United States Patent Office 2,737,298 Patented Mar. 6, 1956

2,737,298

WASTE DISPOSAL PROCESS

Frank J. Hendel, Newark, N. J., assignor to Wigton-Abbott Corporation, Plainfield, N. J., a corporation of New Jersey

No Drawing. Application March 10, 1953, Serial No. 341,605

10 Claims. (Cl. 210—149)

This invention relates to a process for the disposal of wastes containing cyanides. More particularly, the invention relates to an electrolytic process for treating solutions containing cyanides to convert the cyanides either to less toxic cyanates, or to completely break down the cyanides and cyanates to liberate the nitrogen component thereof as a gas.

Current methods for the destruction of cyanides in liquid industrial wastes generally involve chlorination under alkaline conditions according to reactions of the following type:

(1) $NaCN+Cl_2+2NaOH=NaCNO+2NaCl+H_2O$

and

(2) $2NaCN+5Cl_2+10NaOH=2NaHCO_3+10NaCl+N_2+4H_2O$

The choice between these two reactions depends upon whether the conversion to cyanate is sufficient to permit safe disposal, or whether complete breakdown of the cyanide to nitrogen is required before the wastes can be disposed of.

The cost of the chemicals required in these reactions, particularly when full destruction of cyanides to nitrogen is required, and the special equipment needed for chlorination and for the handling of caustic used in reactions, present serious problems and add excessively to the overhead in electroplating, and other processes which yield substantial amounts of cyanide wastes.

I have now discovered a new and practical procedure for treating cyanide wastes to convert the cyanides therein, either to cyanates or to free nitrogen, without any need for handling free chlorine and caustic, while at the same time effecting the conversion at only a fraction of the cost involved in the chemical process above mentioned.

The new process, in accordance with my invention, comprises adding to a solution of cyanides an alkali metal halide, and subjecting the resulting solution to electrolysis for a time, which may be varied from a minimum required to decompose all cyanide present, to a maximum required to decompose all cyanide originally present to free nitrogen.

In this process, any alkali metal halide can be employed, but, since economy is a primary factor, it is preferable to use a cheap form of sodium chloride, such as rock salt, brine, or even sea water, and the salt can be added in solution, or as a solid which is permitted to dissolve as electrolysis proceeds. It is to be noted in this connection, however, that the alkali metal halide, although taking part in the process and being essential to the process, is not consumed. In other words, the alkali metal halide behaves somewhat in the manner of a catalyst. This will be more readily apparent from the following breakdown of reactions which may be considered to take place in the electrolysis and involving the alkali metal halide:

(3) $10NaCl \rightleftharpoons 10Na^+ + 10Cl^-$

(4) On cathode: $10Na^+ + 10- = 10Na$

(5) On cathode: $10Na+10H_2O=10NaOH+5H_2$

(6) On anode: $10Cl^- + 10+ = 5Cl_2$

In the electrolysis, there is no separation of anolyte from catholyte and hence the chlorine and sodium hydroxide which are formed at the anode and cathode may react with cyanides and/or with themselves, according to the reaction:

(7) $2NaOH+Cl_2=NaC10+NaCl+H_2O$

The sodium hypochlorite formed in this reaction, however, is as powerful an oxidizing agent as free chlorine, and will convert cyanides to cyanates or even to nitrogen. Furthermore, the nascent chlorine as it is formed in the electrolysis reacts faster with cyanides and with cyanates than does the chlorine introduced as a gas in accordance with procedures heretofore employed. Thus, the possibility of interreaction between the chlorine and sodium hydroxide as formed does not interfere with the cyanide destruction in the electrolysis.

When reactions 2 and 3 to 6 are combined, the following reaction is obtained as representing what takes place in the electrolysis:

(8) $2NaCN+6H_2O+10+ + 10- = 2NaHCO_3+N_2+5H_2$

In this reaction, hydrogen evolves at the cathode and nitrogen evolves at the anode, and it will be noted that in the overall reaction, the initial sodium chloride has been cancelled or offset by the sodium chloride formed in the reaction.

For complete breakdown of cyanide to nitrogen as indicated in Equation 8, I have found that 5 to 6 kw. h. of electric energy are required for each pound of NaCN or its equivalent. On the other hand, if the presence of cyanates in the resulting solution is permitted, the energy can be reduced to about 2–2.5 kw. h. per pound of NaCN or its equivalent. In this connection, it will be noted that in the initial stages of the electrolysis, i. e., while the primary change involved is conversion of cyanide to cyanate, no nitrogen is evolved at the anode, and, as a practical matter, the time at which the evolution of nitrogen commences can be taken as indicating substantial completion of the breakdown from cyanide to cyanate.

In supplying electric energy for electrolysis, I preferably employ a relatively low voltage, i. e., about 5 to 7 volts. The amperage may be varied to a considerable extent depending upon the nature of the waste solution being treated, and the time required for the electrolysis will accordingly vary inversely with respect to the amperage.

The amount of sodium chloride or other alkali metal halide to be employed depends upon the dilution of the cyanides and upon whether the wastes are treated batchwise, or in a flow-through or continuous process. The lower the quantity of electrolytes in the wastes, the more sodium chloride should be added, and in batch operation less sodium chloride may be used as the chlorine and sodium hydroxide which are formed as intermediates react within the same environment to again form sodium chloride. In flow-through operation, the sodium chloride formed is constantly being carried away, and hence a somewhat greater amount of sodium chloride should be fed with the wastes to insure a proper concentration at all times. In general, for each pound of sodium cyanide or its equivalent, 5 to 10 pounds of sodium chloride should be used in a batch process, whereas in a continuous process this amount should be increased to about 7 to 15 pounds.

Considering briefly the basic cost involved, it will be noted that 15 pounds of rock salt costs about 10 to 15¢, and the cost of 6 kw. h. of electricity may be about 6 to 12¢, making a total of 16¢ to 27¢ per pound of NaCN. This represents but a small fraction of the cost

of materials required in the currently available methods originally mentioned.

Further in the interest of economy, it should be noted that the equipment required is relatively simple and inexpensive. Suitable electrolytic cells for use in the process can be made out of mild steel, or if desired steel lined with concrete. The capacity should be such that at least four hours retention time is insured. This can be achieved by employing a plurality of cells or a single cell of suitable size. Each cell, whether small, or large, should have a number of alternately arranged anodes and cathodes, and in a flow-through system these should be arranged to form a series of baffles so that the waste being treated will flow in zigzag fashion between them. The cathodes may be made of carbon steel, although the anodes should be formed of lead, graphite, or other material suitably resistant to the action of chlorine. The cell should of course be set up either outdoors or in a space suitably ventilated for the elimination of hydrogen as it is evolved at the cathodes.

Wastes to be subjected to electrolysis should have a pH of about 8.5 or more, and this pH should be adjusted by the addition of alkali if it is too low. It may also be desirable to clarify wastes by settling, filtering, or the like, before adding the same to the electrolytic cells. On the other hand, if a waste liquor is strongly alkaline, this alkalinity may be partly reduced by the sodium bicarbonate which is formed in the electrolysis. Further adjustment of the pH of effluent from the cells can be made either by addition of sulfuric acid or the like, or by blending this effluent with other wastes of an acidic nature.

It will also be noted that valuable metals which may remain in the wastes may be deposited in the cathodes and thus recovered. To the extent that metals are deposited in this way at the cathode, the amount of hydrogen liberated may be reduced.

The following example will serve to indicate how the process, in accordance with my invention, can be carried out, but it is to be understood that this example is given by way of illustration, and not of limitation:

Example

0.676 oz. of sodium cyanide was dissolved in one gallon of water and placed in a glass vessel. Two flat electrodes facing each other were submerged. The submerged part was 5" x 3". The distance between the electrodes was 4". The temperature was 70° F. pH–14. The cathode was made of stainless steel, while the anode was made of lead.

Four ounces of sodium chloride in commercial crystalline form was then dumped to the bottom of the vessel. The contents of the vessel were not agitated and hence sodium chloride was dissolving during the electrolysis very slowly. A current of six volts and 10 amps. was applied for three hours. Hydrogen was evolving in great quantities on the cathode. Nitrogen on the anode started to evolve only after one hour of electrolysis.

Time	NaCN, oz./gal.	pH
Start, 9:00 a. m.	0.676	14
10:00 a. m.	0.273	14
11:00 a. m.	0.013	13
End, 12:00 a. m.	0.000	11

Analyses of NaCN content were carried out by titration with KI and $AgNO_3$ solutions. At 12:00 a. m. a check was made for Prussian Blue reaction which can discover even 0.2 p. p. m. of cyanides. No cyanides could be found.

Various changes and modifications in the procedures herein described may occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims, it is to be understood that they constitute part of my invention.

I claim:

1. The process for treating aqueous cyanide waste solution that comprises adding to the said solution the amount of alkali metal halide at least approximately equivalent to the cyanides in the solution, adjusting said solution to an alkaline pH in excess of about 8.5, and subjecting the resulting alkaline solution to electrolysis at a potential of about 5–7 volts until 2 to 6 kw. h. of energy has been consumed for each quantity of cyanide equivalent to one pound of NaCN to thereby decompose all of the cyanides originally present.

2. The process as defined in claim 1 wherein the alkali metal halide is a form of sodium chloride selected from the group consisting of rock salt, brines, and sea water.

3. The process as defined in claim 2 wherein 5 to 15 pounds of sodium chloride is employed for each cyanide equivalent of one pound of NaCN.

4. The process as defined in claim 3 wherein 5 to 10 pounds of sodium chloride is employed and the electrolysis is conducted batchwise.

5. The process as defined in claim 3 wherein 7 to 15 pounds of sodium chloride is employed and the electrolysis is conducted in continuous flow-through operation.

6. The process for treating aqueous cyanide waste solution that comprises adding to the said solution the amount of alkali metal halide at least approximately equivalent to the cyanides in the solution, adjusting said solution to an alkaline pH in excess of about 8.5, and subjecting the resulting alkaline solution to electrolysis at a potential of 5–7 volts until about 2–2.5 kw. h. of energy has been consumed for each quantity of cyanide equivalent to one pound of NaCN, to thereby convert the cyanides present in said solution substantially to cyanates.

7. The process for treating aqueous cyanide waste solution that comprises adding to the said solution the amount of alkali metal halide at least approximately equivalent to the cyanides in the solution, adjusting said solution to an alkaline pH in excess of about 8.5, and subjecting the resulting alkaline solution to electrolysis at a potential of 5–7 volts until about 5–7 kw. h. of energy has been consumed for each quantity of cyanide equivalent to one pound of NaCN, to thereby decompose the cyanides present in said solution substantially to free nitrogen.

8. The process for treating aqueous cyanide waste solution that comprises adding to the said solution 5 to 15 pounds of sodium chloride for each quantity of waste solution containing cyanides equivalent to one pound of NaCN, adjusting said solution to an alkaline pH in excess of about 8.5, and subjecting the resulting solution to electrolysis at a potential of 5–7 volts until at least 2 kw. h. of energy has been consumed for each such quantity of waste solution to thereby decompose all cyanides present in said waste solution.

9. The process as defined in claim 8 wherein the electrolysis is continued until 2–2.5 kw. h. of energy has been consumed to thereby convert cyanides in said waste solution substantially to cyanates.

10. The process as defined in claim 8 wherein the electrolysis is continued until 5–6 kw. h. of energy has been consumed to thereby decompose cyanides in said waste solution substantially to free nitrogen.

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