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SODIUM DICHROMATE AND MOLYBDIC ACID TO INCREASE THE CATHODE EFFICIENCY OF CHLORATE CELLS

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6 Claims

ABSTRACT OF THE DISCLOSURE

Molybdic acid functions synergistically with sodium dichromate in chlorate cells to increase the hydrogen efficiency at a steel cathode. Hence, the concentration of soluble hexavalent chromium in the chlorate cell liquor may be decreased to prevent the development of colored impurities in the crystallized chlorate product, without loss of efficiency.

BACKGROUND OF THE INVENTION

The electrolytic production of chlorates has been effected in cells provided with steel cathodes. To avoid corrosion of the steel cathode and to improve the overall chlorate efficiency of the cell, hexavalent chromium has been conventionally added to the cell liquor. The hexavalent chromium is usually added to the cell liquor in the form of sodium dichromate in at least an amount of two grams per liter of solution.

Hexavalent chromium may be introduced into a chlorate cell liquor in any suitable form. For example, soluble hexavalent chromium may be supplied as Na_2CrO_4 (alkali metal chromate), $\text{Na}_2\text{Cr}_2\text{O}_7$ (alkali metal dichromate) or CrO_3 (chromic acid). Throughout this specification, when reference is made to $\text{Na}_2\text{Cr}_2\text{O}_7$ (alkali metal dichromate) it is to be understood that any source of soluble hexavalent chromium may be substituted with equivalent results.

The chlorate containing cell liquors are conventionally concentrated before introduction into a crystallizer or during the processing within the crystallizer. Due to the evaporation of the solution containing chlorate, the concentration of sodium dichromate increases to from about 5–6 grams per liter of solution based upon an initial concentration of 2 grams per liter. This represents about a 2–3 fold increase based on hexavalent chromium.

The sodium chlorate crystals recovered from the crystallizer have a yellow color, imparted from the high dichromate concentration in the solution from which chlorate is ultimately crystallized. This yellow color is objectionable because the chlorate must be further treated to remove the color. Müller, in U.S. 2,756,201, issued July 24, 1956, found that dull chromium plated iron cathodes in place of iron cathodes would avoid the necessity for using sodium dichromate to prevent excessive reduction at the cathode.

However, the problem remains that to be able to use a steel cathode in a chlorate cell while maintaining nearly 100 percent hydrogen efficiency at the cathode, some additive such as sodium dichromate is required. The percent cathode efficiency, as it is used throughout this specification, is based upon the rate of hydrogen evolution at the cathode with a constant current in the cell.

Attempts to avoid the use of dichromate have been largely unsuccessful or impractical. For example, the use of colorless additives which will perform the function of

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dichromate, or techniques for reducing the quantity of dichromate in the chlorate cell have been attempted.

It was believed that the dichromate level in chlorate cells could not be significantly decreased unless the chromium content in the steel cathode was increased. Furthermore, the use of colorless complex anions such as borate, tungstate and molybdate do not give good cathode efficiencies in chlorate cells containing a steel cathode.

It is an object of this invention to produce chlorates, in a chlorate cell employing a steel cathode, which are relatively free from characteristic color imparted by hexavalent chromium compounds.

Also, it is an object of this invention to produce a chlorate product relatively free from colored impurities while maintaining a near 100 percent cathode efficiency.

BRIEF SUMMARY OF THE INVENTION

We have discovered that the addition of trace amounts (0.05–0.20 gram per liter) of sodium dichromate to chlorate cell liquors containing as low as 0.10 gram per liter of 85 percent molybdic acid results in steel cathode efficiencies of nearly 100 percent. The upper limit of molybdic acid is defined by its solubility. However, for practical purposes the upper limit of the molybdic acid concentration is about 2 grams per liter. Molybdic acid, molybdenum trioxide or an alkali metal molybdate are examples of sources of molybdenum that may be used to introduce hexavalent molybdenum into the chlorate cell liquors. Any source of soluble hexavalent molybdenum is applicable to the process disclosed herein although for the purposes of exemplifying the invention, reference is made to molybdic acid (MoO_3 —85 percent). The action of molybdic acid in combination with sodium dichromate is an example of true synergism. The reduced quantities of sodium dichromate present results in a product relatively devoid of the undesirable color characterizing a chlorate product from electrolysis in the presence of about 2 grams per liter sodium dichromate.

DETAILED DESCRIPTION OF THE INVENTION

Mixtures of sodium dichromate and molybdic acid act synergistically to increase the cathode efficiency at steel cathodes in chlorate cells, at concentrations where neither additive alone is effective.

For the purpose of illustrating our invention in the following examples, the typical, catholyte solution from a diaphragm chlorate cell of the type described in copending application 510,592, now U.S. Pat. No. 3,464,901, and 510,617 filed by Morris P. Grotheer and Edward H. Cook, Jr., on Nov. 30, 1965, and by Morris P. Grotheer, John E. Currey and Edward H. Cook, Jr. on Nov. 30, 1965, respectively. It is to be understood that although for the purpose of illustration, a diaphragm cell liquor was used, this invention is applicable to any chlorate cell using a steel cathode.

All the experiments presented in the following examples were conducted at 80 degrees centigrade.

Example 1

A typical catholyte solution containing 500 grams per liter NaClO_3 , 120 grams per liter NaCl , 40 grams per liter NaOH was electrolyzed with a mild steel, 6 x 6 mesh cathode. With the addition of no additive, the cathode efficiency was calculated from the rate of hydrogen evolution at a constant current. The percent cathode efficiency in the absence of any additive was zero.

Examples 2–11

The following table presents a compilation of the cathode efficiencies obtained from different additives. The

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sodium dichromate was added to the catholyte described in Example 1 as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and molybdic acid was added as 85 percent MoO_3 . These experiments were run in the listed order.

TABLE I

Additive	Percent cathode efficiency
(2) 2 grams per liter H_3BO_3 -----	0
(3) 2 grams per liter $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ -----	72
(4) 2 grams per liter (85%) MoO_3 -----	82
(5) 5 grams per liter (85%) MoO_3 -----	92
(6) 10 grams per liter (85%) MoO_3 -----	90
(7) 2 grams per liter (85%) MoO_3 plus 0.15 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	98
(8) 1 gram per liter (85%) MoO_3 plus 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	98
(9) 0.5 gram per liter (85%) MoO_3 plus 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	99
(10) 0.1 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	98
(11) None -----	0

Between each of the preceding examples, the cathode was etched in dilute HCl to insure removal of Fe_2O_3 prior to exposure in the electrolysis solution.

Experiment 10 presents a higher cathode efficiency than has ever been observed at that concentration of $\text{Na}_2\text{Cr}_2\text{O}_7$. It is assumed, although we do not intend to be bound by the theory, that exposure to the solutions of Examples 4-9 resulted in the deposition of some molybdenum on the surface of the steel cathode that was not fully removed by the HCl etching treatment. Still, some sodium dichromate was essential to prevent hypochlorite and chlorate ion reduction at the cathode as is demonstrated by Example 11.

Examples 12-15

To determine the effects of low $\text{Na}_2\text{Cr}_2\text{O}_7$ concentration, the following experiments were performed. The cathode was etched prior to exposure to the chlorate cell liquor described in Example 1 by treatment with both dilute HNO_3 and dilute HCl to insure the removal of any deposited metal.

TABLE II

Additive	Percent cathode efficiency
(12) 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	47
(13) 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	88
(14) 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	80
(15) 0.20 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	97.5

A comparison of these examples with Examples 4-6 demonstrates that while the increased concentration of sodium dichromate eventually increased the cathode efficiency to 98 percent and above, increasing the molybdic acid concentration as high as 10 grams per liter never produces cathode efficiencies much above 90 percent.

A comparison of Example 10 in Table I with Examples 13 and 14 demonstrates the unusual cathode efficiency of Example 10 resulting possibly from the deposition of molybdenum on the cathode during Examples 4-9 which would not be completely removed by the HCl etching alone.

The data presented in Examples 13 and 14 demonstrates that as the cathode efficiency decreases experimental error increases. As the cathode efficiency approaches 100 percent, experimental error diminishes to the point that repetitive runs vary ± 1 percent. At the higher cathode efficiencies the surface of the cathodes does not contain ferric oxide impurities whereas at lower cathode efficiencies the steel cathode surface contains an amount of ferric oxide which varies considerably from experiment to experiment.

Examples 16-21

To the diaphragm cell liquors containing sodium dichromate concentrations as presented in Examples 12, 13

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and 14, MoO_3 (85%) was added. By comparison with the results tabulated as experiments 12, 13 and 14, the synergistic effect of molybdic acid and sodium dichromate is evident. Examples 16-18 reflect the addition of increasing amounts of MoO_3 (85%) to the sodium of Example 12 during operation of the cell. Examples 19 and 20 reflect the addition of MoO_3 (85%) to the solutions of Examples 13 and 14, respectively, during cell operation.

TABLE III

Additive	Percent cathode efficiency
(16) 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.2 gram per liter MoO_3 (85%) -----	81.5
(17) 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.4 gram per liter MoO_3 (85%) -----	96
(18) 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.6 gram per liter MoO_3 (85%) -----	97.5
(19) 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.10 gram per liter MoO_3 (85%) -----	98
(20) 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.10 gram per liter MoO_3 (85%) -----	84
(21) 0.10 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.4 gram per liter MoO_3 (85%) -----	94

In comparing Examples 19 and 20 with Examples 13 and 14, it will be noted that by adding molybdic acid at the same concentration the relative improvement from a good cathode efficiency (Example 13) is greater than the improvement over a poorer cathode efficiency (Example 14).

Examples 22-24

The addition of increasing amounts of sodium dichromate to a diaphragm chlorate cell liquor as described in Example 1 which already contained 0.10 gram per liter MoO_3 (85%) produced the following results.

TABLE IV

Additive	Percent cathode efficiency
(22) 0.10 gram per liter MoO_3 (85%) -----	60
(23) 0.10 gram per liter MoO_3 (85%) plus 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	80
(24) 0.10 gram per liter MoO_3 (85%) plus 0.15 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ -----	88

From the data tabulated in Tables III and IV it may be seen that the addition of molybdic acid to a chlorate cell liquor already containing sodium dichromate was more effective than the reverse order of addition.

Examples 25-31

These experiments were conducted by introducing both MoO_3 (85%) and $\text{Na}_2\text{Cr}_2\text{O}_7$ into the chlorate cell liquor prior to starting the electrolysis to determine the minimum amounts of additive needed. Dilute HNO_3 and dilute HCl were used to etch the steel cathode between each run.

TABLE V

Additive	Percent cathode efficiency
(25) 0.2 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.2 gram per liter MoO_3 (85%) -----	100
(26) 0.15 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.15 gram per liter MoO_3 (85%) -----	98
The steel cathode used in Example 26 was then removed from the solution, air dried for 20 minutes, and returned to the solution -----	100
The steel cathode used in Example 26 was then air dried over the weekend, placed back in solution -----	97

The following experiments were conducted without etching the steel cathode between runs with dilute HNO_3 and dilute HCl. Etching was omitted, to simulate the loss of additive as it would occur during continuous operation of an electrolytic cell.

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TABLE VI

Additive	Percent cathode efficiency
(27) 0.2 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.2 gram per liter MoO_3 (85%) -----	95
(28) 0.1 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.1 gram per liter MoO_3 (85%) -----	95
(29) 0.05 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.05 gram per liter MoO_3 (85%) -----	93
(30) 0.02 gram per liter $\text{Na}_2\text{Cr}_2\text{O}_7$ plus 0.02 gram per liter MoO_3 (85%) -----	90
(31) No additive -----	75

Examples 25-31 show the minimum concentrations of sodium dichromate and sodium molybdate needed to obtain good cathode efficiencies. In general, cathode efficiencies improved with time. Whenever an initial cathode efficiency of 95 percent or above was observed, within a few hours the performance rose to 100 percent efficiency.

Example 31 provides additional evidence that the steel surface of the cathode has become coated either with molybdenum, a molybdenum-chromium mixture or a molybdate-chromate mixture.

These experiments demonstrate the synergistic action of sodium dichromate and molybdic acid in increasing the efficiency of a steel cathode in a diaphragm chlorate cell. In the absence of molybdic acid and acid etching, about 2 grams per liter sodium dichromate is required to insure good cathode efficiencies. With acid cleaning of the steel cathode, the dichromate concentration may be decreased to about 0.2 gram per liter although higher concentrations are needed to insure sustained cathode efficiencies. Combinations of molybdic acid and sodium dichromate are effective with initial concentrations ranging between 0.15-0.20 gram per liter of each component.

Molybdic acid alone is not sufficient to produce an acceptable cathode efficiency at the concentrations studied. However, once the steel cathode has been conditioned by exposure as a cathode in a solution containing both molybdic acid and sodium dichromate, lower concentrations of these additives can be used. This phenomenon is believed to result from the deposition of molybdenum, molybdenum-chromium or molybdate-chromate mixtures on the cathode. However, no conclusive evidence of such deposits has been obtained to support this theory.

Having disclosed our invention, it is apparent to those skilled in the art that modifications may be made which do not depart from the spirit of our contribution. The

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specific examples presented in this disclosure are illustrative of the invention and are not intended to be limitations upon the true scope of the invention. For example, in addition to the molybdic acid additive specifically disclosed herein, other adjuvants such as tungstates, vanadates and manganates may be employed.

What is claimed is:

1. A process for the production of an alkali metal chlorate essentially free from colored impurities which comprises electrolyzing an alkali metal chloride in an electrolytic cell equipped with a steel cathode in the presence of an amount of hexavalent molybdenum sufficient to reduce the amount of hexavalent chromium additive necessary to maintain hydrogen efficiencies at the cathode near 100 percent.

2. The process of claim 1 in which hexavalent molybdenum was introduced into the chlorate cell liquors as 85 percent molybdic acid.

3. The process of claim 2 in which the hexavalent chromium was introduced as sodium dichromate in an amount less than 0.20 gram per liter of solution.

4. The process of claim 3 in which the ratio of 85% molybdic acid to sodium dichromate is between 1:12 and 12:1.

5. The process of claim 3 in which the molybdic acid and sodium dichromate are present in the chlorate cell liquors in equal amounts.

6. A process for maintaining a near 100 percent hydrogen efficiency at a steel cathode of a chlorate electrolytic cell which comprises performing the electrolysis in the presence of hexavalent molybdenum in conjunction with a source of soluble hexavalent chromium, said hexavalent chromium being present in an amount less than two grams per liter of solution.

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TA HSUNG TUNG, Primary Examiner