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[54] **PROCESS FOR REMOVING HEXAVALENT CHROMIUM FROM CHLORATE CONTAINING LIQUORS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 219,375, Jan. 20, 1972, abandoned.

[52] **U.S. Cl.** **423/475,** 423/472, 423/607

[51] **Int. Cl.** **C01b 11/00,** C01b 11/14

[58] **Field of Search** 423/475, 472, 607, 184, 423/179

[56] **References Cited**

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[57] **ABSTRACT**

A method has been devised for removing hexavalent chromium values from concentrated aqueous alkali metal chlorate solutions by treating said solutions with a soluble sulfide, neutralizing the treated mixture and thereafter separating an insoluble trivalent chromium product from the solution. Hypochlorites, when present, may be simultaneously removed from the chlorate solution by reaction with excess sulfide reagent.

11 Claims, No Drawings

PROCESS FOR REMOVING HEXAVALENT CHROMIUM FROM CHLORATE CONTAINING LIQUORS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 219,375 filed Jan. 20, 1972, now abandoned.

BACKGROUND OF INVENTION

The present invention relates to a method for removing hexavalent chromium values from concentrated aqueous solutions of alkali metal chlorates. More particularly it relates to the simultaneous removal of alkali metal dichromates and alkali metal hypochlorites from concentrated aqueous solutions of alkali metal chlorates by treating said solutions with water soluble sulfides.

It is known to prepare alkali metal chlorates, specifically sodium chlorate, by the electrolysis of brine wherein the alkali metal hydroxide formed at the cathode reacts with the chlorine formed at the anode. The cathode which is generally fabricated from iron or similar corrodible metal may, it is known, be protected from oxidation by the inclusion in the electrolyte of substances, such as an alkali metal dichromate, specifically sodium dichromate. The dichromates being highly colored salts are objectionable impurities when permitted to remain in the chlorate product and it is generally the practice to treat the chlorate solution with a soluble metal salt, such as a soluble barium salt, to remove the dichromate impurity as an insoluble barium salt. Such prior art processes have serious objections. Soluble barium salts are not only relatively expensive but also combine with any sulfate salts present producing difficultly filterable precipitates. In addition, excess barium salts must be precipitated, e.g., with sodium carbonate, and removed by filtration before the cell liquor can be processed further. Moreover, barium salts present pollution problems in the disposal of wastes from processes utilizing alkali metal chlorates.

OBJECTS OF THE INVENTION

It is thus a principal object of this invention to devise an economical and efficient method for removing hexavalent chromium values from concentrated aqueous solutions of alkali metal chlorates.

Another object is to devise a process for the simultaneous removal of hexavalent chromium and alkali metal hypochlorite from alkali metal chlorate solutions.

Other objects will be obvious from the following description of the present invention.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that hexavalent chromium values can be substantially completely removed from concentrated aqueous solutions of alkali metal chlorates by treating said solutions contaminated with a hexavalent chromium compound with an amount of a soluble sulfide sufficient to reduce the hexavalent chromium to the trivalent stage, neutralizing the alkaline solution to a pH of below about 5, and thereafter separating the resultant insoluble trivalent chromium product from the chlorate solution. It has been found also that any alkali metal hypochlorite present in the aqueous alkali metal chlorate solution may be removed simultaneously by the addition of a sufficient excess of the soluble sulfide.

Although the exact course of the reaction is not known, it is probable that the reaction proceeds according to the following equations, using sodium dichromate and sodium sulfide as the reactants in acid solution:

$$Na_2Cr_2O_7 + 3\ Na_2S + 3\ H_2SO_4 + H_2O \longrightarrow 2\ Cr(OH)_3 + 3S + 3\ Na_2SO_4 + 2\ NaOH \quad (1)$$

Similarly it may be postulated that the reaction between sodium hypochlorite and sodium sulfide proceeds as follows:

$$4\ NaClO + Na_2S \longrightarrow Na_2SO_4 + 4\ NaCl \quad (2)$$

$$NaClO + Na_2S + H_2O \longrightarrow S + NaCl + 2\ NaOH \quad (3)$$

or combining equations (2) and (3)

$$5\ NaClO + 2\ Na_2S + H_2O \longrightarrow Na_2SO_4 + 5\ NaCl + 2\ NaOH + S \quad (4)$$

Accordingly, although the precise stoichiometry of the reactions occurring in the process of the present invention is not known, it is believed that at least three mol proportions of the soluble sulfide, e.g., sodium sulfide, are necessary to convert one mol proportion of the hexavalent chromium compound, e.g., sodium dichromate, to the trivalent stage and further at least about 0.4 molar proportion of the soluble sulfide is required to "kill" each mol proportion of alkali metal hypochlorite, e.g., sodium hypochlorite, when present in the aqueous alkali metal chlorate composition. Preferably, in carrying out the process of this invention an excess, and especially at least a 100 percent excess, of the amount of soluble sulfide stoichiometrically required to react with the hexavalent chromium values present in the chlorate liquor is used. Thereby, on acidification all of the hexavalent chromium is reduced to an insoluble trivalent chromium product and any hypochlorite present is removed or "killed."

DETAILED DESCRIPTION OF THE INVENTION

In accordance with a preferred mode of carrying out this process of this invention, a concentrated aqueous solution of sodium chlorate, such as is obtained by the electrolysis of brine and which contains about 200 to 400 grams per liter ("gpl") of sodium chlorate about 100 to 200 gpl of sodium chloride and about 0.2 to about 1.5 gpl of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) is heated to and maintained at from about 40° to about 70° C. To this alkaline solution about 0.5 to about 0.7 gpl of sodium sulfide, equivalent to from about 10 to about 20 mols of sodium sulfide per mol of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), is added. The resultant alkaline yellow solution, the pH of which is above about 8 and may be as high as 11 or more, is neutralized to a pH within the range of about 4 to about 5 by the addi-

tion of sulfuric acid. The solution becomes colorless and a precipitate, which is probably a hydrated chromic oxide, appears and is removed by filtration, preferably after adjusting the pH of the slurry to above 5 and especially to about pH of 7, with an alkaline agent such as caustic soda. The clarified solution contains less than about 2 ppm of chromium and is free from sodium hypochlorite.

The reaction between alkali metal chlorates and alkali metal sulfides proceeds very slowly if at all in alkaline media. Since concentrated aqueous solutions of sodium chlorate are alkaline, i.e., have a pH of at least about 8, and especially in the presence of strongly alkaline alkali metal sulfides it is obvious that the reduction of the hexavalent chromium values proceeds the more slowly, if at all, in the strongly alkaline reaction media of this process. It is therefore, highly desirable to render the reaction mixture acid to expedite the reaction. This can be observed by the decolorization of the mixture on addition of acid. However, alkali metal chlorates decompose with the formation of chlorine dioxide in the presence of acids and sodium chloride, especially at pHs below 4, and at temperatures above ambient. Accordingly it is preferred to adjust the pH of the reaction mass to a pH of above 5, once the color of the solution has been discharged, i.e., after completion of the reduction of the hexavalent chromium values and appearance of the hydrated chromic oxide precipitate. This final adjustment is preferably carried out to a pH of above 5 and especially to a pH of about 7 prior to filtration of the insoluble chromic hydroxide.

Any water soluble sulfide can be used in the process of the present invention. Thus for example, sodium sulfide, potassium sulfide, sodium bisulfide, potassium bisulfide, or the free acid, hydrogen sulfide can be used. Hydrogen sulfide when added to the alkaline chlorate liquor would be converted to sodium sulfide or bisulfide. "White Liquor," as used in Kraft pulp manufacturing plants, and which contains approximately 70 gpl NaOH and 30 gpl Na_2S can be used as the source of the soluble sulfide also. Alkali metal polysulfides, e.g. Na_2S_x, can also be used.

Sodium sulfide and sodium bisulfide because of their general availability and low cost are generally preferred.

The amount of soluble sulfide used should be at least that amount which will reduce the hexavalent chromium values to the trivalent state. Based on the stoichiometry postulated above, it is believed that at least 3 mol proportions of sulfide are required to reduce one mol proportion of hexavalent chromium to the trivalent stage. Preferably an excess is used, and accordingly about 6 mols of sulfide and especially from about 10 to 20 mol proportions of sulfide per mol proportion of hexavalent chromium compound present is used. About 10 or 12 to about 13 mol proportions of sulfide per mol proportion of hexavalent chromium compound present in the solution can be used, for example. Such large apparent excesses of sulfide are preferred in order to not only reduce the chromium values but also to simultaneously remove any hypochlorite from the chlorate solution. Some or all of the excess sulfide, over that required to react with the hexavalent chromium and hypochlorite is removed during the process when the mass is rendered acid.

The temperature of the reaction is not critical. Conveniently, the process is carried out at about 40° to about 80° C, and preferably at about 65° C. The latter temperature is that at which the concentrated alkaline chlorate solution is discharged from many electrolysis cells and it is most convenient to treat the solution at this point to remove the chromium values. Temperatures above and below the preferred range can be used although the reactions proceed at a slower rate below about 40° C, and above about 80° C, the energy expended in heating the solution is wasted.

Following formation of the chromic hydroxide precipitate when the solution is acidified to a pH below about 5, the slurry may be filtered. It has been found that at this point, the sludge is not readily filterable. Addition of filter aids improves the filtration at this stage, but it is preferred to neutralize the acid slurry to a pH of about 5 or higher, with an alkaline agent such as caustic soda or the like. By this procedure not only is the decomposition of sodium chlorate minimized but also the separation of the insoluble chromic hydroxide sludge is facilitated. Separation of the insoluble material can be accomplished in a known manner, as, for example, by filtration, centrifugation and the like.

The following examples will illustrate the process of the present invention. Parts and percentages are by weight and temperatures are given in degrees centigrade, unless otherwise specified.

EXAMPLE I

A concentrated aqueous solution of sodium chlorate containing 350 grams per liter ("gpl") of sodium chlorate, 140 gpl sodium chloride and 0.195 gpl sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) was heated to and maintained at 65°. Sufficient of an alkaline aqueous solution of sodium sulfide ("White Liquor" containing about 70 percent NaOH and 30 percent Na_2S) was added to introduce 0.54 gpl sodium sulfide into the solution. The resulting yellow colored solution had a pH of 11. This solution was rendered acid, by the addition of sulfuric acid to a pH between 4.0 and 4.5. The solution was agitated as it became colorless and a precipitate appeared. Thereafter the acidic mixture was neutralized to a pH of about 7 and filtered. The trivalent chromium ion content of the clarified solution was determined by atomic absorption.

This experiment was repeated using sufficient "White Liquor" to introduce 0.63 gpl sodium sulfide into the mass.

The data obtained in these experiments are set out in the following Table I.

TABLE I

Initial Conc. $Na_2Cr_2O_7.2H_2O$	Na_2S Added	Mol Ratio $Na_2S/Na_2Cr_2O_7.2H_2O$	Cr^{+++} in solution
0.195 gpl	0.54 gpl	10.56	1.9 ppm
0.195 gpl	0.63 gpl	12.32	0.3 ppm

EXAMPLE II

The procedure of Example I was repeated using a concentrated sodium chlorate solution containing 360 gpl $NaClO_3$, 216 gpl NaCl and 1.4 gpl $Na_2Cr_2O_7 \cdot 2H_2O$. The results obtained are set out in the following Table II.

TABLE II

Initial Conc. $Na_2Cr_2O_7.2H_2O$	Na_2S Added	Mol Ratio $Na_2S/Na_2Cr_2O_7.2H_2O$	Cr^{+++} in solution
1.4 gpl	5.88 gpl	16.05	1.6 ppm
1.4 gpl	6.18 gpl	16.85	0.7 ppm

EXAMPLE III

To a synthetic chlorate cell liquor containing about 350 gpl $NaClO_3$, to about 150 gpl NaCl and 0.15 gpl $Na_2Cr_2O_7 \cdot 2H_2O$, at about 65 degrees sufficient aqueous sodium bisulfide containing 0.5 gpl sodium bisulfide assaying 71.5 percent in solid state was added to introduce 0.357 gpl NaHS into the solution. The resulting yellow solution, having a pH of about 9, was rendered acid by the addition of sulfuric acid to a pH of 4.2. The mixture was then divided into three equal portions and the portions were neutralized to pH 5, or 6, or 7 with sodium hydroxide and then filtered. The clarified solutions were assayed by atomic absorption for trivalent chromium. Table III is a record of the results obtained.

TABLE III

Initial Conc. $Na_2Cr_2O_7.2H_2O$	NaHS added	Mol Ratio $NaHS/Na_2Cr_2O_7.2H_2O$	Cr^{+++}in Filtered Solution
0.15 gpl	0.357 gpl	12.67	<0.1 at pH 5
0.15 gpl	0.357 gpl	12.67	<0.1 at pH 6
0.15 gpl	0.357 gpl	12.67	<0.1 at pH 7

EXAMPLE IV

A concentrated sodium chlorate solution containing about 350 gpl sodium chlorate, about 140 gpl sodium chloride, 3.5×10^{-3} moles (0.26075 gpl) sodium hypochlorite and 0.29×10^{-3} mole (0.08642 gpl) sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) was treated with 7.0×10^{-3} moles (0.392 gpl) sodium bisulfide at about 65°. The pH of the solution was adjusted to 4.7 by the addition of aqueous sulfuric acid. This amount of sodium bisulfide represents about 100 percent excess over the stoichiometric equivalent amount of NaHS required to reduce the hexavalent chromium to trivalent chromium. The solution was agitated at about 65° for about 30 minutes and then filtered. The filtrate contained less than 0.1 ppm of hexavalent chromium.

This invention has been described in the above specification and the best modes for carrying it out illustrated in the above examples. As will be obvious to those skilled in this art many variations in the details set out therein can be made without departing from the scope or spirit of the invention.

What is claimed is:

1. A process for removing hexavalent chromium values from alkaline aqueous solutions of alkali metal chlorates which comprises the steps of

1. treating a concentrated aqueous solution of an alkali metal chlorate having a pH above about 8 with at least about 3 molar proportions of a water soluble sulfide per molar proportion of hexavalent chromium compound present,
2. neutralizing the resultant solution to a pH of about 4 to about 5 thereby precipitating trivalent chromium as an insoluble product, and
3. separating the insoluble trivalent chromium product from said solution.

2. The process of claim **1** wherein said alkali metal chlorate is sodium chlorate.

3. The process of claim **2** wherein the said solution is treated with an amount of soluble sulfide which is at least sufficient to reduce the hexavalent chromium values to the trivalent stage and also to react with any alkali metal hypochlorite present.

4. The process of claim **2** wherein the said solution is treated with at least about 6 mol proportions of soluble sulfide per mol proportion of hexavalent chromium compound present in said solution.

5. The process of claim **4** wherein the said solution is treated with from about 10 to about 20 mol proportions of soluble sulfide per mol proportion of hexavalent chromium compound present in said solution.

6. The process of claim **5** wherein the said solution is treated with from about 10 to about 13 mol proportions of sodium sulfide per mol proportion of hexavalent chromium compound present in said solution.

7. The process of claim **2** in which the said solution is treated with sodium bisulfide.

8. The process of claim **5** in which the said solution is treated with about 12 to about 13 mol proportions of sodium bisulfide per mol proportion of hexavalent chromium compound present in said solution.

9. The process of claim **5** wherein the said solution, after treatment with the soluble sulfide, and prior to separating the insoluble trivalent chromium product is adjusted to a pH between above about 5 and about 7.

10. The process of claim **1** wherein the process is carried out at a temperature of from about 40° to about 80° C.

11. The process of claim **10** wherein the process is carried out at about 65° C.

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