Patented Feb. 16, 1932 1,845,713

UNITED STATES PATENT OFFICE

GUNNARD E. JOHNSON, OF EAST CHICAGO, REGINALD G. BOWMAN, OF GARY, AND WILLIAM J. KNOX, JR., OF HAMMOND, INDIANA, ASSIGNORS TO ANACONDA LEAD PRODUCTS COMPANY, OF EAST CHICAGO, INDIANA, A CORPORATION OF DELAWARE

METHOD OF PRODUCING WHITE LEAD

No Drawing. Application filed January 17, 1931. Serial No. 509,534.

This invention relates to improvements in the electrolytic process of producing white lead and is more particularly concerned with certain refinements in the control of the process whereby we are enabled to predetermine the character or quality of white lead formed and to accurately control, in continuous operation, the conditions which are essential to the production of the desired product.

In the United States patent to Ralph M. Harrington, No. 1,308,948, it is recognized that the character and quality of the white lead product may be controlled by regulating the amount of carbon dioxide supplied to the catholyte, and it is further recognized that in order to obtain rapid carbon dioxide absorption and at the same time avoid precipitation of white lead on the anode, it is necessary to maintain the catholyte as compared with the anolyte relatively strongly alkaline.

In the operation of the Harrington process on a commercial scale and for a period of years we have encountered certain difficulties and have worked out certain refinements of control for overcoming such difficulties, which refinements constitute the subject matter of the present invention.

In the first place we have found that the composition of the white lead produced varies directly with the HCO_3 ion or bicarbonate content of the anolyte. By virtue of this discovery we are enabled to more accurately and intelligently control the composition of the white lead produced and to bring about such control in a variety of ways, i. e., by any method which may serve to influence the HCO_3 ion content of the anolyte, e. g. (1) by controlling the supply of CO_2 to the catholyte as described in the Harrington patent, (2) by maintaining the supply of CO_2 to the catholyte constant and adding acetic acid to the anolyte at a point outside the cell, (3) by maintaining the supply of CO_2 to the catholyte constant and subjecting the anolyte to an extra electrolytic treatment to convert its sodium acetate content into bicarbonate, and (4) by maintaining the supply of CO_2 to the catholyte constant and supplying sodium bicarbonate as such to the anolyte at a point outside the cell. Still other methods of controlling the bicarbonate content of the anolyte might readily be devised, the foregoing being suggested merely as examples.

In the second place we have found that the carbonate salt content of the anolyte must be kept low—much lower than is required in order to avoid formation of white lead incrustations on the anode—in order to permit washing the white lead free of these salts in the finishing of the white lead separated from the anolyte. This is important in the commercial production of white lead by the electrolytic method, since the presence of any considerable amount of alkali metal carbonate in the white lead product renders it unfit for use as paint pigment. We have found that the difficulty in washing the white lead sufficiently free of adsorbed salts increases with increasing concentration of carbonate salt in the anolyte to a point at which it is practically impossible to eliminate them. This may be explained by adsorption of the salts in the white lead particles, but it seems more probable that a reaction may occur as follows:

$$2(2PbCO_3.Pb(OH)_2)+Na_2CO_3+NaHCO_3=3NaPb_2(CO_3)_2OH+H_2O$$

whereby the carbonate salt becomes chemically combined and therefore very difficult or impossible to remove.

In accordance with our invention, using a bi-fluid cell with a lead anode suspended in the anolyte capable of yielding a solvent for the lead, e. g., sodium acetate, and a suitable inert cathode suspended in the catholyte containing sodium carbonate and separated from the anolyte by a suitable diaphragm, and to which CO_2 is supplied, all as disclosed in the above mentioned Harrington patent, the anolyte solution is sampled and analyzed at regular intervals, say every hour, and its bicarbonate content adjusted to and maintained at the desired figure by any suitable method such as one of those referred to above.

For example, in a cell operated at a current density of 30 amperes per square foot of cathode area and producing approximately .011 pounds of white lead per ampere hour and operating at an anolyte displacement

rate of 18 gallons per minute, the sodium bicarbonate content of the anolyte is maintained at .0561% to produce a white lead containing 11.60% of CO_2. To produce white lead of greater or smaller CO_2 content the acid carbonate content is increased or decreased, respectively, the exact acid carbonate content required for the production of a particular white lead product being determined in each instance by experiment. The carbonate salt content of the anolyte is maintained at not exceeding about twenty-five one-hundredths of one percent, (0.25%) and preferably in the neighborhood of six one-hundredths of one percent (0.06%). The significance of the limited carbonate salt content of the anolyte specified may be appreciated by comparison with the limitation of the carbonate salt content of the anolyte necessary to avoid troublesome precipitation of white lead on the anode in accordance with the Harrington patent. In this case the carbonate salt content of the anolyte may run as high as six tenths of one percent (0.60%), which content, however, will produce white lead containing so much carbonate salt that it is not feasible in commercial operation to wash it sufficiently free of such salt as to produce a first grade white lead paint pigment.

As has been stated, the two principal points of refinement of the process described in the Harrington patent constituting the present invention are (1) limiting the carbonate salt content of the anolyte to a predetermined maximum to permit the substantially complete removal of such salt from the precipitated white lead and the production of a white lead pigment suitable for use as a paint pigment, and (2) control of the composition of the white lead by reference to the bicarbonate content of the anolyte. In explanation of the last named refinement it may be said that the white lead formation is represented by the following reaction equation:

$$3Pb(C_2H_3O_2)_2+4Na_2CO_3+2H_2O=2PbCO_3.Pb(OH)_2+2NaHCO_3+6NaC_2H_3O_2$$

The composition of the basic lead salt precipitated varies with the pH value of the solution in which it is formed. It will be apparent, therefore, that if only Na_2CO_3 and $Pb(C_2H_3O_2)_2$ were supplied to the solution, the $NaHCO_3$ content would progressively increase and the ratio of HCO_3 to OH ions in the resulting precipitated lead salt would increase until finally only $PbCO_3$ would be produced. In other words the CO_2 content of the precipitated white lead bears a direct relation to the $NaHCO_3$ concentration of the anolyte. This has been found to be true in actual operation. In order to control the composition of the white lead produced, therefore, it is necessary to control the $NaHCO_3$ content of the anolyte, e. g., by controlling the ratio of OH to HCO_3 ions transferred to the anolyte from the catholyte through the diaphragm which in turn is controlled by control of the carbonation of the catholyte and/or by one of the other methods above referred to for controlling the bicarbonate content of the anolyte or suitable combinations thereof or other methods which may be devised.

We claim:

1. In the process of producing white lead by electrolysis in a bifluid cell in which the white lead is precipitated in an anolyte capable under electrolysis of yielding a lead solvent and containing bicarbonate salt the steps which consist in determining the bicarbonate concentration in the anolyte corresponding to the precipitation of white lead of the desired composition, and maintaining said bicarbonate content in the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding an acid to the anolyte.

2. In the process of producing white lead by electrolysis in a bifluid cell in which the white lead is precipitated in an anolyte capable under electrolysis of yielding a lead solvent and containing bicarbonate salt the steps which consist in determining the bicarbonate concentration in the anolyte corresponding to the precipitation of white lead of the desired composition, and maintaining said bicarbonate content in the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding a bicarbonate to the anolyte.

In testimony whereof, we affix our signatures.

GUNNARD E. JOHNSON.
REGINALD G. BOWMAN.
WILLIAM J. KNOX, JR.