

1

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COLORED RUTILE BOULES AND A METHOD FOR MAKING THE SAME

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The present invention relates to rutile single crystal boules. More specifically it relates to colored rutile single crystal boules and to the production of such boules.

Rutile is one of the three known crystal modifications of titanium dioxide. When substantially pure a massive single crystal of rutile has gem-like properties with a very light straw color and reflectance, refraction and brilliance greater than that of the diamond. By means of the present invention rutile single crystals may be produced in various colors.

The principal object of the present invention is the preparation of rutile single crystal boules having various colors which may be used as gem material. A further object is to produce rutile boules having a color within the range from yellow through amber to dark red.

In its broadest aspects the present invention contemplates a rutile single crystal boule containing as a coloring agent an oxide of an element selected from the group of elements consisting of cobalt and nickel. These colored boules are prepared according to the method of the present invention by progressively fusing a mixture of finely divided titanium dioxide and a small amount of a coloring agent mentioned above in a flame carrying an excess of an oxidizing gas to form said boule and thereafter oxidizing the boule so formed.

In this description of the present invention the word "boule" is used in its currently accepted meaning to denote a characteristic shape or form of an artificially prepared massive single crystal having a rounded end, or meniscus, a more or less rod-like body portion and a tapering end, giving an over-all appearance in profile of an almond, or carrot.

This application is a continuation-in-part of my co-pending application Serial No. 134,343 filed December 21 1949, now abandoned.

The general method for production of colored single crystal boules to which the present invention relates is that described in application Serial No. 54,562, filed October 14, 1948, now abandoned, bearing common ownership and now abandoned, for the preparation of pure rutile single crystal boule.

According to the preferred method of the present invention, there is employed as starting material a substantially pure TiO_2 which is very fine, fairly uniform and possesses an open structure with units capable of being rapidly melted. A TiO_2 having an ultimate unit particle size of approximately 0.1 micron has proved especially satisfactory. In general, material having an average particle size above about 5 microns should be avoided because such particles do not satisfactorily fuse under the conditions of this invention. A preferred method for preparing a TiO_2 starting material especially adapted for the production of rutile single crystal boules is described in U. S. Patent No. 2,521,392, issued September 5, 1950, wherein the double salt, ammonium-titanium-sulfate, is calcined until all of the ammonia and sulfate has been removed by volatilization.

According to the present invention the small amount

2

of the coloring agent, i. e. an oxide of an element selected from the group consisting of cobalt and nickel, may be mixed with the TiO_2 starting material in any convenient manner, for instance, by dry blending. A more uniform mixture may be prepared by adding salts of one of the elements, such as a sulfate salt, as a powder, slurry or solution to the double salt, ammonium-titanium-sulfate, prior to calcination.

The amount of coloring agent to be added to the TiO_2 starting material is very small and in order to obtain pleasing colors should not exceed more than about 0.13% for cobalt and about 1.0% for nickel, calculated as the element based on the weight of the TiO_2 . The amounts of coloring agents will vary with the different elements to produce the various depths of colors and the range for each element will be subsequently described. The preferred lower limit is about 0.005% at which boules are produced which possess a light yellow color.

In progressively fusing the starting mixture of TiO_2 and an oxide of an element selected from the group consisting of nickel and cobalt, there should be employed a flame which carries an excess of an oxidizing gas, preferably oxygen. Preferably the fusion is carried out at a temperature of from 1825° C. to 1900° C. according to the method described in application Serial No. 54,562, supra, in which the particles of the starting mixture are entrained in a stream of oxygen in a tube constituting the center of a burner consisting of three concentric tubes. In this burner hydrogen is introduced to the flame through the intermediate tube and additional oxygen in excess over the amount required to combine with the hydrogen is introduced through the outer tube. Preferably, the ratio of oxygen to hydrogen by volume should be about 1 to 1 and should not be less than about 8.5 parts of oxygen to 9.5 parts hydrogen by volume.

The flame temperature should be carefully controlled during the formation of the boule. It has been found that satisfactory results are obtained when the temperature is held between about 1825° C. and 1900° C. around the area where the boule is formed. Rutile melts at about 1820° C. and therefore it is necessary to operate so that the temperature at the top of the boule is somewhat above the melting point, e. g. 1825° C. If the temperature is in excess of 1900° C. an excessively large portion of the boule melts at the top and the molten material boils and runs over the sides of the boule.

The excess of oxygen in the flame is necessary because at elevated temperatures, titanium dioxide gives up oxygen and is converted to lower, or sub-oxides of titanium, e. g. Ti_2O_3 . This loss of oxygen proceeds with considerable rapidity under conditions produced by an oxy-hydrogen flame wherein the TiO_2 is fused and the loss is accelerated when the flame is neutral or reducing. Under such conditions the formation of lower, or sub-oxides of titanium, is so great that mixtures of small crystals of various oxides of titanium are produced rather than a single crystal boule.

Even when operating with an excess of oxygen the boule as produced has generally a deep blue-black color indicative of some deficiency in oxygen. Therefore, in order to produce a boule according to the instant invention in which the color ranges from yellow through amber to dark red, the blue-black boule has to be re-oxidized.

The reoxidation of the boule is preferably carried out by heating the blue-black boule in an oxidizing atmosphere, for instance, air or oxygen. The temperature of the treatment should be within the range from about 650° C. to about 1500° C. It has been found that at temperatures to any extent below 650° C. oxygen will not be appreciably incorporated into the rutile single crystal. There is a decided loss in brilliance, lustre and fire when the treatment is carried out above 1500° C.

and at that temperature the rate of oxygen incorporated into the rutile crystal is excessively rapid and difficult to control. Preferably the oxidation should be carried out at about 1100° C. to 1300° C. to properly anneal the boule. The heating should be continued until the boule obtains the desired color.

According to the present invention it is necessary to fully oxidize the blue-black single crystal boule when employing the coloring agents in order to reveal the characteristic colors of such agents. When the boule is only partially oxidized the true color is masked by the blue of the oxygen deficient boule thus producing colors having bluish or greenish tone. The elements when added to TiO₂ feed material produce boules having various colors. The color of the boules varies in depth and tone when the elements are present in different amounts. When any of these elements are present in the boule in very small quantities the color of the boule is yellow varying from a pale yellow to a yellow with a brownish tone. When present in slightly larger quantities the rutile single crystal boule possesses an amber color. When present in still larger quantities the color changes to a deep red or almost black color.

In order to more clearly illustrate this invention, Table I is presented to show the amount of coloring agent which may be mixed with a titanium dioxide feed material to form a single crystal boule having no fractures and having a substantially clear appearance. The percentages of coloring agents added are also presented to show the various color changes which take place with varying amounts of agents added.

Table I

Agents Added	Preferred Upper Limit (calculated as the element)	Percent Element Added	Color
Cobalt Oxide....	0.13	0.005-0.05 Co.... 0.05-0.1 Co.... 0.1-0.13 Co....	yellow. amber. reddish amber.
Nickel Oxide....	1.0	0.005-0.05 Ni.... 0.05-0.1 Ni.... 0.1-1.0 Ni....	yellow. amber. deep red.

The term "preferred upper limit" as shown in column 2 of Table I means the amounts which produce pleasing colors and superior quality boules. These percentages should not exclude larger additions, however, since larger additions still produce good quality boules. It has been found that when larger amounts of these coloring agents are added to the TiO₂ feed material that the boules formed may have an outer skin or scale which upon analysis shows that most of the additional amounts of elements over that shown in the preferred upper limit column are present in the skin in a more concentrated form. Apparently most of the excess migrates to the outer surface and enters the skin or scale portion. If the coloring agents are added in excessive amounts over that which apparently can migrate to the skin, the boule will possess fracture and bubbles of opaque material which is not satisfactory material for the gem trade. Table II is presented to show the results of adding amounts in excess of the preferred upper limit listed in Table I. For illustration the data are presented for additions of cobalt to TiO₂ feed material.

Table II

Addition Agent	Amount Addition Agent (calculated as the element)	Condition of Boule	Color
	Percent		
Cobalt oxide....	0.13	Excellent.....	Reddish amber.
	2.0	Good+outer skin.	Very dark red.
	3.0	do.....	Do.
	4.0	No boule, bad features.	Do.

As shown in Table II the boules may contain large quantities of coloring agent, but in most cases the color is so deep when the agent is added in excess of the preferred upper limit stated in Table I that most boule material possesses a substantially black color. In most cases boules prepared using an amount of agent which falls within the intermediate to high ranges presented in Table I possess the most pleasing colored tones, i. e., the amber to red colors.

Apparently when the coloring agent is added in excess of the preferred upper limit in Table I most of the excess agent migrates from the boule itself and concentrates into the outer skin, leaving a concentration in the boule approximating that of the preferred upper limit as previously stated.

From the above description it has been shown that pleasant appearing colored rutile boules may be formed by the present invention. The coloring agents produce products which range in color from yellow through amber to red to reddish-black tones when added in varying quantities. The precise depth of tone and nature of the color obtained is readily controlled as hereinbefore described by employment of the appropriate amount of the most suitable coloring agent. These colored boules may be cut into gems which possess the required characteristics, particularly that of a pleasing appearance, which are necessary for the gem trade.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

I claim:

1. A colored rutile single crystal boule containing an oxide of an element selected from the group consisting of cobalt and nickel; the cobalt in amount from 0.005% to 0.13%, the nickel present in amount from 0.005% to 1.0% by weight calculated as the element.

2. A colored rutile single crystal boule containing an oxide of cobalt; the cobalt being present in quantity from 0.005% to 0.13%.

3. A colored rutile single crystal boule containing an oxide of nickel; the nickel cobalt being present in a quantity from 0.005% to 1.0%.

4. A method for preparation of a colored rutile single crystal boule which comprises forming an intimate mixture of finely divided titanium dioxide and an oxide of an element selected from the group consisting of cobalt and nickel and fusing said mixture to form a single crystal boule.

5. A method according to claim 4 in which the cobalt is added to said mixture in amount from 0.005% to 0.13% and the nickel is added in amount from 0.005% to 1.0%.

6. A method according to claim 4 in which the oxide added is cobalt.

7. A method according to claim 4 in which the oxide added is nickel.

8. A method for the preparation of a colored rutile single crystal boule which comprises forming an intimate mixture consisting of finely divided titanium dioxide and an oxide of an element selected from the group consisting of cobalt and nickel; fusing said mixture to form a single crystal boule and heating said boule in an oxidizing atmosphere at a temperature of 650° C. to 1500° C. until the blue color tone disappears.

No references cited.