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PREPARATION OF CERIUM SULPHATE

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This invention relates to the preparation of a product consisting essentially of cerium compounds from the decomposition products of the monazite earths. It relates especially to the preparation of valuable white opacifying agents for enamels and glazes, especially those used for opacifying enamels used on sheet metal, from monazite or cerite earths by an inexpensive and relatively simple process. The novel opacifying agents and a method of opacifying enamels with these opacifiers is described and claimed in my copending patent application, Serial No. 183,517 filed January 5, 1938, now Patent 2,163,334 issued June 20, 1939.

In the treatment of monazite or cerite earths, or similar earths, it has been found especially difficult to separate the compounds of cerium from the so-called colored or variegated earths and from lanthanum. Not only is it expensive and tedious to separate these colored products from the compounds of cerium, but satisfactory separation has proven to be a very difficult chemical problem. The colored earths, consisting essentially of compounds of didymium, cause, as indicated by their name, a very intense coloration of the metallic oxides. Enamels opacified with cerium oxide containing a substantial amount of didymium have usually had a coloration ranging from rose to red. In the preparation of white opacifying agents from compounds of cerium it is therefore essential to prepare the cerium substantially free from compounds of the colored earths.

One of the objects of this invention is the preparation of substantially pure cerium compounds, compounds substantially free from the colored and variegated earth compounds, from the monazite earths, cerite earths, or similar natural products. Another object of this invention is to develop a process for freeing the compounds of cerium from the compounds of the colored earths, such as didymium, by a simple, direct and relatively inexpensive process. Still another object of this invention is the preparation of compounds of cerium, free from colored or variegated earth compounds, which may be utilized directly as white opacifying agents by incorporation in suitable frits. These and still other objects of the invention will be apparent from the ensuing disclosure.

It may be stated that my improved process generally involves the conversion of the decomposition products of the monazite earths, or of other cerium-containing earths, into hydroxides of the cerite metals. The resulting products are

dissolved in sulphuric acid before separation of the compounds of didymium, lanthanum, etc. The addition to the solution of compounds containing a fixed alkali should be avoided to as great an extent as possible. The solution containing the sulphates, in which the cerium compounds are necessarily in the tetravalent state, is then diluted with water until a voluminous precipitate is obtained. This precipitate consists essentially of the basic sulphates of tetravalent cerium.

The precipitate is thereupon separated from the solution and may be washed with a dilute acid. Dilute hydrochloric acid containing from 1 to 2% HCl may be utilized in the washing step. The resulting washed product, after drying, may be added directly to suitable frits by milling as now customary with the known opacifying agents in the preparation of white enamels. As previously stated, the use of the basic sulphates of tetravalent cerium as opacifying agents for the preparation of white enamels is claimed in my copending application, Serial No. 183,517, filed January 5, 1938, now Patent 2,163,334 issued June 20, 1939.

The conversion of the cerium into the tetravalent state may be accomplished either by treating the hydroxides of the cerite metals, before dissolving them in sulphuric acid, or subsequent to the treatment with sulphuric acid by oxidation of the resulting solution. The oxidation is preferably an electrolytic oxidation carried out at the anode of an electrolytic cell containing, as the electrolyte, the hydroxides dissolved in sulphuric acid. If desired, both treatments for the conversion of the cerium compounds to the tetravalent state may be employed.

Other suitable oxidizing agents for converting the cerium to the tetravalent state as well as in the form of its hydroxide, even when in the sulphate solution, are oxidizing agents such as oxygen, for example in the form of atmospheric oxygen, hydrogen peroxide, chlorine, hypochlorites, and similar oxidizing agents.

If desired, instead of treating the solution of the sulphates only with water, it is possible to add thereto slight amounts of non-fixed alkalies such, for example, as ammonia. This will result in complete or substantially complete neutralization of the sulphuric acid set free by hydrolysis, thereby precipitating, to as great an extent as possible, the desired compounds of cerium.

In carrying out my improved process it has been found advisable to have present the least possible amount of compounds of fixed alkalies

because during precipitation of the basic ceric sulphate it has been observed that compounds of the colored earths form much more readily in the presence of compounds containing fixed alkalis. The colored earths will react with the alkali sulphates to form relatively insoluble double compounds which precipitate with the basic ceric sulphate during the step wherein the solution is diluted with water. If compounds yielding fixed alkalis are present satisfactory separation of the compounds of cerium from the compounds of the other rare earths will not be obtained. During precipitation of the cerite hydroxide from the cerite salt solutions with fixed alkali lyes small portions of the formed alkali salts combine with the hydroxides, which results in the difficulties discussed during the subsequent solution of the hydroxides in acid.

In order to insure the most complete separation of the alkali compounds from the compounds of the cerite earths, thereby insuring the presence of the least possible amount of alkali compounds in the sulphuric acid solution, I have observed that the salts are preferably introduced in the solid or dissolved state into the alkali solution during the step of preparing the hydroxides of the cerite metals from the salts of the cerite earths. By so proceeding it is possible to separate the precipitated hydroxides in such condition that they may be easily and completely washed substantially free of the alkali compounds.

If the cerite earths are originally present in the form of their sulphates and if these compounds are free from alkali compounds, the precipitation of the cerium therein in the tetravalent state may be directly accomplished by dilution with water. In other words, it is not necessary in such cases first to prepare the hydroxides from the salts, and after dissolving, precipitate them from the resulting solution by dilution.

It is also possible to suspend the hydroxides of the earths, containing the cerium in the tetravalent state and which have been washed free from alkali, in water followed by reacting those hydroxides with a quantity of sulphuric acid such that the resulting solution is but slightly acid in reaction. If necessary, any excess of acidity imparted to the solution may be subsequently neutralized by the addition of a little ammonia, after which the cerium compounds are again precipitated by dilution.

The product precipitated by dilution with water is pure yellow in color and consists essentially of basic ceric sulphates. It may be used directly as a white opacifier for preparing white opaque enamels. However, it may also be subjected to a firing process at temperatures of from 800 to 1100° C., preferably at about 950° C., whereupon its color changes from pure yellow to slightly reddish ivory white. When mixed in a suitable manner with an enamel frit and subjected to firing there is obtained a pure white enamel which meets the most rigid and exacting requirements.

I have also found it advantageous to add small amounts of basic alkali metal or alkaline earth metal compounds, such, for example, as lime, alumina, or silicic acid either alone or combined, to the product secured by precipitation. There is thus obtained richer and more highly active opacifying agents. The amounts of basic compounds of the type specified that need be added are readily determined by experimentation. An amount of approximately 3 to 8% of alkali compounds has been found advantageous. The

addition of larger amounts, amounts close to the upper limit indicated, 8%, has been found to be desirable if the resulting product to which the alkali salts are added has lost a relatively large amount of its water of hydration by heating. Instead of adding the substances named, there may also be added compounds such as alkali metal silicates, and alkaline earth metal silicates such, for example, as water glass.

As examples of my improved method for obtaining white opacifying agents containing compounds of cerium from monazite and cerite earths, the following may be given:

Example 1

100 liters of a neutral aqueous solution containing the sulphates of the rare earths with 40 grams of cerium oxide and 42 grams of variegated earths including lanthanum, yttrium, etc. per liter, was allowed to flow into a 10% solution of caustic soda containing an amount of caustic substantially 5% in excess of that amount equivalent to the solution containing the earth metal compounds. During the process the solution was vigorously stirred and a strong current of air injected.

The resulting liquid containing the hydroxides of the rare earth metals was then slightly alkaline in reaction. Substantially complete oxidation (approximately 97%) of the cerous hydroxide to yellow ceric hydroxide was secured by injecting air into the solution for several hours. Thereupon it became necessary to remove the alkalis (the excess caustic soda and the sodium sulphate formed in the solution) to as complete an extent as possible because of the tendency of the alkali sulphates to form with the variegated earths double sulphates which are only slightly soluble and which might later contaminate the desired cerium-containing product. This is done by decanting five to six times, washing out the soluble sulphates to as great an extent as possible as, for example, by treatment on a filter press, followed by dissolving the hydroxides in sulphuric acid. The concentration of the sulphuric acid employed depends on the aqueous content of the hydroxides. The less the water content of the hydroxide, the more dilute is the sulphuric acid used. For hydroxides which are dried at 80 to 100° C., sulphuric acid of 30 to 40% concentration is sufficient whereas hydroxides secured by moist suction require an acid content of 60 to 90%. If the sulphuric acid is too dilute there results oily, viscous sulphates which dissolve but very slowly in strong sulphuric acid.

The resulting red solution, which contains the cerium in the form of ceric sulphate, is then filtered off from the small amounts of insoluble constituents present. Filtering may be accomplished by means of a filter press or the clear solution may be siphoned off. In this way, utilizing 9.0 kg. of concentrated sulphuric acid for the 52.5 kg. of hydroxides obtained (8% CeO₂, 8% oxides of the remaining earth metals, and 52% moisture), the hydroxides are dissolved in the solution. The addition of the sulphuric acid is carried out with continuous stirring and cooling.

After filtration, the resulting 45.5 liters of red solution is permitted to run in a thin stream into 220 liters of water at room temperature. This operation is carried out with thorough stirring. In order to complete the precipitation, ammonia is permitted to drip into the solution while the hydrolysis takes place and after hydrolysis has been completed. The amount of ammonia so

added is such as to maintain the solution weakly acid toward Congo red.

The basic sulphates of probable formula $4\text{CeO}_2 \cdot 3\text{SO}_3 \cdot 10(\text{OH})$ were precipitated quickly. After a short time the clear supernatant liquid begins to become cloudy and an additional small amount of basic sulphate precipitates. After several hours precipitation is complete leaving a clear solution which is then filtered. The variegated earths, lanthanum and other earth metals which give colored oxides, pass into the filtrate and may be recovered therefrom by any suitable procedure.

The precipitated basic sulphates of cerium are contaminated with approximately 1% of didymium. They may be freed almost completely from this impurity by stirring 3 to 4 times with water containing 3% by volume (1.3% by weight) of hydrogen chloride. Each stirring is continued for approximately 3 hours, the supernatant clear solution being decanted after settling. The wash waters are then permitted to run off.

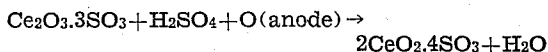
After drying at a temperature of 80 to 100° C. the basic sulphate of cerium is obtained in the form of a fine, yellow powder which may be utilized directly as a mill addition in enamelling operations. The yield from this procedure was 6.5 kg. of dry basic sulphates, approximately 97%.

Example 2

The procedure followed was substantially identical with that described in Example 1 except that the resulting basic sulphates of cerium were fired in a muffle furnace at a temperature of at least 900° C., preferably 950 to 1000° C. The resulting oxide was substantially pure white in color and was very valuable as a white opacifier in enamelling operations. Utilizing these fired basic ceramic sulphates as white opacifiers, opacity equivalent to that obtained with 2% stannic oxide could be secured by utilizing less than 2% cerium oxide.

Example 3

Instead of oxidizing cerium hydroxide in air with an alkaline medium as in Example 1 the cerium may also be converted by electrolytic oxidation at the anode in an electrolytic cell into the tetravalent state. Hydrogen chloride or sulphuric acid may be used in the electrolyte. The equation for the chemical reaction occurring is as follows:



In order to secure tetravalent cerium it is essential to have present at least one molecule of a bivalent acid such as sulphuric acid per molecule of Ce_2O_3 . The variegated earths are inert during the electrolytic oxidation.

It is not possible to utilize in the electrolytic oxidation solutions of the sulphates of high concentration, owing to the relatively low solubility of these sulphates. It is necessary to oxidize acid solutions, thereby requiring the use of larger amounts of ammonia during the hydrolysis than that utilized in Example 1. The hydrolysis and washing of the basic sulphates, and their subsequent firing to obtain a substantially pure white product was carried out as in the foregoing examples. Using an anodic current density of 0.2 amp. per sq. cm., a cathodic current density of 0.66 amp. per sq. cm. and an electromotive force of 10 volts, substantially 100% oxidation of the cerium to the tetravalent form is secured. The yield is 78% based on the current utilized.

Example 4

The basic sulphates of cerium obtained in accordance with the procedures outlined in the foregoing examples may be combined with basic compounds of the alkali or alkaline earth metals with alumina and silicic acid. These basic compounds are preferably added after freeing the basic sulphates of cerium from the variegated or colored earth compounds. The basic substances specified may be present separately or together, or they may be employed in mutual chemical combination, such as, for example, alkali metal compounds and silicic acid in the form of sodium silicate or water glass. The addition of such compounds to the opacifiers has been found of especial value in combination with the hydroxide content (of the basic sulphates and/or of the alkali compounds).

10 kg. of basic sulphate of cerium dried at 80° C. (having a composition as follows: 51.25% CeO_2 , 19% SO_3 and 29.75% H_2O) is combined with 0.4 kg. of NaOH. In place of the NaOH 1.0 kg. of SiO_2 (in the form of hydrate) or 3.5 kg. of water glass (40° Bé.) may be utilized. The basic sulphates of cerium are ground with the addition agents to a paste and then dried at approximately 100° C. The product is a fine powder and is especially suitable for enamelling. It possesses 2.5 times the opacifying action as the same amount of stannic oxide.

It should be understood that the foregoing details are to be considered as illustrative and not restrictive. Various changes may be made in the spirit of my invention, which changes are intended to be comprehended within the scope of the appended claims. The breadth of my invention is to be determined in accordance with the claims and is not to be restricted to specific numerical amounts or to procedures which have been cited in the foregoing examples merely as illustrative.

I claim:

1. A process for the preparation of cerium compounds suitable for use in an enamel opacifying agent which comprises the steps of dissolving a natural product containing cerite earths in sulphuric acid, converting the cerium content to the tetravalent form and introducing said sulphuric acid solution into a caustic alkali solution, washing the resulting cerite earth hydroxides to substantially remove alkali compounds, dissolving said hydroxides in sulphuric acid, and diluting the resulting solution to precipitate basic ceric sulphate.

2. A process as defined by claim 1 wherein the cerium compounds are converted into compounds of tetravalent cerium by separate treatment prior to dissolving the raw material in sulphuric acid.

3. A process as defined in claim 1 wherein the cerium compounds are converted into compounds of tetravalent cerium by anodic oxidation of the solution obtained by dissolving said natural material containing cerite earths in sulphuric acid.

4. A process as defined in claim 1 wherein the basic cerium sulphate is subjected to a subsequent heat treatment at a temperature within the range 800 to 1100° C. prior to use as an enamel opacifying agent.

5. A process according to claim 1 wherein precipitation of basic cerium sulphate is completed by adding to the diluted solution a small amount of non-fixed alkali, and thereafter washing the precipitate with dilute hydrochloric acid.

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