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J. J. GREBE ET AL
METHOD FOR CONTROLLING OXIDATION OF HALIDE
SOLUTIONS TO LIBERATE FREE HALOGEN
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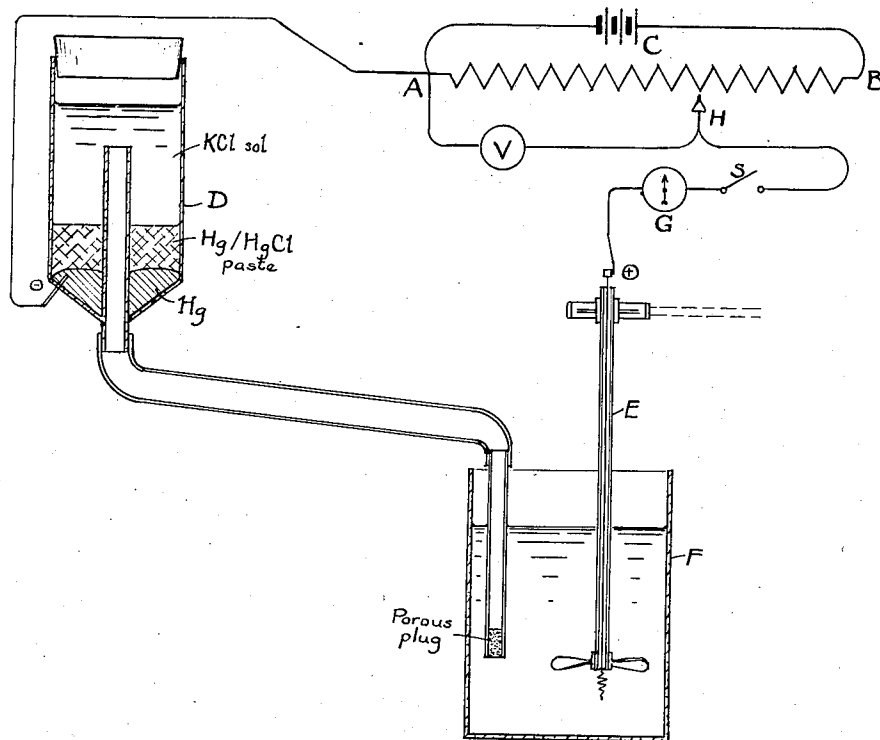


Fig. 1

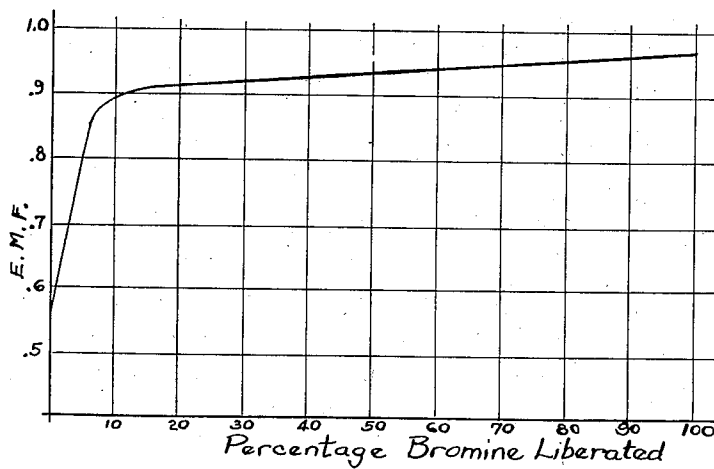


Fig. 2

INVENTORS
John J. Grebe and
Ray H. Bonney
BY Thomas Griswold, Jr.
ATTORNEY

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METHOD FOR CONTROLLING OXIDATION
OF HALIDE SOLUTIONS TO LIBERATE
FREE HALOGENJohn J. Grebe and Ray H. Boundy, Midland,
Mich., assignors to The Dow Chemical Com-
pany, Midland, Mich., a corporation of Mich-
igan

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4 Claims. (Cl. 23-217)

This invention relates to a method for controlling the oxidation of halide-containing solutions for the liberation of the halogen in the elemental state, and has particular regard to a method permitting an immediate and continuous indication to be made of the progress of the oxidation which shows directly the degree of liberation of bromine at any time.

Heretofore the control of bromine liberation, for example, has been based upon chemical analytical methods for determining bromide in the presence of chloride ions, such methods involving tedious manipulation and requiring from ½ hour to 1 hour or more for carrying out. The very considerable time lag between the treatment of the bromide-containing solution and the determination of the result has made virtually impossible any close or immediate control of the oxidation. The usual practice, consequently, has been to oxidize to a calculated excess, based upon the known average bromide content of the solution in process, in order to insure liberating all of the bromine, while the effluent liquor, from which the free bromine has been separated by blowing or steaming out, is analyzed to determine by the residual bromine content thereof whether any material loss has been incurred in the extraction. Obviously, such analytical method does not prevent a loss but merely indicates the fact after it has already occurred, and any irregularity or deviation from calculated conditions cannot be detected until a considerable time after the event, thus rendering ineffectual all attempts to exercise control over the oxidation under varying conditions, or to detect any variation from pre-determined conditions in time to prevent the occurrence of material losses to the process resulting therefrom.

We have developed a potentiometric method for measuring the oxidation of bromide-containing solutions which is based upon the oxidation potential of free bromine in contact with a solution of its ions. Our improved method enables a continuous indication and record of the progress of the oxidation to be made contemporaneously therewith and substantially eliminates the time lag which has seriously limited and handicapped all chemical control methods. By providing suitable means responsive to the aforesaid indication an immediate and positive control of the flow of materials to the reaction may be maintained continuously during the process. To the accomplishment of the foregoing and related ends, the invention, then, consists in the method hereinafter fully described

and particularly pointed out in the claims, the annexed drawing and following description setting forth in detail but a few of the various ways in which the principle of the invention may be used.

In said annexed drawing:—

Fig. 1 is a diagrammatic representation of an apparatus adapted for determining the oxidation potential of a solution in which bromine is being liberated. Fig. 2 is a chart showing the relationship between the observed potential and the degree of liberation of free bromine in sea water.

The oxidation, or solution, potential of a non-metal in contact with a solution of its ions at 25° C. is expressed by the formula;

$$E = e_0 - \frac{0.0591}{n} \log c$$

where E = E. M. F. in volts; e_0 = E. M. F. in volts of a solution of normal ion concentration; n = valence of the ion, and c = concentration of ions in gram ions per liter. The potential E increases as the ionic concentration of the solution decreases. When free bromine is present in a solution of bromide ions there exists a certain definite potential between the molecular bromine and Br^- ions which is capable of being measured. This potential is represented by a value which is characteristic for bromine and differs from the potential of other negative ions, e. g. Cl^- ions, being lower than the value for the latter ions under equivalent conditions and higher than the value for other non-metallic ions. The actual value thereof depends primarily upon the concentration of bromide ions present, but also is influenced by the simultaneous presence of other ions and by the property of free bromine in aqueous bromide solutions to form complex ions. Whatever the actual value as measured under any given conditions, this value will regularly increase as the concentration of free bromine increases and that of the bromide ions remaining in solution decreases, until a maximum point is reached whereat all of the bromine has been liberated and no bromide ions remain. When the liberation of bromine is effected by the action of chlorine, any further increase in the observed potential above the aforesaid maximum point will be due to the presence of free chlorine having a higher oxidation potential value than that of bromine. By determining the limits for any bromide solution between which the oxidation potential varies as bromine is liberated therefrom and installing a suitable instrument to

register or record such potential, it is possible to follow the progress of the bromine liberation directly to the point whereat such action is complete, so that it will be known precisely when the supply of chlorine or other oxidant is to be shut off. There is no appreciable time lag, and the accuracy of the observation is not in any way interfered with by variations or irregularities in the operation. In fact, all such irregularities will be shown immediately whenever they occur.

Our improved method of measurement is carried out by means of a pair of electrodes immersed in the bromide solution under process and connected with a suitable instrument for indicating the potential difference of the electrodes. One such electrode is a standard of known potential and the second is one capable of adsorbing bromine on its surface and acting as a bromine gas electrode, such as a platinum electrode. Fig. 1 of the drawing shows diagrammatically a convenient apparatus assembly.

AB is a resistance element connected with a source of current C, e. g. a storage battery. A standard calomel electrode D, of known potential is connected to the negative terminal A. Electrode D is of the usual type, consisting of a stoppered and sealed glass tube containing a layer of mercury at the bottom, covered by a layer of a paste made of calomel and mercury intimately mixed with and moistened by a standard potassium chloride solution, and the tube filled nearly to the stopper with more of the potassium chloride solution. A smaller tube may be sealed into the larger tube as shown and is provided with an extension, conveniently a rubber tube, terminating in a porous porcelain plug for immersing in the solution to be tested. The form of standard calomel electrode shown is simple and convenient to use, but any other suitable form may be used, if desired. The positive electrode E consists of a piece of platinum wire, preferably smooth, encased at the upper end with an insulating glass tube and having the lower end, in the form of a spiral, exposed for immersing in the test solution. The electrode may also be provided with a propeller and pulley, supported by a suitable bearing, so as to be rotated and to serve as a stirrer. The platinum electrode E, when immersed in a solution containing free bromine, adsorbs some of the bromine on its surface and functions thus as a bromine gas electrode. The extension tube of electrode D and electrode E are allowed to dip into the solution to be tested which is contained in vessel F, the whole constituting the test cell. Electrode E is connected in series with galvanometer G, switch S and a sliding contact H on resistance element AB. A voltmeter V is connected to terminal A and sliding contact H in parallel with the test cell.

To operate the apparatus, the solution to be tested, containing free bromine and bromide ions, is placed in vessel F, switch S is closed and sliding contact H is adjusted to give a zero reading on galvanometer G. The voltage reading on voltmeter V shows the difference in potential between electrodes D and E. The single potential of D being known, that of E can be directly calculated by adding the reading of V algebraically thereto, although for practical purposes the direct reading of V alone is sufficient to indicate the condition of oxidation of the test solution. The potential of electrode E will vary with the relative concentration of free bromine and bro-

mid ions present, as already explained. For continuous testing purposes, in order to follow the course of the liberation of bromine during the operation of the process, samples of the solution under treatment may be tested at intervals, or, preferably, a continuous stream of the solution may be caused to flow through vessel F, the voltage reading at any moment showing the degree of liberation of the bromine. Under suitable conditions, also, the electrodes may be immersed directly in the solution in the apparatus wherein the oxidation is carried out. Since the observed voltage is subject to a temperature factor, it is necessary to carry out the measurements at about constant temperature, or, if that is not feasible, to provide a temperature compensating device to provide for variations in the temperature of the solution being tested. Such device may conveniently consist in an added resistance of known temperature coefficient connected in series with element AB and the source of current C, and immersed directly in the test solution. As the temperature of the solution rises, the resistance of the compensating device increases and correspondingly reduces the voltage drop along AB to balance the reduction in voltage between electrodes D and E which results from the temperature rise, and conversely as the temperature of the test solution falls below the standard.

For continuous reading the electrode system may be connected to a potentiometer combining resistance element AB, battery C, galvanometer G and voltmeter V in one self-contained apparatus which automatically adjusts itself to maintain the zero reading of the galvanometer, and continuously indicates or records on a chart the voltage between the test electrodes. Equipment of such last-mentioned description is now commercially available. Furthermore, by combining with the potentiometer suitable mechanical or electrical devices responsive thereto, the instrument may be utilized to control the oxidation automatically according to the potential indication, e. g. by controlling the supply of chlorine or the flow of solution under treatment. One means of accomplishing such control consists in providing electrical contacts at selected points on AB at either side of the desired position of sliding contact H, so that movement of H to the extent provided either way from the desired point results in closing a motor operating circuit and starting the motor which in turn is connected by a suitable mechanical drive for opening or closing a valve. Various other means of actuating control valves or of otherwise controlling the supply of materials, however, may be employed, such as will be apparent to those familiar with the use of automatic control devices.

As a standard electrode we prefer to employ the saturated calomel electrode, consisting of the system $\text{Hg}/\text{HgCl}/\text{saturated KCl solution}$ containing an excess of solid KCl crystals, the single potential of which is 0.245 volt at 18°C. , referred to the standard hydrogen scale. Such electrode is convenient for use in plant control work as it is not subject to variation in concentration and can be used for long periods without change. However, a calomel electrode of lower concentration, e. g. a normal or a N/10 calomel electrode, or any other suitable electrode of known potential may be substituted, if so desired.

In order to liberate bromine in the elemental state from a bromide-containing solution, the latter must have a neutral or acid reaction. If initially alkaline, the solution is to be acidified,

preferably with a strong mineral acid, otherwise a portion of the bromine content upon oxidation will be converted to soluble oxidized compounds until the alkalinity is neutralized in this way at the expense of the bromine. In strong saline solutions containing a high concentration of ions bromine may be substantially completely liberated by treating the same with chlorine under conditions of approximate neutrality, corresponding to a hydrogen ion concentration expressed as $\text{pH}=7$. In more dilute solutions a slight acid reaction to counteract the tendency of free bromine to be hydrolyzed is necessary in order to obtain a quantitative liberation of bromine, the degree of acidity required varying with the dilution. In the case of sea water, which contains approximately 3.5 per cent total solids, chiefly chlorides, we have found an acidity between about $\text{pH}=3$ and $\text{pH}=4$ is required for the quantitative liberation of bromine. In a sea water acidified to a lower degree, i. e. having a pH value greater than 4, a portion of the bromine will be hydrolyzed to bromic acid sufficient to raise the acidity and accordingly lower the pH value to the aforementioned value between $\text{pH}=3$ and $\text{pH}=4$, thereby causing a loss of bromine in the extraction, as more particularly described in our co-pending application Serial No. 472,820, filed Aug. 4, 1930.

For any given solution of a bromide containing a definite total concentration of ions from which bromine is to be liberated, e. g. by chlorinating, the oxidation potential increases from a characteristic minimum value, whereat the formation of free bromine commences, to a characteristic maximum whereat all of the bromine is liberated in the elemental state and no bromide ions remain. Further addition of chlorine in excess produces a continued rise of the observed oxidation potential, due to the effect of free chlorine.

In applying our improved method of control, therefore, it is required first to determine the maximum and, if desired, the minimum values for the oxidation potential of bromine in the solution being treated. This may be done in various ways. For instance, the bromine content of a sample of the solution is determined by chemical analysis according to the usual method; chlorine water of known strength is then gradually added to another sample of the solution in exact amount calculated to liberate all of the bromine, while measuring the oxidation potential of the solution according to the method just described. The minimum value is found when the addition of chlorine is begun, and the maximum when the addition thereof is just finished. The result may be checked by blowing the liberated bromine out of the solution with air until it is bromine-free, adding a weighed quantity of a bromide equivalent to the original bromine content and repeating the above determination. For every type of bromide-containing solution there is a characteristic range of oxidation potential values which depends upon the initial concentration of bromide ions and also upon the collateral effect of other ions present. Having determined such range of values for any particular type of solution, and having charted the same, the degree of bromine liberation in subsequent operations may be read directly from the chart when the oxidation potential of the solution is measured, thereby giving a substantially simultaneous indication of the progress of the oxidation.

The oxidation potential range of bromine in sea water acidified to $\text{pH}=3$ is shown in the curve in Fig. 2, the data therefor having been determined by the method hereinbefore described and representing the average of a large number of samples. It accordingly constitutes an approximately average curve which would be subject only to minor variations in working with sea water from any region not materially affected by fresh-water dilution or conditions of abnormal evaporation, as in landlocked bays, etc. The first traces of free bromine in the solution being tested cause an immediate rise of the oxidation potential, as measured by the difference in voltage of the saturated calomel electrode and the bromine electrode, to about 0.88 volt. As the liberation of bromine continues and the concentration of bromide ions diminishes the voltage curve breaks sharply between about 0.88 and 0.91 volt and then continues to rise uniformly. We have found that 0.97 volt is the point whereat substantially all of the bromine has been released in the elemental state. Translating these figures to the standard hydrogen scale by adding the value for the single potential of the standard saturated calomel electrode, i. e. 0.245 volt at 18°C ., the values for the single potential of bromine liberated from sea water are between 1.095 and 1.215 volt. If another standard electrode having a different single potential were used, for instance, a normal calomel electrode having a single potential of 0.286 volt at 18°C ., the observed reading of the voltmeter would be lower than given above by the difference between the single potentials of the two standard electrodes (viz. 0.286 volt—0.245 volt=0.041 volt) but when converted to the standard hydrogen scale the single potential of the bromine electrode would have the same value regardless of the particular standard electrode employed.

The values for the single potential of bromine between 1.095 and 1.215 volt on the standard hydrogen scale are characteristic of sea water containing about 3.5 per cent total solids in solution and about 60 parts bromine per million, and which has been acidified to $\text{pH}=3$. The values hold approximately for other degrees of acidity between $\text{pH}=6$ and $\text{pH}=3$. The actual figures for any solution would be dependent upon both the bromine content and the content of other ions present. If the bromine content were to be increased without materially altering the total solids, the minimum value given above would be lowered in proportion, but the maximum value, whereat all of the bromine is liberated in the free state, would remain substantially the same. Conversely, decreasing the total bromine content would raise the lower value without changing the upper value. The effect of the presence of other ions is to depress the single potential of bromine, so that for solutions having the same bromine content as sea water but a higher content of total solids the bromine single potential would be lowered, and for solutions with a lower percentage of total solids the bromine single potential would be raised accordingly. For any particular type of solution, however, the correct values for the range of bromine single potential may be readily found by the method herein described, and once known may be applied for measuring the degree of bromine liberation in the solution in question by means of the voltage indication. In the case of sea water, which has a nearly uniform composition in all parts of the world, the values given above may be applied

with reasonable accuracy regardless of the source of such sea water, excluding of course cases where local fresh water dilution materially alters the composition.

5 In the extraction of bromine from sea water, therefore, the same is preferably to be acidified to a pH value between about 3 and 4, and the acid solution is then to be treated with chlorine until the oxidation potential thereof reaches a
10 value of approximately 1.215 volt on the standard hydrogen scale. Under practical conditions the final value may vary between about 1.20 and 1.23 volt. The efficiency and economy of the process depends upon the proper control of the
15 chlorination within the limits as stated, particularly under conditions of continuous operation such as obtained in commercial practice. If the oxidation potential falls below the stated values, the degree of chlorination is not sufficient to
20 liberate all of the bromine. On the other hand, if the oxidation potential exceeds the preferred range, a material excess of chlorine will have been used, which means not only a waste of chlorine, but also added expense for purifying
25 the bromine from such excess of chlorine. Inasmuch as the total amount of bromine present is only about 60 parts per million, requiring theoretically about 27 parts of chlorine for the liberation thereof, it is apparent that a variation of
30 only a few parts per million in the amount of chlorine used can produce either a relatively high percentage loss of bromine or of chlorine. The permissible variation is so small in proportion to the total volume of sea water treated that it has
35 been found practically impossible to maintain an effectual control of the chlorination by other means than by the herein described electro-metric method. By controlling the chlorination to maintain the oxidation potential of the chlorinated sea water at a value between 1.20 and
40 1.23 volt referred to the standard hydrogen scale, it has been found possible to secure a maximum liberation of bromine with a minimum consumption of chlorine. The liberated bromine may
45 then be separated from the aqueous solution in any suitable way, as by blowing out with a voluminous current of air, and the so separated bromine vapors may then be absorbed in an alkaline solution or other suitable absorbing medium,
50 according to any of the known methods.

The herein disclosed method of control of bromine liberation is equally applicable when, instead of being chlorinated, the bromide-containing solution is electrolyzed or oxidized by any
55 of the other known methods for liberating bromine therein. In whatever manner the oxidation is performed, therefore, the liberation of bromine may be directly measured by means of the oxidation potential indication determined as
60 herein described in complete detail.

A similar method of procedure may likewise be followed for measuring the liberation of iodine when oxidizing an iodide solution in analogous manner. The values for the single potential of
65 iodine in contact with iodide ions are roughly one-half those for bromine for equivalent concentrations. For any particular set of condi-

tions, however, the exact values may be readily obtained by the method herein disclosed, and such values employed to give an indication of the process of iodine liberation. Owing to the
80 fact that there is a measurable differential between the oxidation potential values for bromine and iodine, our improved method may also be adapted for indicating the liberation of iodine and bromine consecutively from the same solution.
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Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or
90 steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a process of extracting bromine from sea
95 water wherein the same is acidified and bromine is liberated by addition of chlorine thereto, the method of controlling such chlorination which comprises producing an electromotive force varying in response to variations in the concentration
100 of free bromine in the acidified solution and regulating the addition of chlorine in accordance with such electromotive force to maintain the latter at approximately 1.215 volt referred to the standard hydrogen scale.
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2. In a process of extracting bromine from sea water wherein the same is acidified and bromine is liberated by addition of chlorine thereto, the method of controlling such chlorination which
110 comprises producing an electromotive force varying in response to variations in the concentration of free bromine in the acidified solution and regulating the addition of chlorine in accordance with such electromotive force to maintain the
115 latter at a value approximately between 1.20 and 1.23 volt referred to the standard hydrogen scale.

3. In a method of recovering bromine from a solution containing a minute amount of a bromide on the order of the bromide content of sea
120 water and also containing a high proportion of chlorides relative to the bromide, in which the solution is oxidized to liberate bromine therein, the step which consists in controlling the oxidation in accordance with the potential of free bromine in the solution so as to maintain such potential
125 at a value between about 1.20 and 1.23 volt referred to the standard hydrogen scale.

4. In a method of recovering bromine from a solution containing a minute amount of a bromide on the order of the bromide content of sea
130 water and also containing a high proportion of chlorides relative to the bromide, in which the solution is chlorinated to liberate bromine therein, the step which consists in controlling the introduction of chlorine in accordance with
135 the potential of free bromine in the solution so as to maintain such potential at a value between about 1.20 and 1.23 volt referred to the standard hydrogen scale.

JOHN J. GREBE.
RAY H. BOUNDY.
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