure sodium I may add the concentrated amalgam obtained by the cooling step to a quantity of molten alkali metal in such proportions that the resulting mixture contains 50 to 75% of alkali metal. To this mixture, heated to a temperature of 200 to 300° C., I then may add a suitable quantity of calcium sludge prepared as described above so that the amount of calcium added is equal to 3 to 5 times the weight of the mercury present. The mixture then is maintained with thorough agitation at a temperature of 200-300° C. until the reaction between the calcium and the mercury is completed which usually requires 1-10 minutes. The melt then is filtered at about 110° C. whereby a filtrate of substantially pure sodium is obtained.

The residue obtained from this final filtration after utilizing the above mentioned chemical method of separating the mercury will consist of a sludgy mixture of the reagent; e. g., calcium or other alkaline earth metal, mercury and alkali metal; probably the alkaline earth metal and mercury are present in the form of a solid amalgam. This mixture may be heated in a still or retort to decompose the amalgam or

mercury compound and drive off mercury vapors which may be condensed to provide liquid mercury for the electrolysis cell cathode. The residue from such distillation will consist of a mixture of alkali metal and the recovered reagent; e. g. alkaline earth metal, which may or may not be substantially free from mercury. This metallic residue which contains alkaline earth metal in finely divided form is suitable for use as reagent for treating a further quantity of alkali metal and mercury metal to remove mercury therefrom by the treating method described above. In this manner the alkaline earth metal or other metal reagent used may be used over and over without any substantial losses.

I claim:

1. A process for the production of an alkali metal which comprises electrolyzing an aqueous solution of an alkali metal compound with a mercury cathode to obtain a dilute, non-homogeneous, substantially liquid alkali metal amalgam, flowing said amalgam from the zone of electrolysis with minimum agitation, cooling said liquid amalgam before mixing can occur, sufficiently to precipitate a solid amalgam therein, and separating said solid amalgam from the cooled liquid amalgam and recovering alkali metal from said solid amalgam.

2. A process for the production of an alkali metal which comprises electrolyzing an aqueous solution of an alkali metal compound with a mercury cathode to obtain a dilute, non-homogeneous, substantially liquid alkali metal amalgam, flowing said amalgam from the zone of electrolysis with minimum agitation, cooling said liquid amalgam before mixing can occur to at least 20° C. below its formation temperature thereby precipitating solid amalgam and separating said precipitated solid amalgam from the cooled liquid amalgam and recovering alkali metal from said solid amalgam.

3. A process for the production of sodium which comprises electrolyzing an aqueous solution of a sodium salt with a mercury cathode to obtain a dilute, non-homogeneous, substantially liquid alkali metal amalgam, flowing said amalgam from the zone of electrolysis with minimum agitation, cooling said liquid amalgam before mixing can occur to at least 20° C. below its formation temperature thereby precipitating solid amalgam and filtering said precipitated solid amalgam from the cooled liquid amalgam and recovering sodium from said solid amalgam.

4. A process for the production of sodium which comprises electrolyzing an aqueous solution of a sodium salt at a temperature of 60 to 80° C. with a mercury cathode to obtain a dilute, non-homogeneous, substantially liquid alkali metal amalgam, flowing said amalgam from the zone of electrolysis with minimum agitation, cooling said liquid amalgam before mixing can occur to a temperature of 10 to 30° C. thereby precipitating solid amalgam and filtering said precipitated solid amalgam from the cooled liquid amalgam and recovering sodium from said solid amalgam.

HARVEY N. GILBERT.