UNITED STATES PATENT OFFICE

2,270,783

ELECTROCHEMICAL METHOD OF PRODUCING WHITE LEAD

Gunnard E. Johnson, Hammond, Reginald G. Bowman, Gary, and William J. Knox, Jr., Hammond, Ind., assignors to International Smelting and Refining Company, East Chicago, Ind., a corporation of Montana

No Drawing. Application December 6, 1937, Serial No. 178,352

4 Claims. (Cl. 204—88)

This invention relates to the production of white lead and has for an object the provision of certain improvements in processes for producing white lead. More particularly, the invention contemplates the provision of certain improvements in processes for producing white lead by electrolysis.

The present-day commercial process for producing white lead electrolytically is carried out in a so-called bi-fluid cell having a lead anode and an iron cathode separated by a porous diaphragm. The anode is surrounded by an electrolyte (the anolyte) containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by an electrolyte (the catholyte) containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between the catholyte and anolyte in the cell except through the diaphragm in the cell.

In practice, a small amount of Na_2CO_3, not exceeding about .05%, is added to the anolyte before placing the electrolytic cells in operation. When the current is turned on, the lead dissolves from the surface of the anode and is immediately precipitated as white lead at a slight distance from the anode surface. The precipitate is carried down through the cell by the descending current of anolyte in a thick cloud without depositing on the anode surface. Hydrogen and the hydroxide ions are liberated at the cathode. The hydroxide and carbonate ions of the hydrolyzed sodium carbonate (Na_2CO_3) of the catholyte migrate through the diaphragm toward the anode, replenishing the anions removed from the anolyte by precipitation of the lead ions. By this electrolytic migration, the electro-chemical equivalent amount of anions required to precipitate the lead cations as they are dissolved at the anode are transported to the anolyte. Slight traces of carbonate can be detected in the anolyte but it is entirely free of dissolved lead salts. However, there is no sodium carbonate (Na_2CO_3) present in the solution film in contact with the anode.

The foregoing outlines the major reaction. In practice, in order to replenish and conserve chemicals and to restore the loss in volume of catholyte due to decomposition of water at the cathode, evaporation and mechanical losses, anolyte is added to the catholyte in a small continuous stream. This introduces sodium acetate into the catholyte which is also acted upon by the current, the acetate ions replacing a part of the hydroxide and carbonate ions that migrate to the anolyte. This is compensated for by permitting a certain amount of seepage of catholyte into anolyte through the diaphragm. The seepage is controlled by selecting a diaphragm fabric of the desired porosity for a given hydrostatic solution head of catholyte of a selected composition in the cathode compartment. The addition of relatively small amounts of anolyte to catholyte and catholyte to anolyte permits adjusting the sodium concentration of the two electrolytes and the conservation of chemicals, since all make-up solution can then be added to the anolyte in the form of filtrate from the filters. All anolyte in the filter cakes is replaced by water by a counter current washing operation and returned to the anolyte circulation system. In addition, wash water filtrate is also returned as required to replenish the losses enumerated above. As the volume of solutions transferred between the two electrolytes is very small the anolyte as previously stated is essentially free of the reacting salts and they are only brought into the zone where the white lead is precipitated in electro-chemical equivalent amounts, there is never an excess present to alter the reaction or influence the size of the particle.

The white lead which is removed continuously from the cell by the circulation of the anolyte, is removed from the anolyte by settling and filtering. The filter pulp is washed, dried, ground and air floated, and is then barrelled in a dry pulverulent form. The clear anolyte is recirculated through the cell.

The composition of the anolyte during its passage through the cell remains unchanged except for a small increase in the acetate concentration. This is controlled by dilution with wash water from the filter. The catholyte is depleted in carbonate ions and a small percent of acetate ions, and enriched in hydroxide ions during its passage through the cathode compartment of the cell. The excess of hydrate ions is neutralized and the loss in carbonate ions restored by passing the catholyte through carbonation towers, in which a stream of descending solution passes through a rising stream of CO_2 gas from a coke burning boiler. The acetate loss is replenished as noted by running a small stream of anolyte into the catholyte after it is discharged from the cells.

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.

We discovered that the composition of the white lead produced varies directly with the HCO_3 ion or bicarbonate content of the anolyte. Our investigations have indicated that the white lead formation is represented by the following reaction equation:

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

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 sodium carbonate (Na_2CO_3) and lead acetate ($Pb(C_2H_3O_2)_2$) were supplied to the solution, the sodium bicarbonate ($NaHCO_3$) 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 carbon dioxide (CO_2) content of the precipitated white lead bears a direct relation to the sodium bicarbonate ($NaHCO_3$) 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.

Our discovery of the effect of the HCO_3 ion or bicarbonate content of the anolyte on the composition of the white lead produced is described in our United States Patent No. 1,845,713, dated February 16, 1932, which covers control of the bicarbonate content of the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding an acid or a bicarbonate to the anolyte.

Our aforementioned patent also points out that it is desirable that the carbonate salt content of the anolyte 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.

Our present invention provides for control of the bicarbonate content of the anolyte by means of excess carbonation of the catholyte and the addition to the anolyte of an alkali metal hydroxide. "Excess carbonation," as used herein and as understood in the art, means carbonation in excess of that required to maintain the bicarbonate ion concentration of the anolyte at the value necessary for the production of a white lead product of desired composition. The alkali metal hydroxide may be added to the anolyte in any suitable manner as, for example, by dissolving the hydroxide in the anolyte outside the cell, by adding a preformed solution of the hydroxide to the anolyte outside the cell, or by adding catholyte high in hydroxide (after electrolysis and prior to carbonation) to the anolyte outside the cell. Each of these procedures effects the desired control of the bicarbonate ion concentration in the anolyte, and hence the composition of the precipitated white lead, in a manner such that the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell. The solution of hydroxide for addition to the anolyte may be formed by employing as solvent the filtrate normally employed as make-up solution. The invention permits simplification of the carbonation operation and provides a simple method of maintaining a supply of anolyte of the proper concentration with respect to bicarbonate. Instead of controlling the carbonation operation to completely or partially neutralize the catholyte solution from the cell (depleted in carbonate ion and high in hydroxide) and, in the case of the partially neutralized catholyte, adding an acid or bicarbonate to the anolyte to compensate for the incomplete neutralization, the carbonation operation may be permitted to proceed to the point at which excess carbonation is effected without the necessity for exercising extreme caution to secure exact neutralization or accurate deficient carbonation. The invention simplifies the process also by eliminating the necessity for exact control of addition of catholyte to anolyte by electrolysis and by seepage through the diaphragm to meet changes in operating conditions. The composition of anolyte thus harmfully altered can be adjusted readily by the method of the inveption. In the preferred method of the invention, the carbonation operation is so controlled as to effect substantially uniform and excess carbonation of the catholyte for each particular set of operating conditions designed to produce a product of particular composition.

In accordance with our invention, using a bifluid cell with a lead anode suspended in an anolyte capable of yielding a solvent for the lead, e. g., sodium acetate, and a suitable inert cathode suspended in a catholyte containing sodium carbonate and separated from the anolyte by a suitable diaphragm, and to which an excess of carbon dioxide (CO_2) is supplied in the carbonation operation, 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 the addition of an alkali metal hydroxide, as pointed out above.

For example, in a cell operated at a current density of 30 amperes per square foot of cathode area and producing approximately .011 pound of white lead per ampere hour and operating at an anolyte displacement rate of 18 gallons per minute while maintaining uniform and excess carbonation of the catholyte, the sodium bicarbonate content of the anolyte is maintained at

0.0561% through adjustment by the addition of sodium hydroxide thereto to produce a white lead containing 11.60% of carbon dioxide (CO_2). To produce white lead of greater or smaller CO_2 content the acid carbonate content of the anolyte may be increased or decreased by the addition of lesser or greater amounts, respectively, of sodium hydroxide. The exact acid carbonate content required for the production of a particular white lead product should be 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 less than six 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.

We claim:

1. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and of a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and by incorporating hydroxyl ions in the anolyte in the form of a soluble metal hydroxide in such an amount that the amount of added metal ions of said hydroxide is not substantially in excess of the amount of metal ions lost in the course of normal operation of the cell, the amount of metal hydroxide incorporated in the anolyte being sufficient to establish therein bicarbonate ions in the desired concentration, whereby the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

2. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and adding to the anolyte a sufficient amount of uncarbonated catholyte containing hydroxyl ions to establish in the anolyte bicarbonate ions in the desired concentration, whereby addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

3. In the process of producing white lead of constant particular composition 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 ion concentration in the anolyte corresponding to the precipitation of white lead of the particular composition, and maintaining said bicarbonate ion content in the anolyte by maintaining a uniform and excess carbonation of the catholyte and by adding an alkali metal hydroxide to the anolyte in such an amount that the amount of added alkali metal ions is not substantially in excess of the amount of alkali metal ions lost in the course of normal operation of the cell but sufficient to establish in the anolyte bicarbonate ions in the desired concentration for precipitation of white lead of the particular composition.

4. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of (1) an anolyte capable under electrolysis of yielding a lead solvent and containing a carbonate and a bicarbonate and (2) a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises maintaining the carbonate concentration in the anolyte at or below a predetermined maximum which is substantially less than the concentration resulting in objectionable deposition of white lead on the anode, and adjusting the bicarbonate ion concentration in the anolyte by subjecting a portion of the catholyte to excess carbonation and by adding to the anolyte the remaining portion of uncarbonated catholyte containing sodium hydroxide to establish in the anolyte bicarbonate ions in the desired concentration, whereby the concentration of ions not entering into the composition of the precipitated white lead is not increased in the course of normal operation of the cell.

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The present-day commercial process for producing white lead electrolytically is carried out in a so-called bi-fluid cell having a lead anode and an iron cathode separated by a porous diaphragm. The anode is surrounded by an electrolyte (the anolyte) containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by an electrolyte (the catholyte) containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between the catholyte and anolyte in the cell except through the diaphragm in the cell.

In practice, a small amount of Na_2CO_3, not exceeding about .05%, is added to the anolyte before placing the electrolytic cells in operation. When the current is turned on, the lead dissolves from the surface of the anode and is immediately precipitated as white lead at a slight distance from the anode surface. The precipitate is carried down through the cell by the descending current of anolyte in a thick cloud without depositing on the anode surface. Hydrogen and the hydroxide ions are liberated at the cathode. The hydroxide and carbonate ions of the hydrolyzed sodium carbonate (Na_2CO_3) of the catholyte migrate through the diaphragm toward the anode, replenishing the anions removed from the anolyte by precipitation of the lead ions. By this electrolytic migration, the electro-chemical equivalent amount of anions required to precipitate the lead cations as they are dissolved at the anode are transported to the anolyte. Slight traces of carbonate can be detected in the anolyte but it is entirely free of dissolved lead salts. However, there is no sodium carbonate (Na_2CO_3) present in the solution film in contact with the anode.

The foregoing outlines the major reaction. In practice, in order to replenish and conserve chemicals and to restore the loss in volume of catholyte due to decomposition of water at the cathode, evaporation and mechanical losses, anolyte is added to the catholyte in a small continuous stream. This introduces sodium acetate into the catholyte which is also acted upon by the current, the acetate ions replacing a part of the hydroxide and carbonate ions that migrate to the anolyte. This is compensated for by permitting a certain amount of seepage of catholyte into anolyte through the diaphragm. The seepage is controlled by selecting a diaphragm fabric of the desired porosity for a given hydrostatic solution head of catholyte of a selected composition in the cathode compartment. The addition of relatively small amounts of anolyte to catholyte and catholyte to anolyte permits adjusting the sodium concentration of the two electrolytes and the conservation of chemicals, since all make-up solution can then be added to the anolyte in the form of filtrate from the filters. All anolyte in the filter cakes is replaced by water by a counter current washing operation and returned to the anolyte circulation system. In addition, wash water filtrate is also returned as required to replenish the losses enumerated above. As the volume of solutions transferred between the two electrolytes is very small the anolyte as previously stated is essentially free of the reacting salts and they are only brought into the zone where the white lead is precipitated in electro-chemical equivalent amounts, there is never an excess present to alter the reaction or influence the size of the particle.

The white lead which is removed continuously from the cell by the circulation of the anolyte, is removed from the anolyte by settling and filtering. The filter pulp is washed, dried, ground and air floated, and is then barrelled in a dry pulverulent form. The clear anolyte is recirculated through the cell.

The composition of the anolyte during its passage through the cell remains unchanged except for a small increase in the acetate concentration. This is controlled by dilution with wash water from the filter. The catholyte is depleted in carbonate ions and a small percent of acetate ions, and enriched in hydroxide ions during its passage through the cathode compartment of the cell. The excess of hydrate ions is neutralized and the loss in carbonate ions restored by passing the catholyte through carbonation towers, in which a stream of descending solution passes through a rising stream of CO_2 gas from a coke burning boiler. The acetate loss is replenished as noted by running a small stream of anolyte into the catholyte after it is discharged from the cells.

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.

We discovered that the composition of the white lead produced varies directly with the HCO_3 ion or bicarbonate content of the anolyte. Our investigations have indicated that the white lead formation is represented by the following reaction equation:

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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 sodium carbonate (Na_2CO_3) and lead acetate ($Pb(C_2H_3O_2)_2$) were supplied to the solution, the sodium bicarbonate ($NaHCO_3$) 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 carbon dioxide (CO_2) content of the precipitated white lead bears a direct relation to the sodium bicarbonate ($NaHCO_3$) 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.

Our discovery of the effect of the HCO_3 ion or bicarbonate content of the anolyte on the composition of the white lead produced is described in our United States Patent No. 1,845,713, dated February 16, 1932, which covers control of the bicarbonate content of the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding an acid or a bicarbonate to the anolyte.

Our aforementioned patent also points out that it is desirable that the carbonate salt content of the anolyte 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.

Our present invention provides for control of the bicarbonate content of the anolyte by means of excess carbonation of the catholyte and the addition to the anolyte of an alkali metal hydroxide. "Excess carbonation," as used herein and as understood in the art, means carbonation in excess of that required to maintain the bicarbonate ion concentration of the anolyte at the value necessary for the production of a white lead product of desired composition. The alkali metal hydroxide may be added to the anolyte in any suitable manner as, for example, by dissolving the hydroxide in the anolyte outside the cell, by adding a preformed solution of the hydroxide to the anolyte outside the cell, or by adding catholyte high in hydroxide (after electrolysis and prior to carbonation) to the anolyte outside the cell. Each of these procedures effects the desired control of the bicarbonate ion concentration in the anolyte, and hence the composition of the precipitated white lead, in a manner such that the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell. The solution of hydroxide for addition to the anolyte may be formed by employing as solvent the filtrate normally employed as make-up solution. The invention permits simplification of the carbonation operation and provides a simple method of maintaining a supply of anolyte of the proper concentration with respect to bicarbonate. Instead of controlling the carbonation operation to completely or partially neutralize the catholyte solution from the cell (depleted in carbonate ion and high in hydroxide) and, in the case of the partially neutralized catholyte, adding an acid or bicarbonate to the anolyte to compensate for the incomplete neutralization, the carbonation operation may be permitted to proceed to the point at which excess carbonation is effected without the necessity for exercising extreme caution to secure exact neutralization or accurate deficient carbonation. The invention simplifies the process also by eliminating the necessity for exact control of addition of catholyte to anolyte by electrolysis and by seepage through the diaphragm to meet changes in operating conditions. The composition of anolyte thus harmfully altered can be adjusted readily by the method of the invention. In the preferred method of the invention, the carbonation operation is so controlled as to effect substantially uniform and excess carbonation of the catholyte for each particular set of operating conditions designed to produce a product of particular composition.

In accordance with our invention, using a bifluid cell with a lead anode suspended in an anolyte capable of yielding a solvent for the lead, e. g., sodium acetate, and a suitable inert cathode suspended in a catholyte containing sodium carbonate and separated from the anolyte by a suitable diaphragm, and to which an excess of carbon dioxide (CO_2) is supplied in the carbonation operation, 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 the addition of an alkali metal hydroxide, as pointed out above.

For example, in a cell operated at a current density of 30 amperes per square foot of cathode area and producing approximately .011 pound of white lead per ampere hour and operating at an anolyte displacement rate of 18 gallons per minute while maintaining uniform and excess carbonation of the catholyte, the sodium bicarbonate content of the anolyte is maintained at

0.0561% through adjustment by the addition of sodium hydroxide thereto to produce a white lead containing 11.60% of carbon dioxide (CO_2). To produce white lead of greater or smaller CO_2 content the acid carbonate content of the anolyte may be increased or decreased by the addition of lesser or greater amounts, respectively, of sodium hydroxide. The exact acid carbonate content required for the production of a particular white lead product should be 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 less than 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.

We claim:

1. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and of a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and by incorporating hydroxyl ions in the anolyte in the form of a soluble metal hydroxide in such an amount that the amount of added metal ions of said hydroxide is not substantially in excess of the amount of metal ions lost in the course of normal operation of the cell, the amount of metal hydroxide incorporated in the anolyte being sufficient to establish therein bicarbonate ions in the desired concentration, whereby the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

2. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and adding to the anolyte a sufficient amount of uncarbonated catholyte containing hydroxyl ions to establish in the anolyte bicarbonate ions in the desired concentration, whereby addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

3. In the process of producing white lead of constant particular composition by electrolysis in a bifluid cell in which 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 ion concentration in the anolyte corresponding to the precipitation of white lead of the particular composition, and maintaining said bicarbonate ion content in the anolyte by maintaining a uniform and excess carbonation of the catholyte and by adding an alkali metal hydroxide to the anolyte in such an amount that the amount of added alkali metal ions is not substantially in excess of the amount of alkali metal ions lost in the course of normal operation of the cell but sufficient to establish in the anolyte bicarbonate ions in the desired concentration for precipitation of white lead of the particular composition.

4. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of (1) an anolyte capable under electrolysis of yielding a lead solvent and containing a carbonate and a bicarbonate and (2) a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises maintaining the carbonate concentration in the anolyte at or below a predetermined maximum which is substantially less than the concentration resulting in objectionable deposition of white lead on the anode, and adjusting the bicarbonate ion concentration in the anolyte by subjecting a portion of the catholyte to excess carbonation and by adding to the anolyte the remaining portion of uncarbonated catholyte containing sodium hydroxide to establish in the anolyte bicarbonate ions in the desired concentration, whereby the concentration of ions not entering into the composition of the precipitated white lead is not increased in the course of normal operation of the cell.

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The present-day commercial process for producing white lead electrolytically is carried out in a so-called bi-fluid cell having a lead anode and an iron cathode separated by a porous diaphragm. The anode is surrounded by an electrolyte (the anolyte) containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by an electrolyte (the catholyte) containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between the catholyte and anolyte in the cell except through the diaphragm in the cell.

In practice, a small amount of Na_2CO_3, not exceeding about .05%, is added to the anolyte before placing the electrolytic cells in operation. When the current is turned on, the lead dissolves from the surface of the anode and is immediately precipitated as white lead at a slight distance from the anode surface. The precipitate is carried down through the cell by the descending current of anolyte in a thick cloud without depositing on the anode surface. Hydrogen and the hydroxide ions are liberated at the cathode. The hydroxide and carbonate ions of the hydrolyzed sodium carbonate (Na_2CO_3) of the catholyte migrate through the diaphragm toward the anode, replenishing the anions removed from the anolyte by precipitation of the lead ions. By this electrolytic migration, the electro-chemical equivalent amount of anions required to precipitate the lead cations as they are dissolved at the anode are transported to the anolyte. Slight traces of carbonate can be detected in the anolyte but it is entirely free of dissolved lead salts. However, there is no sodium carbonate (Na_2CO_3) present in the solution film in contact with the anode.

The foregoing outlines the major reaction. In practice, in order to replenish and conserve chemicals and to restore the loss in volume of catholyte due to decomposition of water at the cathode, evaporation and mechanical losses, anolyte is added to the catholyte in a small continuous stream. This introduces sodium acetate into the catholyte which is also acted upon by the current, the acetate ions replacing a part of the hydroxide and carbonate ions that migrate to the anolyte. This is compensated for by permitting a certain amount of seepage of catholyte into anolyte through the diaphragm. The seepage is controlled by selecting a diaphragm fabric of the desired porosity for a given hydrostatic solution head of catholyte of a selected composition in the cathode compartment. The addition of relatively small amounts of anolyte to catholyte and catholyte to anolyte permits adjusting the sodium concentration of the two electrolytes and the conservation of chemicals, since all make-up solution can then be added to the anolyte in the form of filtrate from the filters. All anolyte in the filter cakes is replaced by water by a counter current washing operation and returned to the anolyte circulation system. In addition, wash water filtrate is also returned as required to replenish the losses enumerated above. As the volume of solutions transferred between the two electrolytes is very small the anolyte as previously stated is essentially free of the reacting salts and they are only brought into the zone where the white lead is precipitated in electro-chemical equivalent amounts, there is never an excess present to alter the reaction or influence the size of the particle.

The white lead which is removed continuously from the cell by the circulation of the anolyte, is removed from the anolyte by settling and filtering. The filter pulp is washed, dried, ground and air floated, and is then barrelled in a dry pulverulent form. The clear anolyte is recirculated through the cell.

The composition of the anolyte during its passage through the cell remains unchanged except for a small increase in the acetate concentration. This is controlled by dilution with wash water from the filter. The catholyte is depleted in carbonate ions and a small percent of acetate ions, and enriched in hydroxide ions during its passage through the cathode compartment of the cell. The excess of hydrate ions is neutralized and the loss in carbonate ions restored by passing the catholyte through carbonation towers, in which a stream of descending solution passes through a rising stream of CO_2 gas from a coke burning boiler. The acetate loss is replenished as noted by running a small stream of anolyte into the catholyte after it is discharged from the cells.

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.

We discovered that the composition of the white lead produced varies directly with the HCO_3 ion or bicarbonate content of the anolyte. Our investigations have indicated that the white lead formation is represented by the following reaction equation:

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

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 sodium carbonate (Na_2CO_3) and lead acetate ($Pb(C_2H_3O_2)_2$) were supplied to the solution, the sodium bicarbonate ($NaHCO_3$) 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 carbon dioxide (CO_2) content of the precipitated white lead bears a direct relation to the sodium bicarbonate ($NaHCO_3$) 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.

Our discovery of the effect of the HCO_3 ion or bicarbonate content of the anolyte on the composition of the white lead produced is described in our United States Patent No. 1,845,713, dated February 16, 1932, which covers control of the bicarbonate content of the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding an acid or a bicarbonate to the anolyte.

Our aforementioned patent also points out that it is desirable that the carbonate salt content of the anolyte 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.

Our present invention provides for control of the bicarbonate content of the anolyte by means of excess carbonation of the catholyte and the addition to the anolyte of an alkali metal hydroxide. "Excess carbonation," as used herein and as understood in the art, means carbonation in excess of that required to maintain the bicarbonate ion concentration of the anolyte at the value necessary for the production of a white lead product of desired composition. The alkali metal hydroxide may be added to the anolyte in any suitable manner as, for example, by dissolving the hydroxide in the anolyte outside the cell, by adding a preformed solution of the hydroxide to the anolyte outside the cell, or by adding catholyte high in hydroxide (after electrolysis and prior to carbonation) to the anolyte outside the cell. Each of these procedures effects the desired control of the bicarbonate ion concentration in the anolyte, and hence the composition of the precipitated white lead, in a manner such that the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell. The solution of hydroxide for addition to the anolyte may be formed by employing as solvent the filtrate normally employed as make-up solution. The invention permits simplification of the carbonation operation and provides a simple method of maintaining a supply of anolyte of the proper concentration with respect to bicarbonate. Instead of controlling the carbonation operation to completely or partially neutralize the catholyte solution from the cell (depleted in carbonate ion and high in hydroxide) and, in the case of the partially neutralized catholyte, adding an acid or bicarbonate to the anolyte to compensate for the incomplete neutralization, the carbonation operation may be permitted to proceed to the point at which excess carbonation is effected without the necessity for exercising extreme caution to secure exact neutralization or accurate deficient carbonation. The invention simplifies the process also by eliminating the necessity for exact control of addition of catholyte to anolyte by electrolysis and by seepage through the diaphragm to meet changes in operating conditions. The composition of anolyte thus harmfully altered can be adjusted readily by the method of the invention. In the preferred method of the invention, the carbonation operation is so controlled as to effect substantially uniform and excess carbonation of the catholyte for each particular set of operating conditions designed to produce a product of particular composition.

In accordance with our invention, using a bifluid cell with a lead anode suspended in an anolyte capable of yielding a solvent for the lead, e. g., sodium acetate, and a suitable inert cathode suspended in a catholyte containing sodium carbonate and separated from the anolyte by a suitable diaphragm, and to which an excess of carbon dioxide (CO_2) is supplied in the carbonation operation, 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 the addition of an alkali metal hydroxide, as pointed out above.

For example, in a cell operated at a current density of 30 amperes per square foot of cathode area and producing approximately .011 pound of white lead per ampere hour and operating at an anolyte displacement rate of 18 gallons per minute while maintaining uniform and excess carbonation of the catholyte, the sodium bicarbonate content of the anolyte is maintained at

0.0561% through adjustment by the addition of sodium hydroxide thereto to produce a white lead containing 11.60% of carbon dioxide (CO_2). To produce white lead of greater or smaller CO_2 content the acid carbonate content of the anolyte may be increased or decreased by the addition of lesser or greater amounts, respectively, of sodium hydroxide. The exact acid carbonate content required for the production of a particular white lead product should be 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 less than 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 limit 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.

We claim:

1. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and of a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and by incorporating hydroxyl ions in the anolyte in the form of a soluble metal hydroxide in such an amount that the amount of added metal ions of said hydroxide is not substantially in excess of the amount of metal ions lost in the course of normal operation of the cell, the amount of metal hydroxide incorporated in the anolyte being sufficient to establish therein bicarbonate ions in the desired concentration, whereby the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

2. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and adding to the anolyte a sufficient amount of uncarbonated catholyte containing hydroxyl ions to establish in the anolyte bicarbonate ions in the desired concentration, whereby addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

3. In the process of producing white lead of constant particular composition 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 ion concentration in the anolyte corresponding to the precipitation of white lead of the particular composition, and maintaining said bicarbonate ion content in the anolyte by maintaining a uniform and excess carbonation of the catholyte and by adding an alkali metal hydroxide to the anolyte in such an amount that the amount of added alkali metal ions is not substantially in excess of the amount of alkali metal ions lost in the course of normal operation of the cell but sufficient to establish in the anolyte bicarbonate ions in the desired concentration for precipitation of white lead of the particular composition.

4. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of (1) an anolyte capable under electrolysis of yielding a lead solvent and containing a carbonate and a bicarbonate and (2) a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises maintaining the carbonate concentration in the anolyte at or below a predetermined maximum which is substantially less than the concentration resulting in objectionable deposition of white lead on the anode, and adjusting the bicarbonate ion concentration in the anolyte by subjecting a portion of the catholyte to excess carbonation and by adding to the anolyte the remaining portion of uncarbonated catholyte containing sodium hydroxide to establish in the anolyte bicarbonate ions in the desired concentration, whereby the concentration of ions not entering into the composition of the precipitated white lead is not increased in the course of normal operation of the cell.

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

Patented Jan. 20, 1942 2,270,783

UNITED STATES PATENT OFFICE

2,270,783

ELECTROCHEMICAL METHOD OF PRODUCING WHITE LEAD

Gunnard E. Johnson, Hammond, Reginald G. Bowman, Gary, and William J. Knox, Jr., Hammond, Ind., assignors to International Smelting and Refining Company, East Chicago, Ind., a corporation of Montana

No Drawing. Application December 6, 1937, Serial No. 178,352

4 Claims. (Cl. 204—88)

This invention relates to the production of white lead and has for an object the provision of certain improvements in processes for producing white lead. More particularly, the invention contemplates the provision of certain improvements in processes for producing white lead by electrolysis.

The present-day commercial process for producing white lead electrolytically is carried out in a so-called bi-fluid cell having a lead anode and an iron cathode separated by a porous diaphragm. The anode is surrounded by an electrolyte (the anolyte) containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by an electrolyte (the catholyte) containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between the catholyte and anolyte in the cell except through the diaphragm in the cell.

In practice, a small amount of Na_2CO_3, not exceeding about .05%, is added to the anolyte before placing the electrolytic cells in operation. When the current is turned on, the lead dissolves from the surface of the anode and is immediately precipitated as white lead at a slight distance from the anode surface. The precipitate is carried down through the cell by the descending current of anolyte in a thick cloud without depositing on the anode surface. Hydrogen and the hydroxide ions are liberated at the cathode. The hydroxide and carbonate ions of the hydrolyzed sodium carbonate (Na_2CO_3) of the catholyte migrate through the diaphragm toward the anode, replenishing the anions removed from the anolyte by precipitation of the lead ions. By this electrolytic migration, the electro-chemical equivalent amount of anions required to precipitate the lead cations as they are dissolved at the anode are transported to the anolyte. Slight traces of carbonate can be detected in the anolyte but it is entirely free of dissolved lead salts. However, there is no sodium carbonate (Na_2CO_3) present in the solution film in contact with the anode.

The foregoing outlines the major reaction. In practice, in order to replenish and conserve chemicals and to restore the loss in volume of catholyte due to decomposition of water at the cathode, evaporation and mechanical losses, anolyte is added to the catholyte in a small continuous stream. This introduces sodium acetate into the catholyte which is also acted upon by the current, the acetate ions replacing a part of the hydroxide and carbonate ions that migrate to the anolyte. This is compensated for by permitting a certain amount of seepage of catholyte into anolyte through the diaphragm. The seepage is controlled by selecting a diaphragm fabric of the desired porosity for a given hydrostatic solution head of catholyte of a selected composition in the cathode compartment. The addition of relatively small amounts of anolyte to catholyte and catholyte to anolyte permits adjusting the sodium concentration of the two electrolytes and the conservation of chemicals, since all make-up solution can then be added to the anolyte in the form of filtrate from the filters. All anolyte in the filter cakes is replaced by water by a counter current washing operation and returned to the anolyte circulation system. In addition, wash water filtrate is also returned as required to replenish the losses enumerated above. As the volume of solutions transferred between the two electrolytes is very small the anolyte as previously stated is essentially free of the reacting salts and they are only brought into the zone where the white lead is precipitated in electro-chemical equivalent amounts, there is never an excess present to alter the reaction or influence the size of the particle.

The white lead which is removed continuously from the cell by the circulation of the anolyte, is removed from the anolyte by settling and filtering. The filter pulp is washed, dried, ground and air floated, and is then barrelled in a dry pulverulent form. The clear anolyte is recirculated through the cell.

The composition of the anolyte during its passage through the cell remains unchanged except for a small increase in the acetate concentration. This is controlled by dilution with wash water from the filter. The catholyte is depleted in carbonate ions and a small percent of acetate ions, and enriched in hydroxide ions during its passage through the cathode compartment of the cell. The excess of hydrate ions is neutralized and the loss in carbonate ions restored by passing the catholyte through carbonation towers, in which a stream of descending solution passes through a rising stream of CO_2 gas from a coke burning boiler. The acetate loss is replenished as noted by running a small stream of anolyte into the catholyte after it is discharged from the cells.

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.

We discovered that the composition of the white lead produced varies directly with the HCO_3 ion or bicarbonate content of the anolyte. Our investigations have indicated that the white lead formation is represented by the following reaction equation:

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

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 sodium carbonate (Na_2CO_3) and lead acetate ($Pb(C_2H_3O_2)_2$) were supplied to the solution, the sodium bicarbonate ($NaHCO_3$) 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 carbon dioxide (CO_2) content of the precipitated white lead bears a direct relation to the sodium bicarbonate ($NaHCO_3$) 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.

Our discovery of the effect of the HCO_3 ion or bicarbonate content of the anolyte on the composition of the white lead produced is described in our United States Patent No. 1,845,713, dated February 16, 1932, which covers control of the bicarbonate content of the anolyte by maintaining a uniform and deficient carbonation of the catholyte and adding an acid or a bicarbonate to the anolyte.

Our aforementioned patent also points out that it is desirable that the carbonate salt content of the anolyte 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.

Our present invention provides for control of the bicarbonate content of the anolyte by means of excess carbonation of the catholyte and the addition to the anolyte of an alkali metal hydroxide. "Excess carbonation," as used herein and as understood in the art, means carbonation in excess of that required to maintain the bicarbonate ion concentration of the anolyte at the value necessary for the production of a white lead product of desired composition. The alkali metal hydroxide may be added to the anolyte in any suitable manner as, for example, by dissolving the hydroxide in the anolyte outside the cell, by adding a preformed solution of the hydroxide to the anolyte outside the cell, or by adding catholyte high in hydroxide (after electrolysis and prior to carbonation) to the anolyte outside the cell. Each of these procedures effects the desired control of the bicarbonate ion concentration in the anolyte, and hence the composition of the precipitated white lead, in a manner such that the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell. The solution of hydroxide for addition to the anolyte may be formed by employing as solvent the filtrate normally employed as make-up solution. The invention permits simplification of the carbonation operation and provides a simple method of maintaining a supply of anolyte of the proper concentration with respect to bicarbonate. Instead of controlling the carbonation operation to completely or partially neutralize the catholyte solution from the cell (depleted in carbonate ion and high in hydroxide) and, in the case of the partially neutralized catholyte, adding an acid or bicarbonate to the anolyte to compensate for the incomplete neutralization, the carbonation operation may be permitted to proceed to the point at which excess carbonation is effected without the necessity for exercising extreme caution to secure exact neutralization or accurate deficient carbonation. The invention simplifies the process also by eliminating the necessity for exact control of addition of catholyte to anolyte by electrolysis and by seepage through the diaphragm to meet changes in operating conditions. The composition of anolyte thus harmfully altered can be adjusted readily by the method of the invention. In the preferred method of the invention, the carbonation operation is so controlled as to effect substantially uniform and excess carbonation of the catholyte for each particular set of operating conditions designed to produce a product of particular composition.

In accordance with our invention, using a bifluid cell with a lead anode suspended in an anolyte capable of yielding a solvent for the lead, e. g., sodium acetate, and a suitable inert cathode suspended in a catholyte containing sodium carbonate and separated from the anolyte by a suitable diaphragm, and to which an excess of carbon dioxide (CO_2) is supplied in the carbonation operation, 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 the addition of an alkali metal hydroxide, as pointed out above.

For example, in a cell operated at a current density of 30 amperes per square foot of cathode area and producing approximately .011 pound of white lead per ampere hour and operating at an anolyte displacement rate of 18 gallons per minute while maintaining uniform and excess carbonation of the catholyte, the sodium bicarbonate content of the anolyte is maintained at

0.0561% through adjustment by the addition of sodium hydroxide thereto to produce a white lead containing 11.60% of carbon dioxide (CO_2). To produce white lead of greater or smaller CO_2 content the acid carbonate content of the anolyte may be increased or decreased by the addition of lesser or greater amounts, respectively, of sodium hydroxide. The exact acid carbonate content required for the production of a particular white lead product should be 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 less than 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.

We claim:

1. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and of a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and by incorporating hydroxyl ions in the anolyte in the form of a soluble metal hydroxide in such an amount that the amount of added metal ions of said hydroxide is not substantially in excess of the amount of metal ions lost in the course of normal operation of the cell, the amount of metal hydroxide incorporated in the anolyte being sufficient to establish therein bicarbonate ions in the desired concentration, whereby the addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

2. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of an anolyte capable under electrolysis of yielding a lead solvent and containing a bicarbonate and a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises adjusting the bicarbonate ion concentration in the anolyte by subjecting the catholyte to excess carbonation and adding to the anolyte a sufficient amount of uncarbonated catholyte containing hydroxyl ions to establish in the anolyte bicarbonate ions in the desired concentration, whereby addition of ions not entering into the composition of the precipitated white lead is not substantially greater than the loss of such ions in the course of normal operation of the cell.

3. In the process of producing white lead of constant particular composition 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 ion concentration in the anolyte corresponding to the precipitation of white lead of the particular composition, and maintaining said bicarbonate ion content in the anolyte by maintaining a uniform and excess carbonation of the catholyte and by adding an alkali metal hydroxide to the anolyte in such an amount that the amount of added alkali metal ions is not substantially in excess of the amount of alkali metal ions lost in the course of normal operation of the cell but sufficient to establish in the anolyte bicarbonate ions in the desired concentration for precipitation of white lead of the particular composition.

4. In a process of producing white lead of constant particular composition by electrolysis in a bifluid cell involving the use of (1) an anolyte capable under electrolysis of yielding a lead solvent and containing a carbonate and a bicarbonate and (2) a catholyte containing a carbonate which is altered during the course of the process by removal of carbonate ions, and involving carbonation of the catholyte to restore carbonate ions thereto and re-use of the regenerated catholyte, the composition of the precipitated white lead being controlled by reference to the bicarbonate ion concentration in the anolyte, the improvement which comprises maintaining the carbonate concentration in the anolyte at or below a predetermined maximum which is substantially less than the concentration resulting in objectionable deposition of white lead on the anode, and adjusting the bicarbonate ion concentration in the anolyte by subjecting a portion of the catholyte to excess carbonation and by adding to the anolyte the remaining portion of uncarbonated catholyte containing sodium hydroxide to establish in the anolyte bicarbonate ions in the desired concentration, whereby the concentration of ions not entering into the composition of the precipitated white lead is not increased in the course of normal operation of the cell.

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

INTERNATIONAL SMELTING AND REFINING COMPANY

20 North Wacker Drive, Chicago, Ill.

F. O. CASE
Manager of Midwest District

February 2nd, 1942

Mr. Frederick Laist
Vice-President
International Smelting and Refining Company
25 Broadway
New York City

Re: Johnson et al. Application Serial No. 178,352, for: Electro-Chemical Method of Producing White lead - New patent No. 2,270,783

Dear Mr. Laist:

This will acknowledge receipt of Mr. James W. Laist's letter of January 29th concerning the above patent.

One copy of this patent is being forwarded to Mr. Johnson for his files and the other is being retained in this office.

Very truly yours,

F. O. Case

FOCvlc

cc: Mr. James W. Laist