

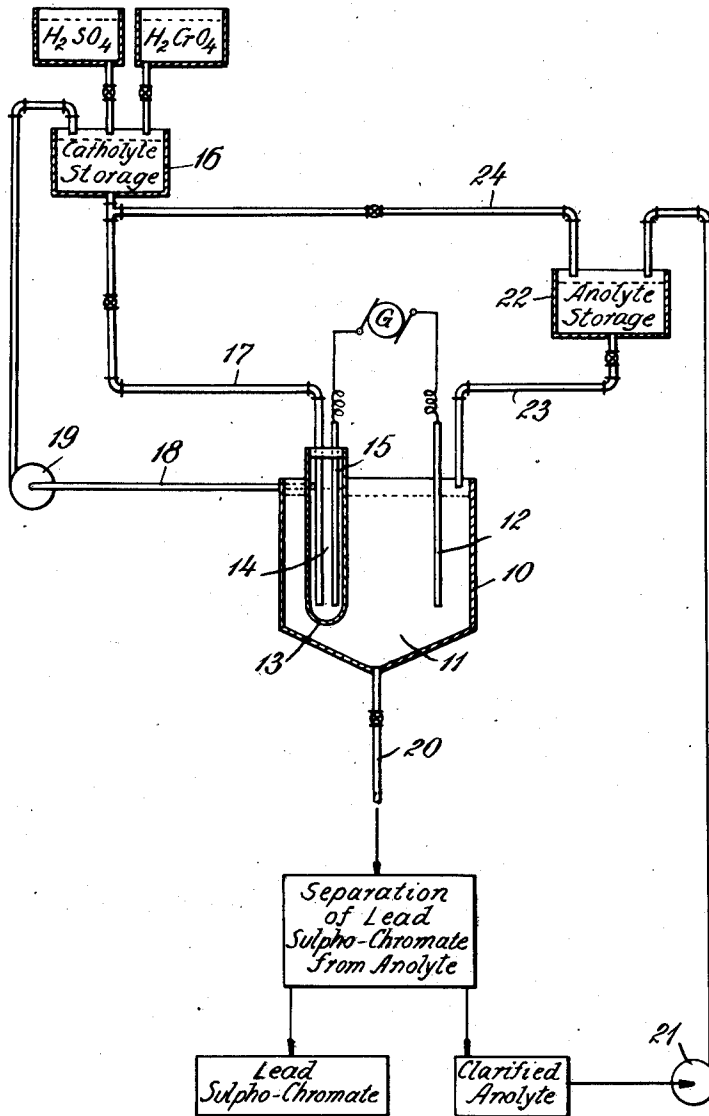
March 3, 1942.

S. W. STOCKDALE ET AL

2,275,054

ELECTROLYTIC PRODUCTION OF LEAD SULPHO-CHROMATES

Filed July 18, 1939



INVENTORS
STEPHEN W. STOCKDALE
ELBERT F. WEAVER

BY
Pennie Davis Manning Edmunds
ATTORNEYS

UNITED STATES PATENT OFFICE

2,275,054

ELECTROLYTIC PRODUCTION OF LEAD SULPHO-CHROMATES

Stephen W. Stockdale, Hammond, Ind., and Elbert F. Weaver, Calumet City, Ill., assignors to International Smelting and Refining Company, a corporation of Montana

Application July 18, 1939, Serial No. 285,104

3 Claims. (Cl. 204-89)

This invention relates to the production of sulpho-chromates, and is concerned more particularly with the provision of a new and improved method for producing lead sulpho-chromate pigments electrolytically. The "lead sulpho-chromate" products referred to herein are known as such in the color industry and comprise complex salts of lead sulphate and lead chromate.

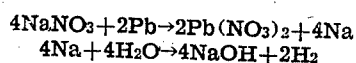
The method of the invention comprises passing an electric current through a bifluid electrolytic cell comprising a lead anode, an anolyte containing a substance capable of serving during electrolysis as a solvent for lead, a diaphragm, a catholyte comprising an aqueous solution containing sulphate ions and chromate ions, and an insoluble cathode. Sulpho-chromates, having the desired chemical composition and physical characteristics, are produced in accordance with this method by controlling the composition of the electrolyte as hereinafter more fully described.

In carrying out a process embodying the new method, a lead anode is immersed in an anolyte containing a substance capable of serving upon electrolysis as a solvent for lead. An aqueous solution of a substance capable of yielding nitrate or acetate ions, such, for example, as sodium nitrate or sodium acetate generally is preferred for use as the anolyte. An insoluble cathode (of iron, for example) is immersed in a catholyte comprising an aqueous solution of a substance capable of yielding sulphate and chromate ions such, for example, as sodium sulphate and sodium chromate. The anolyte and catholyte are physically separated by means of a permeable diaphragm which prevents the two solutions from intermingling, but enables an electric current to pass between anode and cathode and permits the migration of ions from one electrolyte to the other.

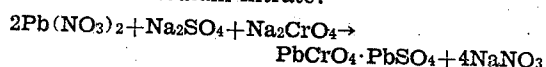
A bifluid electrolytic cell of conventional design, equipped with one or more diaphragms of the type usually employed in producing lead salts electrolytically, may be employed in carrying out the process. The complete apparatus preferably includes means for continuously withdrawing and circulating both the anolyte and the catholyte through a circuit outside the cell during the course of the electrolytic operation. The lead sulpho-chromate product forms in the anolyte and may be separated therefrom in any suitable manner after withdrawal of the anolyte from the cell and before its return thereto. The sulphate and chromate concentrations in the catholyte are maintained at desired values by the addition of

sulphuric acid and chromic acid to the catholyte at a point outside the cell.

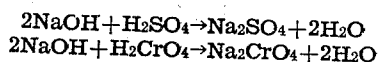
In operating the cell to produce a lead sulpho-chromate product, an electric current is passed from the lead anode through the anolyte, the diaphragm, and the catholyte to the cathode. Satisfactory operation is secured with a potential difference of about 3 to 5 volts between the anode and the cathode, and with a current density of about 25 amperes per square foot of cathode surface. The reactions occurring during electrolysis probably proceed substantially as follows: Assuming that a sodium nitrate solution is used as the anolyte, lead nitrate forms at the anode during electrolysis and sodium ions thereby liberated migrate to the cathode, where they combine with water to form sodium hydroxide and liberate hydrogen:



Sodium sulphate and sodium chromate diffuse through the diaphragm from the catholyte into the anolyte and there react with the lead nitrate to precipitate lead sulpho-chromate and to regenerate the sodium nitrate:



The tendency for the alkalinity of the catholyte to increase as a result of the migration of sodium ions thereto and the production of sodium hydroxide at the cathode is compensated for by the addition of sulphuric acid and chromic acid or their equivalents to the catholyte externally of this cell:



It will be observed that the only reagents consumed during the operation of the electrolytic cell are the lead of the anode and the sulphuric acid and chromic acid which are added to the catholyte. The sodium nitrate is wholly regenerated, and it is necessary to add only such amounts of this reagent as are lost through spillage, leakage from the cell and conduits, and similar operating losses. Accordingly the new process is substantially more economical to operate than heretofore known processes for producing sulpho-chromate pigments.

In some cases it is advantageous to maintain the catholyte at a slightly greater hydrostatic head than the anolyte. In this manner any tendency of the sodium nitrate to diffuse through

the diaphragm from the anolyte into the catholyte is diminished and at the same time diffusion of sodium sulphate and sodium chromate from the catholyte into the anolyte is aided.

The chemical composition and physical properties of the product of the cell may be varied considerably by varying the conditions prevailing in the cell during electrolysis. The factors which exert particular influence in this direction and which should be properly controlled to secure a lead sulpho-chromate product having optimum physical properties for use as a pigment and to facilitate operation of the electrolytic cell are the following:

1. Concentration of salts in the electrolyte

Concentration of sulphate in the anolyte should be maintained at about 0.075% to 0.15% by weight Na_2SO_4 , and concentration of chromate in the anolyte should be maintained at about 0.075% to 0.15% by weight Na_2CrO_4 . Corrosion of the anode is facilitated by maintaining these concentration values, and accumulation of soluble lead in the anolyte is thereby prevented. Soluble lead, if present in appreciable quantities in the anolyte, will contaminate the cell product and render it unsuitable for use as a pigment. The concentration of sulphate in the catholyte preferably is maintained at about 1% to 3% by weight Na_2SO_4 , and the concentration of chromate in the catholyte preferably is maintained at about 2.5% to 3% by weight Na_2CrO_4 . By maintaining these concentration values in the catholyte, the rate of transfer of chromate and sulphate ions to the anolyte is easily established at a value to maintain proper ion concentrations in the anolyte.

2. Alkalinity of the electrolyte

The alkalinity of the anolyte should be maintained at a value corresponding to a pH of 6.5 to 7.5. Below this value the tone and clarity of the product is adversely affected, and above this value the product becomes red in color, thus lessening its value as a light yellow pigment. The alkalinity of the catholyte should be maintained at a value corresponding to a pH of between 7 and 8. Slightly above a pH of 8 free NaOH is present in the catholyte and the cell product becomes basic in character. The desired catholyte alkalinity preferably is maintained by adding sulphuric acid and chromic acid to the catholyte in suitable proportions and in suitable total amounts, as this procedure provides a very precise method of controlling the concentration of sodium chromate and sodium sulphate in the catholyte, either to maintain an established concentration of these salts or to effect any desired increase or reduction in the concentration of either constituent.

3. Temperature of the electrolyte

The temperature of the electrolyte preferably is maintained at about 20° C. to 25° C. Within this temperature range transition of the generally preferred light yellow rhombic crystals into the darker yellow monoclinic crystals is inhibited.

A preferred process in accordance with the invention is illustrated in the accompanying diagrammatic flow sheet. An electrolytic cell tank 10 is substantially filled with an anolyte 11 comprising an aqueous solution of salt such as sodium nitrate or sodium acetate capable of serving during electrolysis as a solvent for lead. For example, an aqueous solution containing 2% to 8% by weight of sodium nitrate may be employed as the

anolyte. Immersed in the anolyte is a lead anode 12.

Suitably spaced from the anode and also immersed in the anolyte is a diaphragm 13, which advantageously is in the form of a fabric bag. The diaphragm bag 13 contains a catholyte 14 comprising an aqueous solution containing sodium sulphate, preferably in a concentration between about 1% to 3% by weight Na_2SO_4 , and sodium chromate, preferably in a concentration between about 2.5% and 3% by weight Na_2CrO_4 . As indicated above, the catholyte may be maintained under a slight hydrostatic head with respect to the anolyte. An insoluble cathode 15, for example a cathode of iron, is immersed in the catholyte.

In order to provide for circulating of catholyte through the catholyte compartment within the diaphragm bag 13, catholyte is continuously introduced from a storage tank 16 through a conduit 17 extending to a point adjacent the bottom of the catholyte compartment. Catholyte overflows continuously from the catholyte compartment through a spout (not shown) and passes through a conduit 18 to a pump 19, by means of which it is returned to the catholyte storage tank 16.

Sulphuric acid and chromic acid are added to the catholyte outside the catholyte compartment (preferably to the catholyte in the storage tank 16) in such relative proportions and in such total amounts as are required to maintain the desired concentrations of chromate and sulphate in the catholyte and to maintain the pH thereof at a proper value.

The cathode 15 and the anode 12 are connected to a suitable source of electric current, and upon closing the electrical circuit the reactions described above take place with the formation of lead sulpho-chromate in the anolyte. The anolyte with the insoluble lead sulpho-chromate suspended therein is continuously withdrawn from the bottom of the cell tank 10 through a conduit 20. The solid sulpho-chromate product is separated from the withdrawn anolyte in any suitable manner, for example by a decantation operation or a filtration operation. The separated lead sulpho-chromate is dried in preparation for marketing, and the clarified anolyte is forced by a pump 21 to an anolyte storage tank 22. Anolyte from the storage tank is fed continuously through a conduit 23 into the anolyte compartment of the cell tank 10 at a rate sufficient to maintain a constant level of anolyte therein.

As pointed out above, the anolyte necessarily contains a small percentage of dissolved chromate and dissolved sulphate which enters the anolyte from the catholyte chiefly by migration through the diaphragm 13 during electrolysis. If desired, in order to insure maintenance of proper sulphate and chromate concentrations in the anolyte, small quantities of catholyte may be introduced into the anolyte outside the cell, as by passing regulated small quantities of catholyte through a conduit 24 from the catholyte storage tank 16 to the anolyte storage tank 22.

The sulpho-chromate product of the cell may be produced in desired tones of color from light yellow to lemon yellow, depending upon the relative proportions of sulphate to chromate established and maintained in the anolyte. A product of light shade is obtained when a relatively high proportion of sulphate is present in the anolyte, and a product of relatively dark shade is pro-

duced when the chromate concentration in the anolyte is relatively high. Other factors, as indicated above, also influence the color and tone of the product.

We claim:

1. The method of producing a lead sulphochromate product electrolytically which comprises passing an electric current through a bifluid electrolytic cell comprising a lead anode, an anolyte containing a substance capable of serving during electrolysis as a solvent for lead, a diaphragm, a catholyte comprising an aqueous solution of sodium sulphate and sodium chromate, and an insoluble cathode, and controlling the chemical composition and physical characteristics of the sulphochromate product by maintaining in the catholyte sodium sulphate in an amount equal to about 1% to 3% by weight Na_2SO_4 and sodium chromate in an amount equal to about 2.5% to 3% by weight Na_2CrO_4 .

2. The method of producing a lead sulphochromate product electrolytically which comprises passing an electric current through a bifluid electrolytic cell comprising a lead anode, an anolyte containing a substance capable of serving during electrolysis as a solvent for lead, a diaphragm, a catholyte comprising an aqueous solution of sodium sulphate and sodium

chromate, and an insoluble cathode, and controlling the chemical composition and physical characteristics of the sulphochromate product by maintaining in the anolyte sodium sulphate in an amount equal to about 0.075% to 0.15% by weight Na_2SO_4 and sodium chromate in an amount equal to about 0.075% to 0.15% by weight Na_2CrO_4 .

3. The method of producing a lead sulphochromate product electrolytically which comprises passing an electric current through a bifluid electrolytic cell comprising a lead anode, an anolyte containing a substance capable of serving during electrolysis as a solvent for lead, a diaphragm, a catholyte comprising an aqueous solution of sodium sulphate and sodium chromate, and an insoluble cathode, and adding sulphuric acid and chromic acid to the catholyte in such relative proportions and in such total amount as to maintain in the catholyte a concentration of sodium sulphate of about 1% to 3% by weight Na_2SO_4 , a concentration of sodium chromate of about 2.5% to 3.0% by weight Na_2CrO_4 , and a hydrogen ion concentration equivalent to a pH of about 7 to 8.

STEPHEN W. STOCKDALE.
ELBERT F. WEAVER.