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D. L. SCHECHTER ETAL
PROCESS FOR THE PREPARATION OF SODIUM PEROXIDE BY
THE OXIDATION OF A SODIUM AMALGAM
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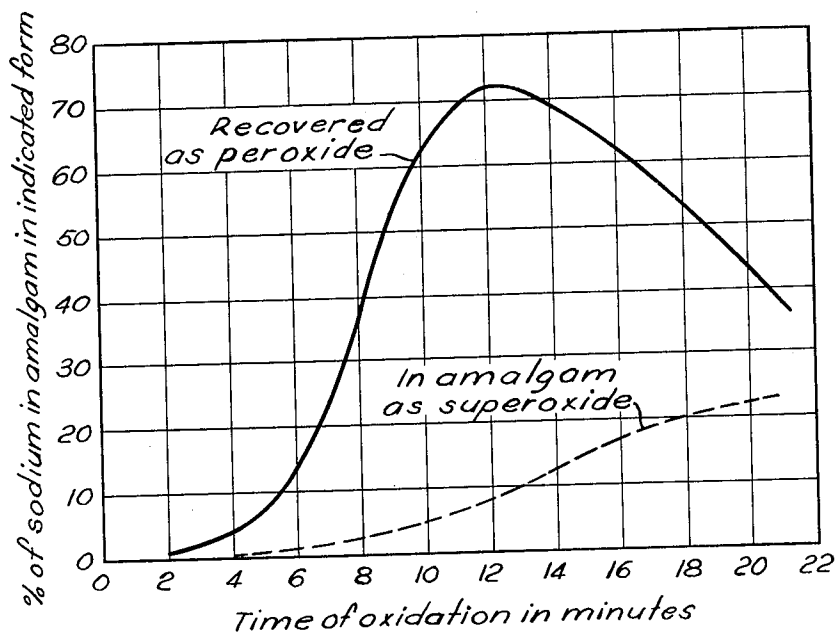


Fig. 1

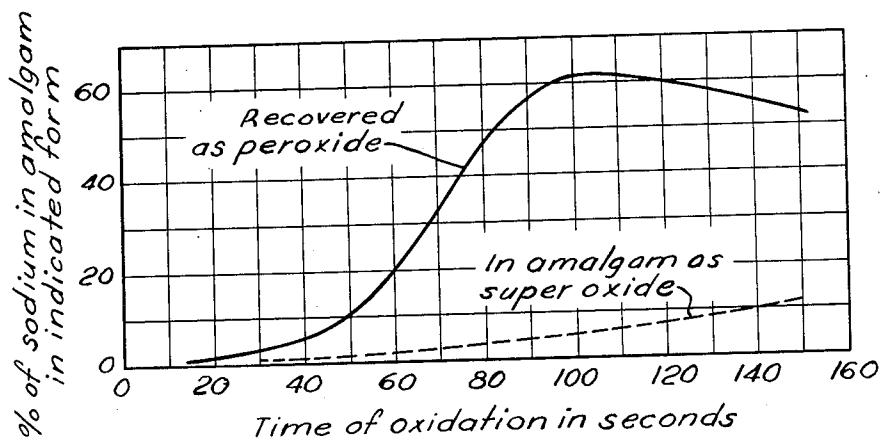


Fig. 2

INVENTORS.
Dale L. Schechter
Charles K. Bon
James J. Leddy
BY *Griswold & Burdick*
ATTORNEYS

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**PROCESS FOR THE PREPARATION OF SODIUM
PEROXIDE BY THE OXIDATION OF A SODIUM
AMALGAM**

Dale L. Schechter, Charles K. Bon, and James J. Leddy,
Midland, Mich., assignors to The Dow Chemical Com-
pany, Midland, Mich., a corporation of Delaware
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This invention pertains to the preparation and recovery of alkali metal peroxides. More particularly, it pertains to the preparation of peroxides by oxidation of an alkali metal-containing amalgam and recovering the resulting peroxide therefrom.

Numerous processes have been suggested for the preparation of peroxides by the oxidation of an alkali metal-containing amalgam. However, heretofore none of the processes proposed have been entirely satisfactory. While the alkali metal in the amalgam may be oxidized, a high proportion of the alkali metal is not oxidized to peroxide. The yield of peroxide is further decreased by the decomposition of the peroxide prior to its recovery. In addition, during the oxidation step a considerable portion of the mercury is also oxidized. This results in a continual loss of mercury. In the event that the amalgam is recycled to an electrolytic cell the mercury oxide or sludge may also be recycled; however, energy has to be expended to reconvert the mercury oxide sludge to mercury, decreasing the sodium amalgam producing efficiency of the cell.

It is therefore an object of this invention to provide a process for the preparation of alkali metal peroxides by the oxidation of an alkali metal containing amalgam wherein the major proportion of the alkali metal in the amalgam is converted and recovered as the peroxide. A further object is to provide a process for the oxidation of an alkali metal in an amalgam with the minimum oxidation of the mercury. Another object is to provide a process for the recovery of the peroxide from the oxidized amalgam.

The above and other objects are attained according to the invention by the oxidation of the alkali metal in an amalgam by contacting the amalgam in a liquefied state containing from about 0.1 to 5.0 mole percent of an alkali metal, such as sodium, with an oxygen-containing gas stream to oxidize the alkali metal in the amalgam to the peroxide and superoxide to an extent that not more than 20 percent, preferably 10 percent, of the alkali metal in the amalgam is converted to superoxide. After the alkali metal in the amalgam has been oxidized to the desired extent, the oxidized amalgam is intermixed with an aqueous medium to dissolve the peroxide from the oxidized amalgam. The solution of peroxide obtained after contact with the oxidized amalgam is immediately treated to remove the mercury oxide which may have become dispersed in the solution after which the peroxide is recovered from the solution. By the above process over 75 percent of sodium in an amalgam may be recovered as sodium peroxide.

In the work leading to this invention, it was found that the mercury oxide formed during the oxidation step not only is undesirable due to decrease in efficiency when the denuded mercury is recycled to the electrolytic cell but that the mercury oxide has a catalytic effect in promoting the decomposition of the peroxide formed. In the presence of water, mercury oxide will catalytically decompose the sodium peroxide to the respective hydroxide.

Thus, when leaching an amalgam which has contained at some point during the oxidation an appreciable amount of superoxide, a considerable amount of the mercury oxide will have been formed so that a significant portion

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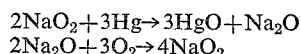
of the peroxide is reduced to hydroxide before the peroxide can be separated or recovered. As the result, it is necessary to carry out the oxidation of the alkali metal in the amalgam under conditions such that the oxidation of the mercury is minimized.

To effect the oxidation with the minimum mercury oxide or sludge formation, it was found that it is essential that the amalgam be subjected to the oxidizing atmosphere under controlled conditions to prevent excess formation of superoxide. In the oxidation of alkali metals in amalgams, the alkali metal is oxidized to three levels, a monoxide, a peroxide and a superoxide. Initially upon contact with an oxidizing atmosphere the alkali metal is converted to the monoxide and then further oxidized. It is expected that there may exist an equilibrium ratio between the particular oxides present in the amalgam. The oxidation of sodium amalgam to the peroxide is very rapid and a major portion of the sodium in the amalgam can be converted to the peroxide in a contact time of a matter of seconds. The amount of superoxide formed is not appreciable until about 60 to 85 percent of sodium in the amalgam is converted to the peroxide. When the content of superoxide in the amalgam exceeds about 20 percent of sodium present in the amalgam, the recoverable yield of peroxide rapidly decreases. The effect of superoxide concentration is shown on the attached graphs. The details and the data from which the figures were obtained are shown in the examples.

In FIGURES 1 and 2 the percent of the alkali metal in the specific form in the amalgam is plotted as the ordinate and the oxidation time in minutes is plotted as the abscissa. The percent of sodium recovered as peroxide is shown as the solid line curve and the amount of superoxide determined is shown by the broken line curve. The superoxide content of the amalgam was calculated from the measured amount of oxygen liberated upon leaching. As shown in FIGURE 1, when the oxidation time was increased from 6 minutes to 13 minutes, the peroxide recovery very rapidly increased from around 10 percent to about 73 percent. After 13 minutes, the peroxide recovered rapidly decreased so that at a contact time of around 21 minutes less than 40 percent of the sodium in the amalgam was being recovered as peroxide. The superoxide formation increased continually. When the superoxide content was about 10 percent, after about 13 minutes contact time, the recoverable sodium peroxide decreased rapidly. To obtain FIGURE 2, the apparatus was operated in a manner similar to that used to obtain FIGURE 1 except that the oxygen rate being charged to the oxidizer was increased about 3 times to more rapidly oxidize the amalgam. The curves obtained are similar to those shown in FIGURE 1 except that the critical superoxide concentration was reached more rapidly and at a peroxide concentration of a little over 60 percent. When more efficient mixers are used, the oxidation time can be decreased to a matter of 30 to 60 seconds or less, with conversions to peroxide well above seventy percent. In this short contact time the superoxide formation will reach the undesirable concentration at about 65 percent conversion of the alkali metal in the amalgam to the peroxide.

As a result of the work leading to this invention, it is believed that the superoxide formation is detrimental to the yields in that the presence of the superoxide results in the oxidation of the mercury to mercury oxide. At the levels of oxidation of the amalgam, where the superoxide is maintained at a fairly low concentration, the amount of mercury oxide formed is relatively small. However, upon attaining a critical concentration, the yield of the peroxide recovered decreases rapidly. It may be that the presence of mercury oxide may have some catalytic effect in accelerating the oxidation reaction of the mercury by the superoxide. The formation of mercury oxide

is believed to result from the reaction of mercury with the superoxide. After the superoxide reaches a critical concentration, it is believed that a cyclic reaction results whereby the superoxide reacts with mercury to form mercury oxide and sodium monoxide which is again re-oxidized to the superoxide. The above reactions may be illustrated by the following equations:



While the contact time to obtain the maximum recoverable sodium peroxide will vary with the conditions employed as well as the physical methods used for contacting the amalgam with the oxidizing atmosphere, the amalgam is generally subjected to the oxidizing atmosphere for a period of time not greater than 5 minutes. It is preferred to subject the amalgam under conditions such that the maximum peroxide recoverable will be obtained with a contact time of from 0.1 to 2 minutes. With a short contact time the mercury inventory is decreased.

The oxidation of the amalgam is usually carried out at a temperature below 40° C., although a temperature as high as 60° C. may be used with a short contact time of from 5 to 10 seconds. Generally it is preferred to carry out the oxidation at a temperature in the range of 20° to 30° C. While the reaction may be carried out at a temperature just above the solidification of the amalgam, temperatures below -20° C. are seldom used. Amalgams having the desired concentration of alkali metals are too viscous, even though not solidified, to handle conveniently at temperatures below -20° C.

Amalgams containing up to about 5.0 mole percent of the alkali metal may be used. However, generally an amalgam having from about 0.4 to 1.5 mole percent is preferred. With the alkali metal in the preferred range, the amalgam is sufficiently fluid at the oxidation temperature to be easily handled and is of sufficient concentration to permit the preparation of the peroxide without handling unduly large amounts of amalgam. However, concentrations of the alkali metal as low as or even below 0.1 mole percent may be used. The costs are somewhat higher with such low concentration amalgam due to the increase in amount of amalgam which has to be processed.

Any method of intermixing a heavy fluid with a gas which does not atomize or finely disperse the mercury may be used to intimately intermix the amalgam with the oxidizing air or oxygen containing stream to obtain efficient contact. Rotary mixers or agitators which provide fresh surface by shearing action are preferred. An example of one type of a mixer which may be used is the rotating disc-type mixer. The discs are partially immersed in the amalgam so that on rotation new surface of mercury is exposed to the oxidizing atmosphere by the amalgam clinging to the surface of the discs. With efficient mixers the contact time can be reduced to 5 seconds or less.

It is desirable to recover the peroxide from the oxidized amalgam shortly after oxidation. The superoxide present in the amalgam, even in the low concentrations, will continue to oxidize the mercury so that most of the superoxide will have reacted in about 20 to 30 minutes. Generally the peroxide may be recovered from the oxidized amalgam by contacting the amalgam with water or an aqueous solution to leach the peroxide and superoxide. The peroxide and superoxides are readily leached from the amalgam with the superoxide reacting with water to form peroxide and oxygen.

Since the catalytic effect of mercury oxide in presence of water rapidly decomposes the peroxide, the solution is separated from the oxidized amalgam as soon as possible. Also, any mercury oxide and mercury which may have become dispersed in the solution are removed from the solution by passing the solution through a centrifuge, filter, or other means used to remove the dispersed mer-

cury oxide. The contact time of the oxidized amalgam with the aqueous medium and the time after leaching before the dispersed mercury oxide can be removed from the solution must be maintained to less than 5 minutes, preferably less than 1 minute. In the leaching or dissolving step temperatures in the range of 0 to 50° C. may be used. It is preferred to employ a temperature in the range of 5° to 20° C. The amount of water or solution used is generally such that a solution containing usually from 1/2 to 5 weight percent of peroxide is obtained.

An acid or alkaline aqueous medium as well as substantially pure water or a neutral aqueous medium may be used to remove the peroxides. To effect the leaching or extraction of the peroxide from the amalgam in the short time required, it is essential that the oxidized amalgam be intimately intermixed with the water or solution used. Any liquid-liquid contact type of apparatus may be used to effect the leaching operation, however, a mixer type contact may be very conveniently used.

Although the oxidation and leaching steps may be carried out in a batchwise process, it is generally preferred to carry out the reaction in a continuous process. In the process, the amalgam is continually charged into an agitated reactor or oxidizer through which air, oxygen or some other oxygen-containing stream is passed. Substantially anhydrous conditions are maintained. The amalgam is likewise continuously discharged from the oxidizer and immediately charged into a second agitated vessel or leacher where the oxidized amalgam is contacted with an aqueous medium to dissolve the peroxides. In the leacher the oxidized amalgam is continually charged and continually discharged after it has been contacted with the water. In the process the oxidizer is operated such that the average retention time of the mercury in the oxidizer is less than 5 minutes and generally in the preferred range of .1 to 2 minutes. The peroxide solution upon leaving the leacher is passed through a centrifuge or filter to remove any mercury or mercury oxide which may be dispersed in the solution. The time in which the amalgam is contacted with the solution and the solution is treated to remove any mercury oxide dispersed within the solution is very short being preferably in the range of 5 seconds to 1 minute.

The peroxide obtained in the solution free of mercury oxide may be recovered by any of the well known methods or used as produced. Once the solution has been separated from the amalgam containing the mercury oxide or the mercury oxide dispersed in the solution, the peroxide is relatively stable and may be recovered by distillation, evaporation, "salting out" effect, precipitation, or other well known methods. Generally it is preferred to crystallize out the peroxide by lowering the temperature of the solution. Since the solution is usually recycled to the leacher after crystallization, it is not essential to recover all of the peroxide.

The examples below further illustrate the invention.

EXAMPLE 1

A series of runs was made at room temperature where samples of a sodium amalgam of about 335 grams each containing about 0.4 mole percent of sodium were oxidized in a batch oxidizer for different periods of time. The oxidizer was about 2 inches in diameter and was equipped with a fine glass frit at the bottom through which dry oxygen at a rate of about 4.7 liters per minute was introduced into the oxidizer and into contact with the amalgam.

After contacting the amalgam with the oxygen for a predetermined time, the oxygen stream was shut off and the oxidized amalgam was contacted with acid solution containing 50 weight percent of sulfuric acid for a period of 15 to 45 seconds to leach the sodium peroxide. The oxidizer thus was also used as a leacher. The leach solution was analyzed iodometrically using standard sodium thiosulfate as a titrant for the liberated iodine.

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The superoxide was determined by analyzing the gases evolved during the leaching step and calculating the superoxide. The results obtained are given below:

Table I

Run	Average Residence Time of Amalgam in Oxidizer, Minutes	Percent of Sodium in Amalgam Recovered as Sodium Peroxide	Volume of Oxygen Evolved from Leacher, Cubic Centimeters at S.T.P.	Sodium Superoxide in Amalgam, Weight Percent
1	0	0	0	0
2	2	3.6	.2	0.20
3	4	3.8	.7	0.85
4	6	8.3	1.1	1.40
5	7½	36.9	2.3	2.95
6	9	52.6	3.0	3.75
7	10½	65.6	6.3	7.95
8	12	72.3	7.3	9.0
9	14	69.7	8.7	10.8
10	17	55.7	15.0	18.6
11	21	37.4	16.2	20.1

Similar results may be obtained in a continuous process employing a blade-type oxidizer. A blade-type oxidizer was constructed which was a 2 inch in diameter glass tube approximately 11 inches long. At each end of the oxidizer an inlet and an outlet were provided. Within the oxidizer a shaft was inserted along its longitudinal axis to which 27 plastic discs were attached equally spaced along the shaft. The shaft was attached to a variable speed motor so that the discs could be rotated at different speeds within the oxidizer. The oxidizer was positioned so that the longitudinal axis of the oxidizer was inclined with respect to the horizontal plane with the amalgam inlet located at a lower level than the discharge. The amalgam containing about 0.4 mole percent of sodium was introduced into the oxidizer at an inlet provided at the lower elevation and discharged at the distant end of the reactor. The rate of the amalgam passing through the oxidizer was varied to obtain different average residence time of the amalgam in the oxidizer. The amalgam discharged from the oxidizer was passed directly to a leacher which comprised a vessel with a mixer. An aqueous solution was continually passed through the leacher. The amalgam was continually discharged from the leacher by means of an overflow controlled to maintain a given amount of mercury within the leacher.

A series of batch runs similar to that described above to obtain the results given in Table I was repeated except that the rate of oxygen charged into the oxidizer was increased about 3 times that used above. The results obtained are shown in Table II below:

Table II

Run	Average Residence Time of Amalgam in Oxidizer, Seconds	Percent of Sodium in Amalgam Recovered as Sodium Peroxide	Volume of Oxygen Evolved from Leacher, Cubic Centimeters at S.T.P.	Sodium Superoxide in Amalgam, Weight Percent
1	0	0	0	0
2	15	1.1	0.5	0.7
3	30	2.0	0.6	0.8
4	45	6.9	0.8	1.4
5	60	21.4	1.1	3.0
6	75	40.2	2.4	4.5
7	90	56.8	3.5	6.0
8	105	60.4	4.7	9.0
9	120	60.0	7.1	12.0
10	150	55.3	9.4	

EXAMPLE 2

To illustrate the effect the mercury oxide has upon the decomposition of the sodium peroxide, a leacher similar to that described above in Example 1 was used. To the leacher a given amount of amalgam obtained from the oxidizer having an average residence time of 60 seconds was added. The amalgam was intermixed with a pre-

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determined amount of a 12 weight percent aqueous sodium hydroxide solution. Periodically samples of the caustic solution in contact with the oxidized amalgam were taken and analyzed for sodium peroxide content. The results obtained at 25° C. are shown in the table below:

Table III

Run	Time after Intermixing Oxidized Amalgam, Minutes	Na ₂ O ₂ Solution, Weight, Percent
1	0	2.7
2	3	2.3
3	5½	1.6
4	8	1.2
5	10	.7

When the solution after contact with the amalgam was filtered to remove the mercury oxide dispersed in the aqueous solution, a solution containing 30 grams of sodium peroxide per liter was obtained. The concentration remained relatively constant decreasing gradually at the end of two hours to 28 grams of sodium peroxide per liter.

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

What is claimed is:

1. A process for the preparation of sodium peroxide by the oxidation of a sodium amalgam, which comprises contacting the sodium amalgam in a liquefied state said amalgam containing from about 0.4 to 1.5 mole percent of sodium with an oxygen containing gas stream at a temperature below 40° C. for a period of time in the range of from 0.1 to 2 minutes to oxidize the sodium in the amalgam to sodium peroxide and superoxide to the extent that not more than 10 percent of the sodium in the amalgam is oxidized to superoxide, subsequently intermixing the oxidized amalgam with an aqueous medium at a temperature in the range of from 0° C. to 50° C. to decompose the sodium superoxide to sodium peroxide and to leach the sodium peroxide from the oxidized amalgam, separating from the resulting solution mercury oxide dispersed in the solution from the oxidized amalgam during the previous step, said intermixing of oxidized amalgam with the aqueous medium and separation of the dispersed mercury and mercury oxide from the solution being carried out in from 5 seconds to 1 minute, and recovering said sodium peroxide from the resulting solution.

2. A continuous process for the preparation of sodium peroxide by the oxidation of a sodium amalgam, which comprises, passing a sodium amalgam in liquefied state, said amalgam containing from about 0.4 to 1.5 mole percent of sodium, into an agitated reactor, introducing an oxygen-containing gas stream into the reactor to thereby intermix the amalgam with the oxygen-containing gas stream to oxidize the sodium in the amalgam to the extent that not more than 20 percent of the sodium is converted to sodium superoxide, discharging continuously the oxidized amalgam into an agitated leacher, introducing an aqueous medium continuously into the leacher to be intermixed with the oxidized amalgam at a temperature of from 0 to 50° C. to decompose the sodium superoxide and to leach the sodium peroxide from the oxidized amalgam, discharging continuously the resulting solution of sodium peroxide from the leacher, separating from the resulting solution mercury oxide dispersed in the solution from the oxidized amalgam in the leacher, said leaching step and separation step removing the dispersed mercury oxide from the solution being carried out in a combined time of less than 5 minutes.

3. A process for the preparation of sodium peroxide by the oxidation of a sodium amalgam in high yield which comprises:

- (a) contacting a sodium amalgam in a liquefied state with an oxygen containing gas stream at a temperature below 40° C. for a period of from about 0.1 to about 2 minutes, said amalgam containing from about 0.4 to about 1.5 mole percent sodium,
- (b) controllably oxidizing the sodium in said amalgam to sodium peroxide such that at a maximum about 20 percent of said sodium in said amalgam is oxidized to the superoxide.
- (c) intermixing the so-oxidized amalgam with an aqueous medium at a temperature of from about 0° C. to about 20° C. for a period of from about 5 seconds to about 1 minute thereby leaching said sodium peroxide from said oxidized amalgam,

- (d) separating the sodium peroxide containing solution from mercury oxide dispersed therein during the leaching of said sodium peroxide from said oxidized amalgam, and
- (e) recovering said sodium peroxide from the resulting solution.

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