

UNITED STATES PATENT OFFICE

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METHOD OF PRODUCING CHROMATE

Marvin J. Udy, Niagara Falls, N. Y.

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11 Claims. (Cl. 23—56)

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This invention relates to chromium recovery and has for an object the provision of an improved method for recovering chromium from crude chromium-bearing material such as chromite ore. More particularly, the invention contemplates the provision of an improved method or process for recovering chromium in chromate form from chromium-bearing material containing chromium in the form of chromite. A further object of the invention is to provide certain improvements in methods or processes for producing chromate compounds.

According to some heretofore customary practices, chromate compounds are produced by subjecting chromite-bearing materials such as natural chromite ore and chromite ore concentrates to oxidation treatments in the presence of one or more basic substances such as lime and alkali metal compound. Thus, for example, alkali metal chromates may be formed by subjecting charges comprising finely divided chromite-bearing material and an alkali metal compound such as sodium carbonate or sodium sulphate to an oxidizing or roasting treatment at a temperature in the range 750° C. to 1200° C. The product of the oxidizing or roasting treatment may be leached or digested with a solvent for the alkali metal chromate produced to form a solution of the chromate, and the solution may be separated from the insoluble material by filtration.

In order to accomplish effective oxidation, it is important that the roasting charge be kept porous to permit effective contact of an oxidizing gas such as air with the solid components of the charge. Porosity is maintained by dilution of the charge with a refractory substance such as lime (CaO) and by control of temperature to avoid fusion. Customarily, charges employed for the production of alkali metal chromates by air oxidation or roasting comprise natural chromite ore, alkali metal compound in amount sufficient to form alkali metal chromate with substantially all of the chromium of the chromite ore and lime or other diluent material in amount equal to as much as three times the weight of the chromite ore. In the treatment of such charges at the high temperatures required for oxidation, even with the large amounts of diluent material included, it is difficult to avoid fusion with consequent reduction in the efficiency of oxidation, and, even under optimum conditions of operation, it is difficult or impossible to approach or accomplish complete oxidation. Satisfactory oxidation usually requires heating of the charge under oxidizing conditions for many hours.

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Fusion of the roasting charge, in some cases, may be attributed to some extent to the presence in the charge of the large amount of relatively low-melting point alkali metal compound required to form alkali metal chromate with all of the chromium of the chromite ore and to the production of a relatively large amount of low-melting point alkali metal chromate in such cases. Fusion may be avoided to a large extent by employing the alkali metal compound in an amount substantially smaller than that required to form alkali metal chromate with all of the chromium of the chromite ore and thus avoiding the inclusion and production of large amounts of relatively low-melting point compounds. Ineffective or incomplete oxidation may be attributed to the exclusion of the oxygen of the air from contact with the chromite particles resulting from agglomeration of the charge particles or coating of the particles with alkali metal chromate produced in the roasting treatment. In employing rotary kilns and hearth furnaces provided with rabbling means in accordance with heretofore customary procedures, conversion to chromate of about eighty percent (80%) of the chromium of the chromite ore of a roasting or oxidizing charge can be accomplished quite efficiently, but higher degrees of conversion are difficult and relatively expensive to accomplish.

The present invention provides improvements by means of which less dilute oxidation charges, or charges more concentrated with respect to chromium content, may be employed to effect improved recoveries of chromium in the form of chromate in shorter periods of time and with greater ease of handling and greater economy resulting from the use of the more concentrated charges.

The invention is based in part on my observation that oxidation of the chromium of chromite-bearing material proceeds rapidly during the early stages of the oxidizing treatment and on my discovery that, at the conclusion of the oxidizing treatment, the unoxidized chromium still remains as a constituent of undecomposed chromite of the charge subjected to oxidation. I have observed, for example, that in a given charge, containing lime, chromite and an alkali metal compound such as sodium carbonate, in which a maximum of about ninety percent (90%) conversion to chromate can be effected in twelve to fourteen hours, a conversion of as much as eighty percent (80%) is effected within about three hours or less.

I have found that about the same amount of

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chromium will be oxidized in the initial stages of the oxidation treatment whether the amount of alkali metal compound employed is sufficient to form alkali metal chromate with all of the chromium or with only about seventy to eighty percent (70 to 80%) of the chromium.

According to the present invention, the tendency of the charge to oxidize effectively with a limited amount of alkali metal compound is taken advantage of to provide an oxidation charge (containing a limited amount of alkali metal compound) which sinters or fuses less readily under the conditions employed in the oxidation treatment, and the fact that the unoxidized chromium remains as a constituent of the original chromite is taken advantage of to recover the unoxidized chromium by means of a concentration treatment. The use of a relatively small amount of alkali metal compound in the oxidation charge also permits the use of smaller amounts of diluent materials such as lime, and charges containing limited amounts of diluent material and alkali metal compound may be oxidized at higher temperatures with less danger of undesirable sintering or fusing resulting and with consequent increase in the rate of oxidation of the chromium. The components of the charge may also be employed in coarser states of subdivision. Thus, the use of a limited amount of alkali metal compound permits the use of substantially more concentrated and coarser oxidation charges which facilitates subsequent leaching and filtering operations and improves the efficiency of the oxidation treatment by reducing the time of oxidation. Charges consisting largely of particles small enough to pass a 100-mesh screen can be treated substantially as efficiently in the process of the invention as charges consisting largely of much smaller particles can be treated in processes of the type employed heretofore. The invention permits the use of smaller charges than those employed in heretofore customary processes to produce the same amounts of chromate.

Oxidation of the chromite ore in the presence of basic materials such as lime and alkali metal compounds results in decomposition of a large proportion of the chromite mineral of the charge with the production of decomposition products which have apparent specific gravities lower than the specific gravity of chromite mineral remaining undecomposed with the result that the undecomposed chromite mineral may be separated from the solid materials associated therewith by gravity concentration methods such, for example, as tabling and water classification. Compounds such as iron oxide, silica, alumina, and magnesia initially associated with that portion of the chromite mineral which is decomposed in the oxidation treatment are converted in whole or in part into compounds of sufficiently low specific gravities or of such physical forms that they may be floated or washed away from the particles of undecomposed chromite mineral by means of water. My investigations have indicated that iron is the most difficult of the original constituents of the chromite mineral to separate from the undecomposed chromite mineral. The chromite mineral recovered by concentration may be contaminated to some extent with iron in the form of ferric oxide. If desired, this contaminating iron may be removed by treating the concentrate with an acid such as sulphuric acid in aqueous solution.

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According to the present invention, chromium-bearing material such as chromite ore is subjected to an oxidizing treatment under conditions such as to convert chromium contained therein to the chromate condition. Chromate produced in the oxidation treatment is separated or recovered from the oxidation charge (comprising chromate, undecomposed chromite and solid decomposition products containing the iron oxide, silica, magnesia and alumina of the chromite subjected to oxidation) by digesting or leaching the oxidation charge with a liquid solvent for the chromate. The chromate solution is separated from the insoluble materials of the charge by sedimentation or filtration, and the insoluble residue is subjected to a concentration treatment to recover undecomposed chromite.

The chromite ore subjected to oxidation may be natural chromite ore or altered or modified chromite ore produced, for example, by heating natural chromite ore preliminarily with lime to effect alteration of the chromite mineral of the ore. Heating of the ore with lime may be carried out in accordance with procedures outlined in my pending applications Serial No. 252,743, filed January 25, 1939, and Serial No. 351,128, filed August 3, 1940. Heating of the ore with lime effects alteration of the ore and the production of a product containing an altered chromite by substitution of the lime for ferrous oxide of chromite of the original ore and makes the chromium of the ore more readily oxidizable to the chromate condition. In effecting alteration of the ore, a charge comprising natural chromite ore and lime or limestone in intimate admixture may be heated, for example, to a fusing temperature. Fusion may be of the type in which a molten glassy product is formed or it may be of the type in which a sintered product or a fritted product is formed. Temperatures in the range 1200° C. to 1350° C. may be employed to produce sintered or fritted products. Higher temperatures are required to produce molten products.

Any desired amount of lime or limestone relatively to chromite ore may be employed in a charge treated to effect alteration of chromite ore. For example, lime or limestone may be employed in amount sufficient to provide one molecule of calcium oxide for each molecule of the acid components or constituents of the ore, or lime or limestone may be employed in amount sufficient to provide more than one molecule or several molecules of calcium oxide for each molecule of the acid constituents or components of the ore. The components of a charge to be subjected to an alteration treatment preferably are intimately mixed and consist largely of particles small enough to pass a 100-mesh screen or smaller. Intimate mixing can be accomplished effectively by grinding the components together.

A complete preferred process of the invention involves an oxidation treatment with air or other oxygen-containing gas of a charge comprising chromite, a diluent such as lime and an alkali metal compound to oxidize chromium of the chromite to the hexavalent state with the production of chromate, treatment of the oxidized charge to separate chromate from the accompanying material, and a concentration treatment of the solid residue remaining after separation of the chromate to separate and recover chromite of the original charge containing the unoxidized chromium. The concentrate recovered may be reintroduced into the oxidation furnace with ad-

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ditional chromite or it may be accumulated and treated separately.

The charge subjected to roasting or oxidation preferably comprises chromite, lime in amount equal to about one and one-half to two times the weight of the chromite and sodium carbonate in amount sufficient to form sodium chromate with about seventy to eighty percent (70 to 80%) of the chromium of the chromite. The materials of the charge preferably are intimately mixed together and in the form of particles small enough to pass a 100-mesh screen. Mixing may be accomplished effectively by grinding together the components of the charge.

Roasting or oxidation preferably is carried out with air in a rabble furnace at a temperature in the range 750° C. to 1000° C. for a period of about three hours.

Leaching preferably is carried out with an aqueous liquid containing some sodium carbonate in solution. Maintenance of some sodium carbonate in the leaching liquor insures the recovery as sodium chromate of any calcium chromate formed in the course of the oxidizing treatment. The leaching solution may be treated in any suitable manner for the recovery in suitable form of the chromium contained therein as sodium chromate.

The solid insoluble residue remaining after separation of the soluble chromate is subjected to a water classification or concentration treatment, preferably in the form of a table concentration operation in which the undecomposed chromite is separated by gravity from the lighter decomposition products associated therewith. The concentration treatment results in the recovery in the form of a low-volume concentrate of ninety percent (90%) or more of the undecomposed chromite. The chromium content of the original or rough concentrate is only slightly lower than the chromium content of the original chromite subjected to oxidation. A clean concentrate containing about the same chromium content as that of the original chromite may be produced by treating the rough concentrate with an acid such as sulphuric acid to remove iron oxide associated with the chromite particles.

By concentrating the residue remaining after separation of the soluble chromate from the oxidation charge and returning the concentrate to the process for oxidation to chromate an over-all recovery of chromium as chromate in excess of ninety percent (90%) can be accomplished consistently.

I claim:

1. The method of producing chromate which comprises roasting a charge of chromite-bearing material, lime and soda ash while in intimate contact with air at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air

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to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

2. The method of producing chromate which comprises roasting a charge of chromite-bearing material, lime and soda ash while in intimate contact with air at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time such that not substantially more than about 70% to about 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

3. The method of producing chromate which comprises roasting a charge of chromite-bearing material, lime and soda ash while in intimate contact with air at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time not exceeding about three hours and not longer than necessary to decompose about 80% of the chromite and to oxidize the chromium thereof to the hexavalent state, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

4. The method of producing chromate which comprises roasting a charge of chromite-bearing material, lime and soda ash while in intimate contact with air at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time such that not substantially more than about 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, leaching the product of the roasting operation with an aqueous solution of sodium carbonate to produce a solution of chro-

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mate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

5. The method of producing chromate which comprises roasting a charge of chromite-bearing material, lime and soda ash while in intimate contact with air at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time such that not substantially more than about 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, the lime being present in the charge in amount equal to about one and one-half to about two times the weight of the chromite of the chromite-bearing material, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

6. The method of producing chromate which comprises roasting, in intimate contact with air, a charge of chromite-bearing material, lime and soda ash, in which the soda ash is present in amount not substantially in excess of that required to form sodium chromate with about 80% of the chromium of the charge, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of chromium thereof to the hexavalent state with the production of chromate, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

7. The method of producing chromate which comprises roasting, in intimate contact with air, a charge of chromite-bearing material, lime and soda ash, in which the soda ash is present in

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amount not substantially in excess of that required to form sodium chromate with about 80% of the chromium of the charge, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of chromium thereof to the hexavalent state with the production of chromate, for a length of time to cause substantially all of the soda ash to react with the chromite of the charge, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

8. The method of producing chromate which comprises roasting, in intimate contact with air, a charge of chromite-bearing material, lime and soda ash, in which the soda ash is present in amount not substantially in excess of that required to form sodium chromate with about 70% to about 80% of the chromium of the charge, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of chromium thereof to the hexavalent state with the production of chromate, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

9. The method of producing chromate which comprises roasting, in intimate contact with air, a charge of chromite-bearing material, lime and soda ash, in which the soda ash is present in amount not substantially in excess of that required to form sodium chromate, with about 80% of the chromium of the charge and the lime is present in amount equal to about one and one-half to about two times the weight of the chromite of the chromite-bearing material, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact

with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

10. The method of producing chromate which comprises heating a charge comprising chromium-bearing material containing ferrous chromite and lime to a temperature above 1200° C. and at least sufficiently high to cause a sintering of constituents of the charge and to produce a product containing an altered chromite formed by substitution of the lime for ferrous oxide of the chromite of the original chromium-bearing material, roasting a charge comprising the product of said heat treatment and soda ash, while in intimate contact with air, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

11. The method of producing chromate which comprises heating a charge comprising chromium-bearing material containing ferrous chromite and lime to a temperature above 1200° C. and at least sufficiently high to cause a sintering of constituents of the charge and to produce a product containing an altered chromite formed by substitution of the lime for ferrous oxide of the chromite of the original chromium-bearing material, roasting a charge comprising the product of said heat treatment and soda ash, in which the soda ash is present in amount not substantially in excess of that required to form sodium chromate with about 70% to about 80% of the chromium of the

charge, while in contact with air, at a temperature sufficiently high to cause decomposition of the chromite and oxidation of the chromium thereof to the hexavalent state with the production of chromate, for length of time such that not substantially more than about 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state, leaching the product of the roasting operation with an aqueous medium to produce a solution of chromate, separating the chromate solution from the insoluble material of the roasted charge, concentrating the residual insoluble material to separate and recover undecomposed chromite contained therein, and thereafter roasting a charge of fresh chromium-bearing material, lime, soda ash, and the recovered undecomposed chromite while in intimate contact with air to cause decomposition of the chromite thereof and oxidation of chromium thereof to chromate, said last-mentioned roasting operation being conducted for a length of time such that not substantially more than 80% of the chromite is decomposed and the chromium thereof oxidized to the hexavalent state.

MARVIN J. UDY.

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