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PRODUCTION OF CHROMIUM COMPOUNDS

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

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7 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 or process for recovering chromium in the form of relatively pure compounds or concentrates from crude chromium-bearing material such as chromite ore. More particularly, the invention contemplates the provision of an improved method or process for producing chromium oxide-bearing products. A further object of the invention is to provide certain improvements in methods or processes for producing chromic oxide as such or in chemical combination with a basic oxide such as calcium oxide. The invention also contemplates the provision of an improved method or process for producing calcium chromate. A specific object of the invention is to provide an improved method or process for utilizing alkali metal compounds in obtaining relatively pure chromium compounds from crude chromium-bearing materials such as chromite ore.

Throughout the specification and in the claims, the term "chromite ore" is intended to include natural chromite ore, chromite ore concentrates, altered chromite ore and similar chromite mineral-bearing materials.

According to some heretofore customary processes, chromite ores are subjected to oxidizing or roasting treatments in the presence of one or more alkali metal compounds such, for example, as sodium carbonate, sodium hydroxide and sodium sulphate under such conditions as to oxidize the trivalent chromium of the chromite ore to the hexavalent state and produce alkali metal chromates such, for example, as sodium chromate. Sodium chromate thus produced is separated from the product of the roasting or oxidizing treatment by leaching and crystallization and marketed as such or converted to sodium dichromate for marketing. Commercial sodium chromate and sodium dichromate are utilized as raw or intermediate materials in the production of other chromium-bearing compounds. Thus, for example, chromium compounds such as chromic oxide, calcium chromite and calcium chromate are produced by suitable reduction or conversion treatments of commercial sodium chromate or sodium dichromate. Usually, the production of such compounds is carried out independently of the chromate production operations and, consequently, the sodium oxide content of the chromate compound is wasted or, at any rate, is not recovered in a form in which it is readily available for re-use in the chromate production operations. Therefore, chromic oxide,

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calcium chromite and calcium chromate are relatively costly commercial products. Such compounds are highly desirable materials for many industrial uses, but their usefulness is not fully developed because of high costs.

The present invention provides for the production of such compounds under conditions and according to procedures such that the alkali metal oxide content of chromates employed in their production is utilized for the production of additional chromate. A complete preferred process of the invention comprises (1) oxidation or roasting in air of chromite ore in the presence of one or more alkali metal compounds in accordance with well known oxidizing or roasting procedures with the production of alkali metal chromate, (2) separation of the chromate from other materials associated therewith in the oxidized or roasted charge as, for example, by leaching with an aqueous liquid followed by evaporation and crystallization, (3) reduction of the chromate directly or after conversion to dichromate with the production of chromic oxide as such or chromic oxide chemically combined with a basic oxide and one or more alkali metal compounds suitable for use in the oxidation or roasting treatment of chromite ore, and (4) utilization of the one or more alkali metal compounds thus produced in an oxidizing or roasting treatment of additional chromite ore. Through the recovery and re-use of the alkali metal oxide of the chromate, the costs of producing compounds such as chromic oxide, calcium chromite and calcium chromate are reduced materiallly and a wider field of usefulness for such compounds is provided.

The invention also provides improved, more efficient and less expensive methods or processes for utilizing commercial alkali metal chromates and dichromates in the production of compounds such as chromic oxide, calcium chromite and calcium chromate.

According to the invention, an alkali metal chromate, such as sodium chromate (Na_2CrO_4) or sodium dichromate ($Na_2Cr_2O_7$), in finely divided form, is intimately mixed with finely divided solid carbonaceous reducing material and ignited. Finely divided charcoal, coke or coal may be employed satisfactorily as the reducting material. Finely divided charcoal may be employed most advantageously for the production of pure products. Finely divided coke or coal may be employed when relatively impure products are satisfactory. When coal or coke is employed, the products resulting from reduction of the chro-

mium of the chromate through elimination of a portion of the oxygen may be contaminated with coal or coke ash.

My investigations have indicated that reduction of alkali metal chromate and dichromate with carbon through ignition of intimate mixtures of the materials proceeds somewhat according to the following equations:

(1) $Na_2Cr_2O_7+3C—Na_2O\cdot Cr_2O_3+3CO$

(2) $2Na_2Cr_2O_7+3C—2(Na_2O\cdot Cr_2O_3)+3CO_2$

(3) $2Na_2CrO_4+2C—Na_2O\cdot Cr_2O_3+Na_2CO_3+CO$

(4) $4Na_2CrO_4+3C—2(Na_2O\cdot Cr_2O_3)+2Na_2CO_3+CO_2$

It will be noted that the above equations indicate the production of sodium chromite ($Na_2O\cdot Cr_2O_3$) and carbon monoxide or carbon dioxide in reducing sodium dichromate with carbon in different proportions relatively to sodium dichromate and the production of sodium chromite ($Na_2O\cdot Cr_2O_3$), sodium carbonate and carbon monoxide in reducing sodium chromate. When the solid reaction product resulting from the reduction of sodium dichromate with carbon is digested with water (hot or cold), a solution of sodium hydroxide substantially free of sodium carbonate and a solid residue consisting essentially of chromic hydroxide ($Cr(OH)_3$) are produced. When the solid reaction product resulting from reduction of sodium chromate with carbon is digested with water, a solution of sodium hydroxide and sodium carbonate and a solid residue consisting essentially of chromic hydroxide ($Cr(OH)_3$) are produced.

Digestion of the solid products resulting from reduction does not effect hydrolysis or decomposition of all of the sodium chromite ($Na_2O\cdot Cr_2O_3$) contained therein, and the solid residue consisting essentially of chromic hydroxide contains some sodium oxide probably chemically combined with chromic oxide as sodium chromite. The residual sodium oxide may be separated from the bulk of the chromic hydroxide by subjecting the residue resulting from digestion to an oxidizing treatment with air at an elevated temperature (above about 500° C.) and leaching the resulting product with water. The residual sodium oxide is converted to sodium chromate in the oxidizing treatment and the chromic hydroxide is converted to chromic oxide (Cr_2O_3).

Calcium chromite and sodium carbonate may be produced by forming and igniting an intimate mixture of finely divided sodium chromate or sodium dichromate, finely divided calcium oxide and finely divided carbon. It appears that the reactions proceed somewhat according to the following equations:

(5) $Na_2Cr_2O_7+2CaO+2C—(CaO)_2Cr_2O_3+Na_2CO_3+CO$

(6) $2Na_2Cr_2O_7+4CaO+3C—2(CaO)_2Cr_2O_3+2Na_2CO_3+CO_2$

(7) $2Na_2CrO_4+2CaO+3C—(CaO)_2Cr_2O_3+2Na_2CO_3+CO$

The sodium carbonate and calcium chromite produced in accordance with the reactions indicated by the above equations may be separated by digesting the solid reaction products with water, hot or cold. Calcium oxide may be employed as such or in chemical combination with carbon dioxide as calcium carbonate.

Equations 5 to 7 indicate the production of a compound approximating in chemical composition di-calcium chromite. Compounds approximating in chemical composition mono-calcium chromite or tri-calcium chromite may be produced by adjusting the proportions of chromate or di-chromate and calcium oxide employed.

All of the reactions indicated by Equations 1 to 6 above are exothermic and usually proceed to completion without the application of heat from extraneous sources. When the calcium oxide is employed in the form of calcium carbonate and when the production of tri-calcium chromite is sought, it may be advisable to provide additional heat from extraneous sources to insure effective chemical combination of the calcium oxide with the chromic oxide.

Calcium chromate may be produced by roasting in air a solid residue obtained in the digestion of a solid reaction product resulting from the reduction of a chromate or dichromate in the presence of calcium oxide to produce calcium chromite. Substantially complete conversion to calcium chromate may be accomplished by roasting the di-calcium chromite and the tri-calcium chromite. Roasting of the mono-calcium chromite will result in the production of calcium chromate and chromic oxide. Complete conversion to chromate of the mono-calcium chromite may be accomplished by incorporating in the roasting or oxidizing charge at least one molecule of calcium oxide for each molecule of calcium chromite contained therein.

In a complete preferred process of the invention involving the oxidation of chromite ore to produce sodium chromate, sodium carbonate, sodium hydroxide or mixtures of sodium carbonate and sodium hydroxide obtained by digesting the solid products resulting from reduction of sodium chromate and sodium dichromate may be employed in the oxidation treatment. The solutions obtained by digestion of the products of reduction may be evaporated partially or entirely to obtain solid sodium hydroxide or sodium carbonate or both, or to obtain sodium hydroxide, or sodium carbonate or both partly in the solid state and partly in solution for re-use in the oxidation of chromite ore. Solutions containing sodium hydroxide may be passed in contact with gases, such as flue gases, containing carbon dioxide to carbonate the solution, or partly for the purpose of carbonating the solution and partly for the purpose of washing the gases, and produce, and convert the sodium hydroxide to, sodium carbonate or sodium bicarbonate or both.

The production of chromic oxide by reduction of sodium chromate with carbon is illustrated by the following example:

A reaction mixture was formed by grinding together 648 pounds of sodium chromate (Na_2CrO_4) and 46 pounds of carbon in the form of charcoal. The mixture was placed in a crucible, covered with finely divided charcoal and ignited by means of a gas flame. Upon ignition, the reaction proceeded quietly and smoothly.

The amount of carbon employed represents an excess of about thirty percent (30%) over that required to effect reduction of the chromate. It is desirable that sufficient excess carbon be employed to prevent re-oxidation of the reaction product during cooling.

The solid reaction product was cooled under nonoxidizing conditions, digested by grinding in water to form a pulp to effect solution of sodium compounds and filtered. Hot or cold water may be employed for digestion. The filtrate obtained was an aqueous solution of sodium hydroxide and sodium carbonate. The solid residue consisting essentially of chromic hydroxide ($Cr(OH)_3$) was

roasted in air at an elevated temperature (1000° C.) to eliminate water and carbon and convert the chromic hydroxide to chromic oxide. The roasted product was 95 percent chromic oxide.

The chromic oxide-bearing product was leached with water to remove soluble compounds such as sodium chromate contained therein. The residue remaining after leaching was substantially pure chromic oxide. The sodium chromate thus obtained may be returned to the process. Conversion to chromic oxide of 97.5 percent of the chromium of the sodium chromate was effected.

I claim:

1. The method of recovering chromium values from chromite ore which comprises subjecting the ore to an oxidizing treatment in the presence of sodium carbonate to produce sodium chromate, treating the product of the oxidizing treatment to separate sodium chromate from other material associated therewith, subjecting the sodium chromate to a reducing treatment with a carbonaceous reducing agent in the presence of calcium oxide and forming a product comprising sodium carbonate and calcium chromite, separating the sodium carbonate from the calcium chromite, and utilizing the sodium carbonate in an oxidizing treatment of additional ore.

2. The method of producing calcium chromite which comprises subjecting sodium chromate to a reducing treatment with a carbonaceous reducing agent in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, and separating the calcium chromite and the sodium carbonate.

3. The method of producing calcium chromate which comprises subjecting sodium chromate to a reducing treatment with a carbonaceous reducing agent in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, separating the calcium chromite and the sodium carbonate, and subjecting the calcium chromite to an oxidizing treatment to oxidize chromium contained therein to the hexavalent condition.

4. The method of producing calcium chromate which comprises subjecting sodium chromate to a reducing treatment with a carbonaceous reducing agent in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, calcium oxide being employed in amount such that the calcium chromite produced contains more than one molecule of calcium oxide for each molecule of chromic oxide contained therein, separating the calcium chromite and the sodium carbonate, and subjecting the calcium chromite to an oxidizing treatment to oxidize chromium contained therein to the hexavalent condition.

5. The method of producing calcium chromite which comprises subjecting sodium chromate to a reducing treatment at an elevated temperature with solid carbon in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, and separating the calcium chromite and the sodium carbonate.

6. The method of producing calcium chromate which comprises subjecting sodium chromate to a reducing treatment at an elevated temperature with solid carbon in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, separating the calcium chromite and the sodium carbonate, and subjecting the calcium chromite to an oxidizing treatment to oxidize chromium contained therein to the hexavalent condition.

7. The method of producing calcium chromate which comprises subjecting sodium chromate to a reducing treatment at an elevated temperature with solid carbon in the presence of calcium oxide to eliminate a portion of the oxygen of the chromate and form a product comprising calcium chromite and sodium carbonate, calcium oxide being employed in amount such that the calcium chromite produced contains more than one molecule of calcium oxide for each molecule of chromic oxide contained therein, separating the calcium chromite and the sodium carbonate, and subjecting the calcium chromite to an oxidizing treatment to oxidize chromium contained therein to the hexavalent condition.

MARVIN J. UDY.

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