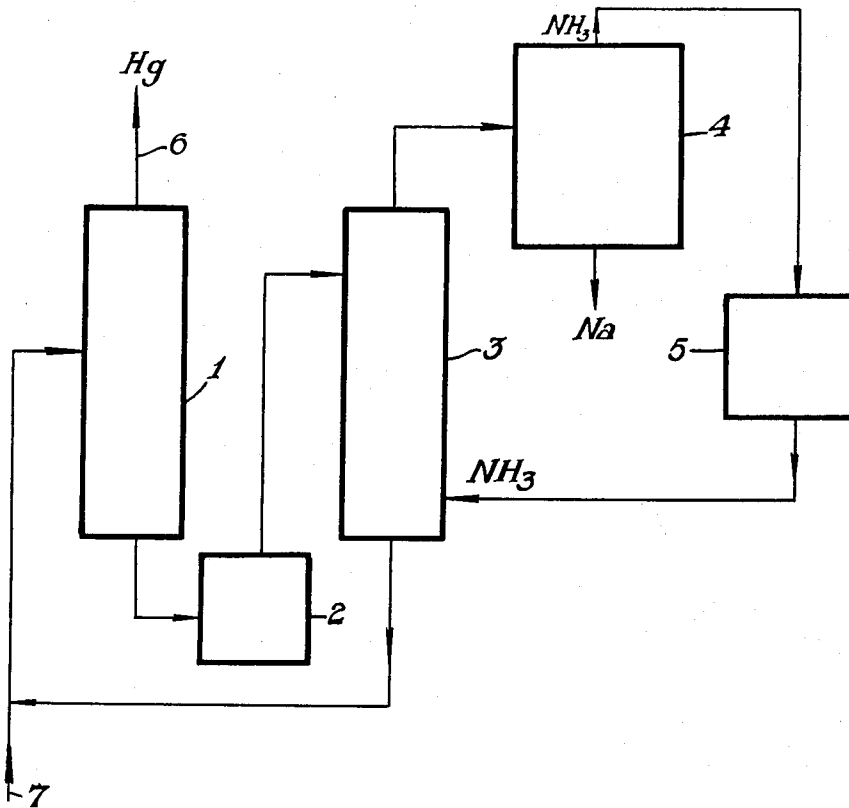


June 12, 1956

L. VANHAREN ET AL
METHOD FOR THE EXTRACTION OF ALKALI METALS
FROM THEIR AMALGAMS
Filed April 1, 1952

2,750,281



Inventors
Lambert Vanharen
Pierre Octors
By Robert E. Burns
Attorney

1

2,750,281

METHOD FOR THE EXTRACTION OF ALKALI METALS FROM THEIR AMALGAMS

Lambert Vanharen and Pierre Octors, Brussels, Belgium, assignors to Solvay & Cie, Brussels, Belgium, a Belgian company

Application April 1, 1952, Serial No. 279,802

Claims priority, application Netherlands April 4, 1951

11 Claims. (Cl. 75—66)

The present invention relates to a new process for the extraction of alkali metals from their amalgams, particularly from amalgams produced by the electrolysis of aqueous solutions of alkali metal salts in a cell provided with a mercury cathode.

It is known that these metals, especially sodium which has acquired a very great importance commercially, are produced on a factory scale almost exclusively by the electrolysis of fused salts.

This process has, however, serious drawbacks, because the reaction must be effected at a very high temperature, for instance above 800° C. when electrolysing fused sodium chloride, and above 300° C. when electrolysing fused caustic soda. The power consumption (approx. 15 kwh./kg. Na) and the deterioration of the apparatus because of corrosion and of high temperatures, make this process very troublesome.

Various processes have already been proposed in order to replace the thermal electrolysis by the extraction of the alkali metal from the amalgam obtained economically by the electrolysis of an aqueous solution of an alkali metal salt in a cell provided with a mercury cathode.

The difficulties inherent in these processes result from the weak concentration of the alkali metal from the amalgams obtained in the first phase of the process.

It has been particularly recommended to extract the alkali metal from an amalgam by the distillation of mercury. This working method is theoretically very economical, because, by judiciously combining the production of an alkali metal with an electric power generator based on the recuperation of the heat of condensation and of the sensible heat of the evaporated mercury, it is possible to obtain this alkali metal with a minimum consumption of energy. However, this process has not found any industrial application because of the insurmountable difficulties encountered in the realisation of the apparatus. In fact, the distillation of mercury from the amalgam in order to achieve a complete separation of the sodium entails working conditions, and particularly the application of temperatures of about 900° C. under atmospheric pressure to which the materials used in the construction of the industrial apparatus are subjected, cannot resist for long.

The alkali metal obtained according to this process has also the disadvantage of containing comparatively large quantities of mercury which must be separated, for instance by a combination with an alkaline earth metal, the affinity of which for mercury is superior to that of the alkali metal.

The quantity of mercury to be separated from the amalgam by distillation may obviously be reduced by the prior concentration of the dilute amalgam obtained by electrolysis: the dilute amalgam is cooled so as to precipitate a more concentrated amalgam which is separated from the mercury that remained liquid. This improvement does not, however, permit of an avoidance of the critical phase of the distillation at a high temperature, so that the process remains practically impossible of realisation.

2

The present invention aims at avoiding the inconveniences of the above described processes and particularly at obtaining a technically pure alkali metal, rigorously freed from mercury, starting from amalgams obtained by the electrolysis of aqueous solutions of alkali metal salts in a cell provided with a mercury cathode.

The present invention is based on the fact that the alkali metal of an amalgam previously concentrated may be extracted by a solvent, particularly by liquid ammonia or by a fused alkali hydroxide.

We are aware of the fact that it has already been proposed to decompose the amalgam in the presence of a solvent of the alkali metal in an electrolytic cell in which the amalgam is the anode, but this process is essentially different and requires two consecutive electrolyses, starting at an elevated power consumption which may be estimated in the case of sodium at about 10 kwh./kg. of alkali metal.

According to the present invention, the dilute amalgam obtained by the electrolysis of an aqueous solution of an alkali metal salt in a cell provided with a mercury cathode is concentrated in such a manner as to achieve a concentration of alkali metal of more than 10% by weight, which may be brought about by working at temperatures not prejudicial to the apparatus, then the concentrated amalgam is treated with a solvent in order to dissolve an important part of the alkali metal contained in the amalgam. The exhausted amalgam is recycled towards the apparatus for concentration, whilst the alkali metal is separated from the solvent.

The concentration of the alkali metal of the amalgam prepared by the electrolysis of an aqueous solution of an alkali metal salt does not usually exceed 0.7% by weight.

At higher concentrations, the amalgam begins to solidify at the temperature usually maintained in the electrolytic cells. This dilute amalgam may be concentrated by distillation at elevated temperatures, preferably in several successive columns, so as to carry the concentration of the alkaline amalgam to such a value as to render economical the extraction with a solvent. The lower concentration limit obviously varies with the nature of the solvent, but the applicants have found that, in the case of the known solvents, the higher concentration limit is at 10% by weight.

Before the distillation, it is obviously possible to effect a prior concentration by cooling the hot dilute amalgam of the cells in such a manner as to precipitate the solid amalgam. In the case of an amalgam of sodium, for instance, it is possible to precipitate NaHg₄ (about 2.8% of Na) which is separated from the liquid mercury. The concentration of the amalgam is then raised by distillation, if necessary under reduced pressure.

According to a preferred method of working the process, the concentration of amalgam which is to be submitted to extraction by a solvent is brought to the maximum value compatible with an economic course of the distillation of mercury; for example, in the case of the production of metallic sodium, the amalgam is preferably brought to a concentration in Na of from 40 to 60%.

At these concentrations, the solubility of Na in the solvent is in fact elevated and the distillation temperature of mercury contained in the amalgam remains within limits consistent with the materials of construction of the apparatus to attack by sodium and mercury. The result is that to a comparatively slight increase in the amount of evaporated Hg corresponds a slight recycling of amalgam and an elevated amount of Na extracted per cycle.

The recommended solvents of alkali metals according to the invention are particularly liquid ammonia, ethylene diamine, methylamine, as well as fused hydroxides of alkali metals. However, other solvents inert with regard

to alkali metals may be suitable in so far as their dissolving power is sufficient to allow the economic extraction of the alkali metals. It is also possible to use a mixture of solvent of the alkali metal or a mixture of a solvent with a non-solvent inert with regard to the alkali metal.

The extraction may be effected in the cold or in the hot from the solid or liquid amalgam. The solution of alkali metal is subsequently evaporated in order to separate the metal from the solvent. The exhausted amalgam is recycled for concentration after having added thereto fresh quantities of dilute amalgam coming from the electrolysis.

It goes without saying that the alkali metal dissolved in liquid ammonia or another solvent may be used without prior separation for the preparation of derivatives of this metal, such as peroxides or amides. On the other hand, it is interesting to note that the alkali metal obtained by evaporation of the solvent is in a very finely dispersed state, in which it is extremely reactive and can therefore also be economically used for the preparation of various derivatives.

An interesting method of carrying the invention into effect consists in the extraction of the alkali metal from the amalgam by the hydroxide of this alkali metal, or of another alkali metal, in the state of fusion.

It has been known that fused caustic soda dissolves sodium (Von Hevesy, Z. f. Electroch., August 1909, p. 529), but it has now been discovered that sodium, combined with mercury or with another metal in an amalgam, may be extracted by fused caustic soda.

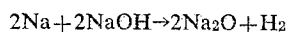
According to the nature of the invention, the amalgam of liquid alkali metal, at a concentration of the alkali metal exceeding 10% by weight, is brought into contact with the fused hydroxide of alkali metal in a tight receptacle in order to extract part of the alkali metal contained in the amalgam, whereafter the exhausted amalgam is separated and returned into the cycle for re-concentration while the alkali metal is separated from the hydroxide of alkali metal.

In the case of the extraction of sodium from its amalgam by caustic soda, this extraction may be effected at a temperature of above 325° C., for instance between 325 and 600° C. Nevertheless, the temperature may also be lowered below the normal melting point of caustic soda by the addition of compounds such as Na₂CO₃, KOH, NaBr, NaI, and the like.

The sodium dissolved in caustic soda may be separated on account of the fact that the solubility of sodium in caustic soda is inverted, that means it decreases when the temperature increases. Thus, on heating the solution, a layer of sodium floating on fused caustic soda separates.

This separation may likewise be effected after cooling, by means of an auxiliary solvent.

In order to understand more easily the statement in the present invention, it has been assumed that the alkali metal dissolves in its fused hydroxide. In reality, the matter in question is not so simple a physical phenomenon and, under certain conditions, the dissolution is accompanied by chemical reactions. It is known, for instance, that, above 450° C., and atmospheric pressure, the sodium reacts with caustic soda to form sodium oxide according to the reaction:



This reaction may be applied in a process in which the extraction of sodium from an amalgam is combined with the production of sodium oxide. Nevertheless, when working under other conditions, particularly at temperatures below 450° C. and/or under hydrogen pressure, it is possible to recuperate the sodium in a non-combined state.

The assumed simplification of the reaction mecha-

nism of the hydroxide of alkali metal cannot therefore be harmful to the value of the process.

The following examples of the extraction of sodium from amalgam are given on the understanding that the invention is not limited to these examples, but that the process of the invention, as indicated above, is applicable to the separation of any alkali metal from its amalgam.

These examples relate to continuous working methods of the process; however, the application may easily be effected in a discontinuous manner by the successive extractions of the alkali metal from amalgam, the exhausted amalgam being treated in an extraction apparatus with fresh solvent until the concentration of the amalgam drops to the limit at which the extraction ceases to be economical.

Example 1

The diagram of the method can be seen from the accompanying drawing.

In a cell provided with a mobile mercury cathode, an aqueous solution of sodium chloride is electrolysed to form an amalgam with 0.4% Na.

250 kg. of this hot liquid amalgam coming from 7 and mixed with 2.08 kg. of exhausted amalgam with 26% Na originating from extraction column 3, are introduced in a continuous manner into distillation column 1 within one hour, where the amalgam is concentrated until an Na-content of 50% by weight is reached, the temperature not exceeding 550° C. From this column, 249 kg. of mercury vapors are separated within one hour, which escape through 6, and which are condensed by utilising the condensation heat and the sensible heat by known methods. The cooled liquid mercury is returned to the electrolysing cell. Furthermore, this column yields, at the same time, 3.08 kg. of concentrated amalgam with 50% Na which is directed to heat exchanger 2 to be cooled to about 70° C.

The amalgam cooled in 2 is pumped into extraction column 3 where it meets in counter-current liquid ammonia coming from 5. The sodium extraction apparatus works under an ammonia pressure of 35 kg./cm.². The outgoing solution leaves the apparatus at its upper part, and is compressed to 62 kg./cm.² in evaporator 4, where 1 kg. of metallic sodium per hour is separated.

The ammonia vapors liberated in the evaporation are expanded in an expansion vessel (not shown) and condensed at 70° C. in condenser 5. The liquid ammonia is reintroduced at the bottom of extraction column 3 under pressure of 35 kg./cm.².

The amount of liquid ammonia circulating by recycling for the extraction of 1 kg. of sodium per hour amounted to about 10 kg. per hour.

Example 2

200 kg. of amalgam with 0.5% of sodium produced by electrolysis, are introduced into distillation column 1 within one hour simultaneously with 1.4 kg. of solid amalgam with 14.3% Na originating from extractor column 3.

2.4 kg. of amalgam with 50% Na are withdrawn from the bottom of the distillation column and are cooled in a heat exchanger, then the liquid amalgam is dispersed in extraction column 3 wherein an ascending stream of liquid ammonia is circulating at -37° C. under atmospheric pressure. The finely dispersed solid amalgam drops to the bottom of the extraction column while losing the sodium which dissolves in the liquid ammonia. The solution is heated to -20° C. in evaporator 4 so as to deposit the sodium by the evaporation of NH₃. These vapors are condensed at -35° C. in 5 and reintroduced into extraction column 3.

The quantity of liquid ammonia necessary for the extraction which circulates by recycling in order to extract 1 kg. of sodium per hour was 5 kg./hour approximately.

5

Example 3

1 kg. of previously fused and dried caustic soda is introduced into a tight receptacle, then 1 kg. of fused sodium amalgam containing 500 gr. of sodium is added. Two liquid layers are formed in the receptacle, one layer of caustic soda and one layer of concentrated amalgam which floats on top. The whole is heated to a temperature of 480° C. so as to extract the sodium from the amalgam by dissolving in caustic soda.

This extraction manifests itself by the inversion of the two liquid layers. In effect, the amalgam becomes poorer in sodium, and its specific weight increases until it becomes superior to that of the fused caustic soda which becomes richer in sodium. An ascendant displacement of the caustic soda thus results which facilitates the exchange of the phase.

At the end of a certain time, the fused amalgam residue (750 gr.) contains only 333 gr. of sodium per kg. of amalgam.

It is withdrawn from the bottom of the receptacle and returned for concentration. The caustic soda containing 250 gr. of sodium per kg. of NaOH is then heated to 600° C. in a closed vessel.

A portion of the sodium, about 150 gr., separates because of the decrease of the solubility due to the increase of the temperature and forms a liquid layer which floats on top. It is separated by decanting. The caustic soda still containing 100 gr. of sodium per kg. of NaOH is advantageously utilised for a subsequent extraction.

Example 4

The caustic soda residue according to Example 3 with a concentration of 100 gr. of sodium per kg. of NaOH is brought back to a temperature of 480° C., and 600 gr. of amalgam containing 500 gr. of sodium per kg. of amalgam are added thereto.

After the extraction of part of the sodium, the exhausted amalgam (450 gr.) with 333 gr. of sodium per kg. of amalgam is separated. The caustic soda phase having absorbed additional 150 gr. of sodium is reheated to 600° C., and 150 gr. of sodium are separated therefrom, corresponding to a difference of the solubility between the two temperatures.

We claim:

1. A process for extracting alkali metals from their amalgams which comprises concentrating an alkali metal amalgam having a concentration of less than 10% by weight of the alkali metal by distilling mercury therefrom to increase the concentration of said alkali metal to a value of at least 10% by weight, bringing the concentrated amalgam thus obtained into contact with a solvent having a solvent action upon said alkali metal but being non-reactive with the mercury and the amalgam, thereby dissolving a portion of the alkali metal from the amalgam, separating the amalgam from the solution of alkali metal in the solvent by physical means, and recovering the alkali metal from the solvent.

2. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the alkali metal in the amalgam is brought to a concentration of 40 to 60% by weight.

6

3. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the solvent is liquid ammonia.

4. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the treatment with the solvent is effected at atmospheric pressure and at a temperature at which the amalgam is solid.

5. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the treatment with the solvent is effected at sub-atmospheric pressure and at a temperature at which the amalgam is liquid.

6. A process for extracting alkali metals from their amalgams as defined in claim 5, wherein the liquid amalgam is dispersed in the solvent and the solvent is maintained at a temperature below the solidification temperature of the amalgam.

7. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the solvent is fused alkali metal hydroxide.

8. A process for extracting alkali metals from their amalgams as defined in claim 7, wherein the alkali metal is recovered from solution in the fused alkali metal hydroxide by heating the solution under hydrogen pressure at a temperature higher than the temperature at which the amalgam was brought into contact with the fused alkali metal hydroxide.

9. A process for extracting alkali metals from their amalgams as defined in claim 7, wherein the amalgam is brought into contact with the fused alkali metal hydroxide under conditions which give rise to the formation of alkali metal oxide with the liberation of hydrogen.

10. A process for extracting alkali metals from their amalgams which comprises concentrating an alkali metal amalgam having a concentration of less than 10% by weight of the alkali metal by distilling mercury therefrom to increase the concentration of said alkali metal to a value of at least 10% by weight, bringing the concentrated amalgam thus obtained into contact with a solvent selected from the group consisting of liquid ammonia, ethylenediamine and methylamine, separating the amalgam from the solution of alkali metal in the solvent by physical means and recovering the alkali metal from the solvent.

11. A process for extracting alkali metals from their amalgams as defined in claim 1, wherein the amalgam separated from the solvent solution of the alkali metal is mixed with a fresh batch of dilute amalgam being charged to the concentration step.

References Cited in the file of this patent

UNITED STATES PATENTS

1,570,467	Ewan	Jan. 19, 1926
2,124,564	Gilbert et al.	July 26, 1938
2,224,814	Gilbert	Dec. 10, 1940

OTHER REFERENCES

Johnson et al.: "Chemical Reviews," vol. 8, April 1931, pages 273 to 301.

MacMullin: Chemical Engineering Progress, volume 46, No. 9 (September 1950), pp. 447-448.