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ELECTROLYTIC BASIC METAL CHROMATE PIGMENT MANUFACTURE

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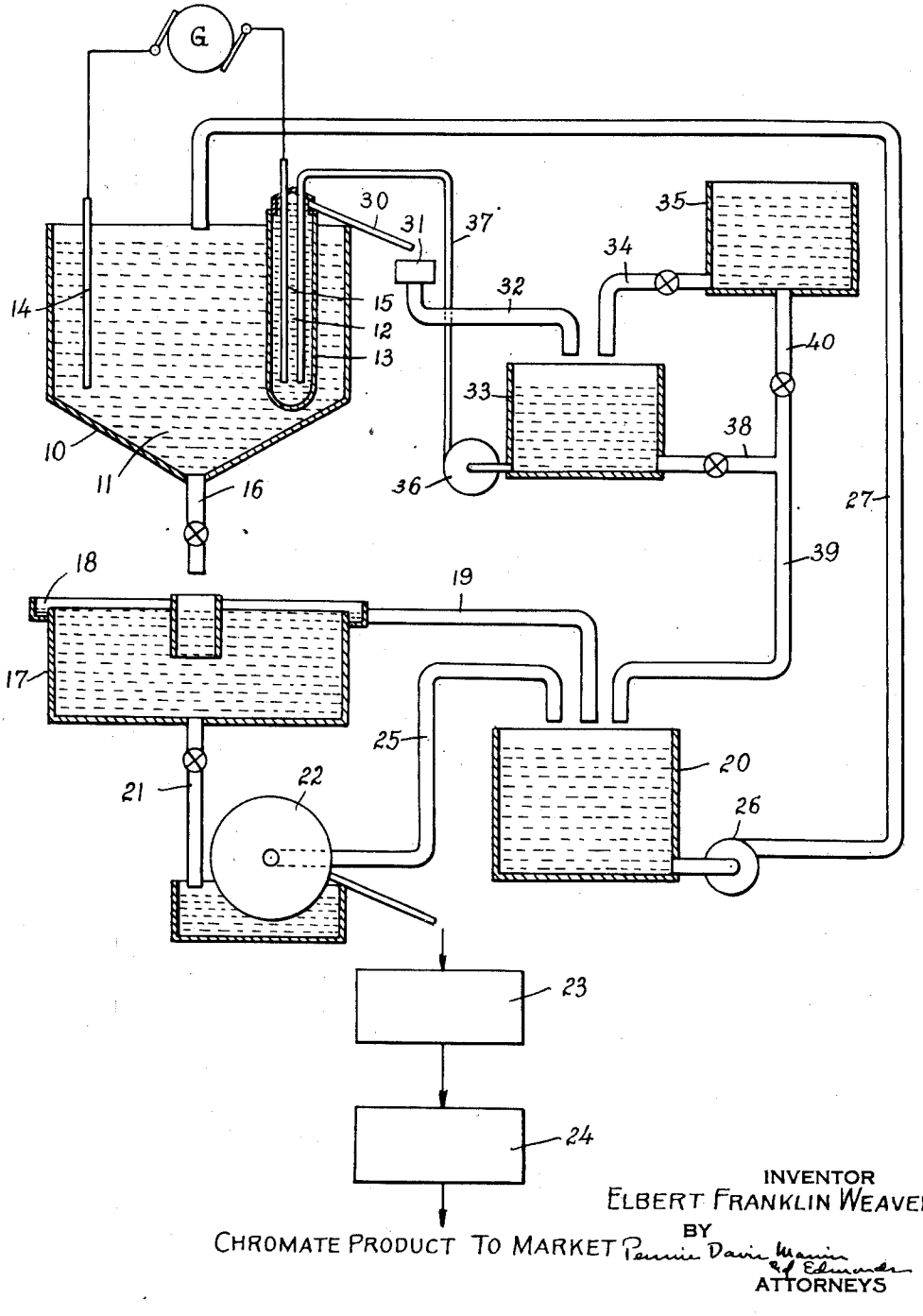


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## ELECTROLYTIC BASIC METAL CHROMATE PIGMENT MANUFACTURE

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7 Claims. (Cl. 204—89)

This invention relates to the production of metal chromates, and has for its principal object the provision of an improved method for manufacturing metal chromate pigments. More particularly, the invention provides an improved electrolytic method for the manufacture of basic metal chromate pigments, in accordance with which it is possible to control the chemical composition and the physical properties of the metal chromate products. This application is a continuation-in-part of my copending application Serial No. 134,520, filed April 2, 1937.

Metal chromates produced electrolytically are not always normal chromates, but may be in the form of basic chromates. Basic chromates may be regarded as combinations in varying proportions of normal metal chromates with corresponding metal oxides. The physical and chemical properties of metal chromate pigments depend almost entirely upon the chemical composition of the particular metal chromate in question, that is, upon the relative proportions of metal chromate to metal oxide in the product.

It has been found that the chemical composition of chromate pigments produced electrolytically depends upon the establishment and maintenance of certain conditions in the electrolytic cell in which the chromate is produced. In producing metal chromates electrolytically in a bifluid cell, I have discovered that the chemical composition and physical properties of the metal chromate product may be controlled particularly closely and effectively by controlling the ratio between the hydroxyl ion concentration and the chromate ion concentration in the anolyte while maintaining the pH of the anolyte at a substantially constant value above about 8.5. The present invention is concerned particularly with the production of metal chromate pigments in a bifluid electrolytic cell, and in accordance with the method of the invention, use is made of the foregoing discovery to control the character of the metal chromate product which it is desired to produce. The invention makes possible predetermination of the character or quality of the metal chromate produced, and accurate control, either in continuous or intermittent operation, of the conditions upon which formation of the desired product depend.

In accordance with the method of the invention, an electric current is passed from a soluble metal anode through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for the metal of the anode, a diaphragm, and a catholyte containing chromate ions to a cathode. The composition and physical properties such as color of the metal chromate produced in the cell is controlled by incorporating chromate ions in the anolyte in such manner as to control the ratio of concentration of hydroxyl ions to concentration of chromate ions therein while maintaining the pH of the anolyte at a substantially constant value above about 8.5. The method of the invention may be carried out continuously in electrolytic cells of conventional design equipped with soluble anodes, insoluble cathodes and diaphragms of the type usually employed in producing insoluble lead salts such as white lead electrolytically.

The apparatus employed in carrying out the invention preferably includes means for circulating both the anolyte and the catholyte through the cell, and circulation of both electrolytes advantageously is carried out continuously during operation of the process. The chromate product of the cell forms in the anolyte and is separated therefrom in any conventional manner subsequent to withdrawal of the anolyte from the cell and prior to its re-introduction into the cell. Suitable provision is made for adding a chromate (source of chromate ions) to the anolyte to control the ratio of concentration of hydroxyl ions to concentration of chromate ions in accordance with the composition of the desired chromate product.

In carrying out the method of the invention, an anode of the metal the chromate of which is to be produce is introduced into the anode compartment of a bifluid electrolytic cell in contact with the anolyte. The anolyte comprises a solution of a substance capable of serving upon electrolysis as a solvent for the metal of the anode, and its pH is maintained at or above about 8.5. An inert or insoluble cathode is introduced into the cathode compartment of the cell in contact with a catholyte of suitable composition. The cathode may be formed of any suitable material, preferably metal, capable of conducting electric current, but it should be of such nature that it is not readily corroded by reagents with which it comes in contact and it should not tend to contaminate the electrolytes or the product of the cell. In general, iron cathodes are satisfactory. The catholyte in contact with the cathode comprises a solution of any suitable soluble chromate, but a catholyte comprising a solution of sodium chromate ordinarily is preferred. The diaphragm separating the anolyte from the catholyte may be of any substance which will permit the passage of an electric current, the

migration of ions from catholtye to anolyte, and the maintenance of anolyte and catholyte substantially separated from one another in the cell. Fabric diaphragms are well suited for use in carrying out the method of the invention.

Advantageously, a catholyte circulation system provides for withdrawing catholyte from the cell and for returning it thereto to circulate the catholyte through the catholyte compartment of the cell. Suitable tanks and pumps may be included in this circulation system in order to facilitate handling of the catholyte. Provision is made for incorporating in the catholyte the chromate required to make up for that consumed in the cell and for such losses as may occur in the course of its circulation outside the reacting zone of the cell.

A similar anolyte circulation system is provided for withdrawing anolyte from the anolyte compartment and for returning it thereto. Suitable pumps and tanks may be included in the anolyte circulation system to facilitate handling of the anolyte. The metal chromate product of the cell, which forms in the anolyte, is separated from the anolyte after its withdrawal from the cell, and before it is returned to the cell. Provision advantageously is made in the anolyte circulation system for adjusting the ratio of chromate ion concentration to hydroxyl ion concentration in the anolyte to a value corresponding to the composition of the desired chromate product, while maintaining the pH of the anolyte substantially constant at a value above about 8.5. Thus, provision may be made for adding a substance capable of yielding chromate ions, such, for example, as a portion of the catholyte, to the anolyte in the course of its passage through the anolyte circulation system outside the reacting zone of the cell. The amount of catholyte so added to the anolyte is insufficient to alter the pH of the anolyte to any appreciable extent, and yet is sufficient to adjust the ratio of hydroxyl ion concentration to chromate ion concentration to the correct value.

In carrying out the process of the invention, it is advantageous to adjust the hydrostatic head of the catholyte in the catholyte compartment of the cell with respect to the hydrostatic head of the anolyte in the anolyte compartment to control, partially at least, the rate at which chromate ions diffuse through the diaphragm from the catholyte into the anolyte. For example, the rate of diffusion (or migration) of chromate ions from the catholyte into the anolyte may be increased somewhat by maintaining the catholyte under a slight hydrostatic head equivalent, say, to a few inches of water, with respect to the anolyte.

When an electric current is passed through a cell such as is described above, the metal of the anode passes into solution in the anolyte. Under the influence of the current chromate ions migrate through the diaphragm from the catholyte into the anolyte and there react with the dissolved metal to form a chromate of the metal. The metal chromate product is separated from the anolyte by suitable means after withdrawal of the anolyte from the cell.

It is possible in accordance with the above described process to produce basic chromate pigments, particularly insoluble basic chromate pigments, of a number of different metals. The particular conditions prevailing during operation of the process of course will depend upon the particular metal chromate being produced and also upon the particularly desired composition of the chromate product. For the purpose of illustrating a specific application of the method of the invention, therefore, the invention is described below with reference to the continuous production of basic lead chromate.

In the production of basic lead chromate, a lead anode is suspended in the anolyte compartment of a bifluid electrolytic cell in contact with an anolyte containing a substance capable of serving during electrolysis as a solvent for lead. An aqueous solution containing one or more acetate salts of potassium, sodium or ammonium, or containing one or more chlorate or nitrate salts of sodium or potassium, may be employed as the anolyte, but in general, an aqueous solution of sodium acetate is satisfactory.

An insoluble cathode, for example, an iron cathode, is suspended in the catholyte compartment of the cell in contact with a catholyte containing a substance capable of yielding chromate ions. An aqueous solution containing a chromate of an alkali or alkaline-earth metal may be employed as the catholyte, but, in general, an aqueous solution of sodium chromate is preferred.

Provision is made for withdrawing catholyte from the catholyte compartment and for returning it thereto, thereby to provide for circulation of the catholyte through the catholyte compartment of the cell. The catholyte in the cell becomes depleted in chromate ions with the attendant formation of sodium hydroxide during the course of the electrolysis, and to maintain a proper chromate concentration in the catholyte, chromate is added thereto at any suitable time after it is withdrawn from the cell and prior to its return thereto. Preferably, the chromate is added in the form of chromic acid in an amount sufficient to react with the sodium hydroxide that has been formed in the catholyte. In this manner, the concentration of sodium chromate in the catholyte and the alkalinity of the catholyte are maintained within a proper range. The thus treated catholyte is returned to the catholyte compartment of the cell.

Provision is also made for withdrawing the anolyte from the cell and for returning it thereto, thereby to circulate the anolyte through the anolyte compartment of the cell, and provision is made in the anolyte circulation system for adjusting the ratio between concentration of chromate ions and concentration of hydroxyl ions in the anolyte to a value corresponding to the composition of the desired chromate product, while maintaining the pH of the anolyte substantially constant at or above about 8.5. This may be accomplished in various ways. For example, any substance capable of furnishing chromate ions to the anolyte without materially affecting its pH may be added to the anolyte during its circulation outside the reacting zone of the cell. Chromic acid, for example, is a satisfactory source of chromate ions for this addition to the anolyte. Chromic acid is a very weak acid and is only very slightly dissociated in water solutions (its dissociation constant is of the order $5\times10^{-7}$). Hence it may be added to the anolyte in the small amounts required without appreciably affecting the pH thereof. A solution of sodium chromate (or other soluble chromate) also may be used as the source of chromate ions added to the anolyte. Generally, however, it is simpler and is preferred to add a portion of the

catholyte, which contains chromate ions in solution, to the anolyte at some point in the course of its circulation outside the anolyte compartment of the cell. The hydroxyl ion concentration in the catholyte is so small relatively to the chromate ion concentration therein that such additions of catholyte to anolyte in the amounts required for control purposes can be made without appreciably affecting the anolyte pH.

Apparatus suitable for use in carrying out the above-described process for the manufacture of basic lead chromate is shown diagrammatically in the accompanying drawing. The apparatus comprises a bifluid electrolytic cell **10** divided into an anolyte compartment **11** and a catholyte compartment **12** by a diaphragm **13** of fabric or other permeable material. An anode **14** of the metal the chromate of which is to be produced (for example, lead) is suspended in the anolyte compartment **11** in contact with the anolyte therein and a cathode **15** of iron or other non-corrodible material extends into contact with the catholyte in the catholyte compartment **12**. The catholyte in the catholyte compartment **12** advantageously is maintained at a slight hydrostatic head with respect to the anolyte in the anolyte compartment. Although only one anode and one cathode are shown in the drawing, any convenient number of anodes and cathodes may be employed if desired. A generator G is connected to the anode and to the cathode.

A valved conduit **16** provides for withdrawing anolyte from the bottom of the anolyte compartment **11** to a suitable settling or thickening tank **17**. The anolyte contains the solid chromate product of the cell, and in the settling or thickening tank **17** this product settles out. The clarified anolyte overflows into a launder **18** arranged about the upper edge of the settling tank **17** and is withdrawn therefrom through a suitable conduit **19** to an anolyte storage tank **20**. The cell product that settles out in the settling tank **17** is withdrawn from the bottom thereof together with a portion of the anolyte through a valved conduit **21** to a vacuum drum type or other suitable filter **22**. The filtered product is washed to recover electrolyte salts adhering to it, and the washed product is passed to a suitable drying chamber **23** and thence to a grinding mill **24** to prepare it for the market. The filtrate from the filter **22** passes through a conduit **25** to the anolyte storage vessel **20**.

A pump **26** provides for returning anolyte from the storage tank **20** through a conduit **27** to the anolyte compartment **11** of the cell **10** at a rate sufficient to balance the rate at which anolyte and cell product are withdrawn from the anolyte compartment.

A catholyte circulation also is provided for circulating catholyte through the catholyte compartment **12** of the cell **10**. Catholyte overflows from the catholyte compartment through an overflow conduit **30** into a launder **31** and passes thence by gravity through a conduit **32** to a catholyte storage vessel **33**.

The chromate ion concentration of the catholyte decreases and its hydroxyl ion concentration increases in the cell **10**, and to restore these concentrations to their proper values, a valved conduit **34** provides for adding chromic acid from a suitable storage vessel **35** to the catholyte in the catholyte storage tank **33**. A pump **36** provides for the return of catholyte from the catholyte storage vessel **33** through a conduit **37** to the catholyte compartment **12** of the cell **10**. The conduit **37** extends substantially to the bottom of the catholyte compartment **12** to insure circulation of catholyte through the catholyte compartment.

To maintain the proper ratio of hydroxyl ion concentration to chromate ion concentration in the anolyte, conduits **38** and **39** provide for withdrawing a portion of the catholyte from the catholyte storage vessel **33** and for introducing it into the anolyte in the anolyte storage vessel **20**. A conduit **40** also may be provided for introducing chromic acid from the chromic acid storage vessel **35** directly into the anolyte in the anolyte storage vessel **20** if such should be desirable or necessary.

When an electric current from a suitable source is passed through a cell such as described above, with sodium acetate as the substance in the anolyte capable of serving as the solvent for lead and with the pH of the anolyte above about 8.5, basic lead chromate will be formed. Under the influence of the current, the sodium acetate reacts with the lead anode, forming lead acetate.

$$2Pb+4NaC_2H_3O_2 \rightarrow 2Pb(C_2H_3O_2)_2+4Na^+$$

The sodium ions liberated by this reaction in the anolyte migrate through the diaphragm into the catholyte and react at the cathode to form sodium hydroxide.

$$4Na^+ + 4H_2O \rightarrow 4NaOH + 2H_2$$

Simultaneously basic lead chromate is formed by a reaction which occurs in the anolyte between the lead acetate, the sodium chromate and the sodium hydroxide present therein.

$$2Pb(C_2H_3O_2)_2 + Na_2CrO_4 + 2NaOH \rightarrow PbCrO_4 \cdot PbO + 4NaC_2H_3O_2 + H_2O$$

Sodium acetate is regenerated by this reaction. Practically all the sodium chromate required comes from the catholyte by migration through the diaphragm, and the amount consumed is made up by addition of chromic acid to the catholyte, thereby neutralizing the sodium hydroxide formed in the catholyte.

$$2NaOH + H_2CrO_4 \rightarrow Na_2CrO_4 + 2H_2O$$

The above-described reactions resulting in the formation of basic lead chromate ($PbCrO_4 \cdot PbO$) occur only if the ratio of sodium hydroxide concentration to chromate concentration is sufficiently high to satisfy the indicated demand for hydroxyl ions. In accordance with the control feature of the invention, this ratio is maintained at the proper value for the particular chromate product being produced while the pH of the anolyte is maintained at a substantially constant value above about 8.5. By properly controlling the ratio of hydroxyl ion concentration to chromate ion concentration in the anolyte at a substantially constant pH, it is possible to produce any one of a number of basic lead chromates ranging in color from deep red to light orange.

The value of the ratio between hydroxyl ion concentration and chromate ion concentration in the anolyte may be controlled in various ways, as mentioned above, without appreciably affecting the pH of the anolyte. Usually, with a diaphragm of suitable permeability, the rate at which chromate ions migrate from the catholyte through the diaphragm to the anolyte is substantially chemically equivalent to the rate at which sodium ions migrate from the anolyte to the catholyte. With an ideal diaphragm (which can be fairly closely approached in actual practice) no adjustment of ion concentrations after first

making up the electrolytes would be necessary (except, of course, to make proper additions of chromic acid to the catholyte as the latter became depleted in chromate ions. From a standpoint of practical control, however, it is desirable to work with a diaphragm which is of slightly less permeability than ideal operation would require. The hydrostatic head of the catholyte with respect to the anolyte is then adjusted from time to time, if necessary, to adjust the rate of chromate ion migration from the catholyte to a value substantially, but not quite, chemically equivalent to the rate of chromate ion consumption in the anolyte. Such additional control as need be exercised is then easily accomplished by making small additions of chromate ions to the anolyte, as by adding small amounts of catholyte to the anolyte outside the reacting zone of the cell.

In producing basic chromates, the hydroxyl ion concentration of the cell is maintained at a substantially constant value above that corresponding to a pH of about 8.5, and the value of the ratio between hydroxyl ion concentration and chromate ion concentration is adjusted to a value corresponding to the particular basic chromate product which it is desired to produce. If the true basic chromate is desired, the pH of the anolyte is maintained at a constant value above about 8.5 and the ratio between the hydroxyl ion concentration and the chromate ion concentration is established and maintained fairly closely in the molar proportion of two to one. If an intermediate basic chromate product is desired, the value of this ratio is reduced to a molar proportion somewhat less than two to one, depending on the degree of basicity of the chromate product sought, while the pH of the anolyte is maintained substantially constant above about 8.5.

To secure most efficient operation of a process embodying the method of the invention, it is advisable to pay some attention to factors other than those indicated above, such, for example, as current density and cell voltage, but these factors do not appear to be critical in determining the character of the cell product. The following data obtained in carrying out a process in accordance with the method of the invention to produce a light orange basic lead chromate, are given as illustrating more or less typical values of these factors:

| | |
|---|---|
| Temperature of electrolyte——°C—— | 55 |
| Current density per square foot of cathode surface——amperes—— | 15–20 |
| Cell voltage——volts—— | 3–6 |

Anolyte composition

| | Per cent |
|---|---|
| $NaC_2H_3O_2$ | 4.0 |
| $Na_2CrO_4$ | 0.040 |
| NaOH | 0.036 |

Catholyte composition

| | |
|---|---|
| $Na_2CrO_4$ | 5.0 |
| NaOH | 0.44 |

Chromate products made in accordance with the invention are superior in quality to corresponding products produced in accordance with heretofore known processes, being of more uniform particle size and having a crystalline structure such that the physical properties of the products are substantially enhanced. Chromates manufactured in accordance with the method of the invention may easily be distinguished from heretofore available chromates by visual comparison of the two products, when the finer texture and crystalline structure of the product of the invention become readily apparent. When suitably ground, chromate products prepared in accordance with the invention yield a better grade of pigment than heretofore available lead chromates. Chromates produced in accordance with the invention are easily ground to the proper degree of fineness for use as pigments and serve admirably as such when used in paints and other pigmented products.

Although the invention has been described above with particular reference to the production of basic lead chromates and is particularly well adapted for use in connection with the production of lead chromate pigments, it is to be understood that the method of the invention is useful in the production of insoluble chromates of metals other than lead. For example, basic copper chromates or basic zinc chromates having improved physical and chemical properties may be produced in accordance with the invention. In producing metal chromates other than lead chromate, it is, of course, necessary to modify the details of operation set forth above in connection with the production of lead chromate. Thus, in the production of a zinc chromate, a sulphate salt of an alkali or alkali earth metal (sodium sulphate, for example) is employed in place of sodium acetate in making up the anolyte; similarly, in the production of a copper chromate in accordance with the invention, a sulphate or chloride salt of an alkali or alkali earth metal (for example, sodium sulphate or sodium chloride) is employed in preparing the anolyte. Other operating details also must be modified when the method of the invention is used in producing metal chromates other than lead chromate, but in general the principles of operation set forth above will apply.

I claim:

1. In the production of basic metal chromates involving the passage of an electric current from a soluble anode of the metal through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for the metal, through a diaphragm, and through a catholyte containing chromate ions to a cathode, the method of controlling the composition and physical properties such as color of the metal chromate produced in the cell which comprises adding chromate ions to the catholyte as a source of chromate ions entering into the basic metal chromate, and adding chromate ions to the anolyte in such manner as to establish and maintain a ratio of concentration of hydroxyl ions to concentration of chromate ions in the anolyte corresponding to the composition of the desired chromate product while maintaining the anolyte at a substantially constant pH above about 8.5.

2. In the production of basic metal chromates involving the passage of an electric current from a soluble anode of the metal through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for the metal, through a diaphragm, and through a catholyte containing chromate ions to a cathode, the method of controlling the composition and physical properties such as color of the metal chromate produced in the cell which comprises adding chromate ions to the catholyte as a source of chromate ions entering into the basic metal chromate and establishing a substantially constant rate of transfer of chromate ions through the diaphragm to the anolyte, withdrawing anolyte from the cell, making small additions of chromate

ions to the withdrawn anolyte to establish and maintain therein a ratio of concentration of hydroxyl ions to concentration of chromate ions corresponding to the composition of the desired chromate product, and returning the thus treated anolyte to the cell with a substantially constant pH of at least about 8.5.

3. In the production of basic metal chromates involving the passage of an electric current from a soluble anode of the metal through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for the metal, through a diaphragm, and through a catholyte containing chromate ions to a cathode, the method of controlling the composition and physical properties such as color of the metal chromate produced in the cell which comprises adding chromate ions to the catholyte as a source of chromate ions entering into the basic metal chromate and establishing a substantially constant rate of transfer of chromate ions through the diaphragm to the anolyte, withdrawing anolyte from the cell, adding catholyte to the withdrawn anolyte in an amount sufficient to establish and maintain a ratio of concentration of hydroxyl ions to concentration of chromate ions corresponding to the composition of the desired chromate product and returning the thus treated anolyte to the cell with a substantially constant pH of at least about 8.5.

4. In the production of a basic lead chromate product involving the passage of an electric current from a soluble lead anode through an anolyte containing a substance capable of serving upon electrolysis as a solvent for lead, through a diaphragm, and through a catholyte containing chromate ions to an insoluble cathode, the method of controlling the chemical composition and physical properties such as color of the chromate product of the cell which comprises adding chromate ions to the catholyte as a source of chromate ions entering into the basic lead chromate, withdrawing anolyte from the cell, adding catholyte to the withdrawn anolyte in an amount sufficient to establish and maintain therein a ratio of hydroxyl ion concentration to chromate ion concentration corresponding to the composition of the desired chromate product and returning the thus treated anolyte to the cell with a substantially constant pH of at least about 8.5.

5. In the production of a basic lead chromate product involving the passage of an electric current from a soluble lead anode through an anolyte containing a substance capable of serving upon electrolysis as a solvent for lead, through a diaphragm and through a catholyte containing chromate ions to an insoluble cathode, the method of controlling the chemical composition and physical properties such as color of the chromate product of the cell which comprises adding chromate ions to the catholyte as a source of chromate ions entering into the basic lead chromate, controlling the rate at which chromate ions are transferred from the catholyte to the anolyte by maintaining the catholyte under a hydrostatic head with respect to the anolyte, withdrawing anolyte from the cell, adding catholyte to the withdrawn anolyte in an amount sufficient to establish and maintain therein a ratio of concentration of hydroxyl ions to concentration of chromate ions corresponding to the composition of the desired chromate product and returning the thus treated anolyte to the cell with a substantially constant pH of at least about 8.5.

6. The method of producing a basic copper chromate product which comprises passing an electric current from a soluble copper anode through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for copper, through a diaphragm, and through a catholyte containing chromate ions to a cathode, adding chromate ions to the catholyte as a source of chromate ions entering into the basic copper chromate, and adding chromate ions to the anolyte in such manner as to control the composition of the copper chromate product by establishing and maintaining a ratio of concentration of hydroxyl ions to concentration of chromate ions in the anolyte corresponding to the composition of the desired chromate product while maintaining the anolyte at a substantially constant pH above about 8.5.

7. The method of producing a basic zinc chromate product which comprises passing an electric current from a soluble zinc anode through an anolyte comprising a substance capable of serving upon electrolysis as a solvent for zinc, through a diaphragm, and through a catholyte containing chromate ions to a cathode, adding chromate ions to the catholyte as a source of chromate ions entering into the basic zinc chromate, and adding chromate ions to the anolyte in such manner as to control the composition of the zinc chromate product by establishing and maintaining a ratio of concentration of hydroxyl ions to concentration of chromate ions in the anolyte corresponding to the composition of the desired chromate product while maintaining the anolyte at a substantially constant pH above about 8.5.

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