

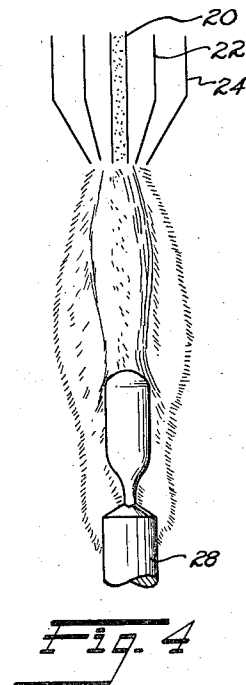
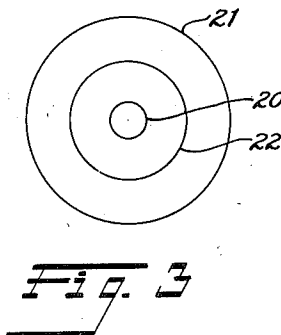
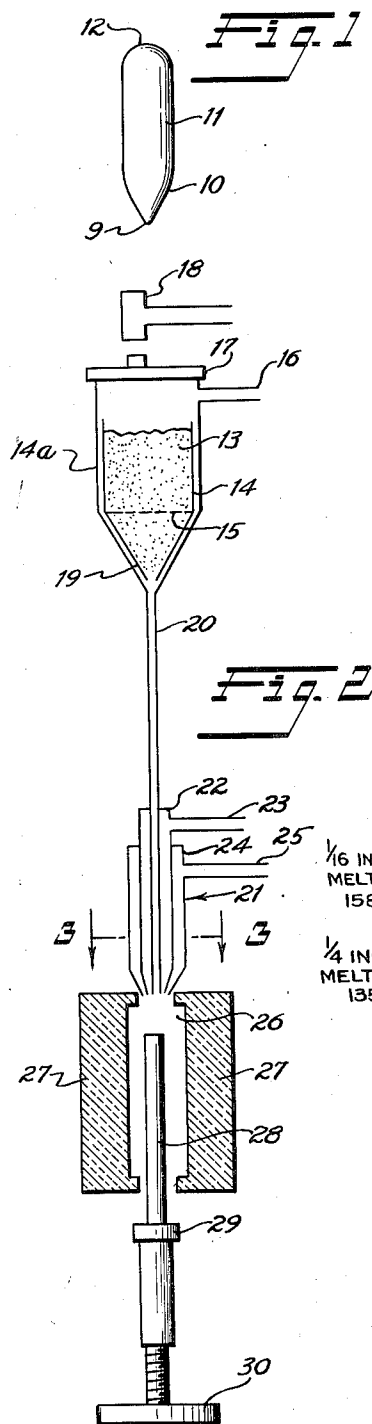
May 14, 1957

C. H. MOORE, JR., ET AL

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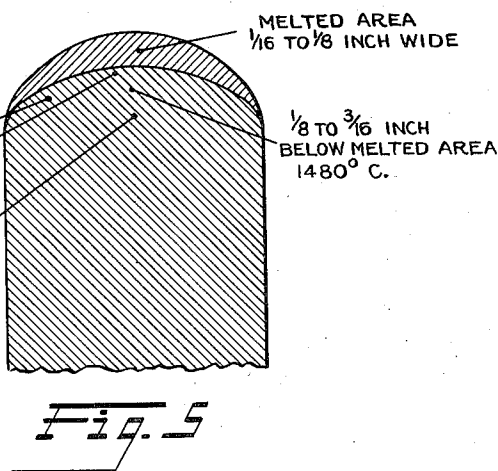
SYNTHETIC RUTILE CRYSTAL AND METHOD FOR MAKING SAME

Filed April 4, 1956



1/6 INCH BELOW
MELTED AREA
1580° C.

1/4 INCH BELOW
MELTED AREA
1350° C.



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2,792,287

SYNTHETIC RUTILE CRYSTAL AND METHOD
FOR MAKING SAME

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12 Claims. (Cl. 23--202)

The present invention relates to rutile crystals of large size and of uniform predetermined color and quality and to the production of such crystals.

This application is a continuation-in-part of applications Serial Nos. 54,562 and 54,563 filed October 14, 1948, both now abandoned, and application Serial No. 286,853 filed May 9, 1952, which also has been abandoned.

The term "boule" as used herein is a term of art used to denote a characteristic crystal form or shape and is applied particularly to the synthetic crystals of the form produced by processes similar to the process of Verneuil.

Rutile is one of the three crystal modifications of titanium dioxide. In nature, rutile generally occurs as tetragonal crystals which are often geniculated and twins are common. Rutile also sometimes appears as thin, hair-like crystals in quartz. Nowhere in nature does rutile occur as a boule nor does rutile occur in nature as a straw-white single crystal.

When substantially pure, a single crystal of rutile has gem-like properties with a very light straw color and reflectance, refraction and brilliance greater than that of diamonds. Its optical properties suggest its usefulness in the form of prisms, lenses and the like for optical instruments. When slightly deficient in oxygen, the color of pure rutile varies through shades of blue to blue-black. The color and other properties of rutile single crystals can also be varied by the inclusion of additives such as metal salts.

The art of growing synthetic crystals is quite old and well known, but prior to the present invention it was impossible to produce synthetic crystals of rutile by known methods. In the course of the researches leading to the present invention, early attempts to prepare rutile single crystal boules by the Verneuil process met with no success largely because certain factors peculiar to rutile were not understood and appreciated.

Titanium dioxide has a strong tendency to give up oxygen at elevated temperatures and form lower oxides of titanium. We have found that at the high temperatures necessary to grow single crystal rutile boules (about 1825° C. to 1900° C.), this tendency is so strong that unless an oxidizing flame is used, there is strong likelihood that some of the TiO₂ will be changed to a lower oxide such as Ti₂O₃ with the result that the boule will be multicrystalline rather than a single crystal.

Even when the boule is formed under properly oxidizing conditions, it is usually blue-black with a metallic luster when broken, indicating an oxygen deficiency. We have found that this blue-black color can be eliminated by oxidizing the boule by heating it in an oxidizing atmosphere. When a single crystal of substantially pure rutile is satisfied with respect to oxygen, that is to say contains stoichiometric proportions of oxygen and titanium, the color is nearly water-white with a very slight straw colored tone. As oxygen is restored to a substantially pure rutile single crystal having the deep blue-black metallic color of the boule as prepared, the color grad-

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ually lightens, passing through a range of color gradations which may be described as deep blue, medium blue, light blue, etc. until the nearly water-white color of a rutile crystal completely satisfied with respect to oxygen is achieved. The oxygen deficiency of blue monocrystalline rutile is so slight that the crystal has both the apparent chemical composition and crystal structure of rutile and at present, no methods are known by which the actual oxygen deficiency can be estimated quantitatively in terms of some standard of measure, e. g. weight or volume. It is evident, however, that the blue color effect results from oxygen deficiency and very small variations of this deficiency produce definite and appreciable color differences. The blue crystals of substantially pure rutile produced according to the present invention may be cut and polished to form beautiful brilliant blue gems.

The properties of rutile single crystals can also be varied in other ways in addition to the control of oxygen content. Metal salts can be added to the powdered TiO₂ starting material to give the resulting crystal desired color or other properties. With such additives present, the boule is formed in the same way in an oxidizing flame, and then the boule or crystal is oxidized in the same way to reduce or eliminate the blue color and bring out the characteristic color due to the additive. For example, when the TiO₂ starting powder contains 0.04% Fe₂O₃, a monocrystalline boule can be formed. The boule when formed usually has the blue-black metallic luster resulting from oxygen deficiency. Heating the boule, or crystals cut from the boule, in an atmosphere of oxygen, causes the blue color to disappear and the boule, when fully oxidized, has a yellow color resulting from that amount of Fe₂O₃. When larger amounts of Fe₂O₃ are added, the color of the fully oxidized boule becomes darker and a boule having 0.2% Fe₂O₃ is clear reddish color. Additions of other metal compounds such as cobalt or nickel have coloring effects similar to iron. With one or more of these additives, boules can be made ranging in color from pale yellow to deep red, larger amounts of the additive giving the deeper color, but in any event the amount of coloring agent is small. Cobalt and nickel are especially useful additives giving clear and pleasing colors from pale yellow, through amber, reddish amber and red to a deep reddish black. U. S. Patent No. 2,715,071, issued August 9, 1955 to Leon Merker describes and claims specific amounts of various additives to secure particular colors.

When very finely powdered alumina is added to the TiO₂ starting material, fully oxidized crystals have a clear water white color and the hardness of the crystals is increased. Satisfactory boules have been made with small amounts of alumina from 0.005% to 0.1%. U. S. Patent No. 2,715,070 issued August 9, 1955 to Charles H. Moore, Jr. describes and claims rutile crystals containing alumina.

Regardless of whether the boule is to be formed of substantially pure rutile or contains a coloring or other modifying agent such as alumina, the boule is formed and its oxygen content controlled in the same way. According to the present invention, any desired degree of oxygen deficiency as indicated by the depth or tint of the blue coloration, may be obtained by stopping the oxidation, or by deoxidizing the crystal, to the desired point.

One of the principal objects of the present invention is to provide a rutile single crystal boule.

Another object is to produce rutile single crystals of such large size that gems and optically useful articles can be prepared therefrom.

Still another object is to provide a method for producing rutile single crystals which may be formed into beautiful, brilliant gems.

Another object is to provide rutile crystals having predetermined properties.

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A further object is to provide a method for controlling the oxygen content of rutile single crystals.

A further object is to provide a method for restoring the oxygen content of oxygen deficient rutile single crystals.

A further object is to provide a novel process for converting dark opaque as-grown rutile crystals to a transparent and substantially colorless condition for use as gemstones.

A further object of the invention is to provide rutile single crystals having predetermined oxygen content, color and properties.

These and other objects and advantages reside in novel features and steps and processes as hereinafter more fully set forth.

Figure 1 illustrates the characteristic shape of a boule.

Figure 2 is a schematic representation of a preferred form of apparatus for carrying out the present invention.

Figure 3 is a cross-section of the burner of the apparatus of Figure 2 taken on the line 3—3 of Figure 2.

Figure 4 is a schematic representation of the flame formation of the boule according to the present invention.

Figure 5 is an enlarged section of the top, or meniscus end of a boule showing the various temperature zones during formation.

A typical boule is illustrated in Figure 1 of the drawing. The boule forms at a point 9, then tapers outwardly in somewhat conical form 10, then has a substantially cylindrical body portion 11 and finally has a rounded end 12. The diameter and length of the body portion 11 can be varied to produce boules of different sizes.

The first factor which must be considered for the successful practice of the present invention is the purity of the titanium dioxide starting material. It is essential that the starting material be free, or at least substantially free from components which prevent or inhibit the crystallization of the TiO_2 in a single crystal of rutile. Such interference may result from crystalline structure or chemical action of the component.

For example, the TiO_2 starting material should be free or substantially free from elements possessing ionic radii incompatible with the rutile crystal lattice. The ionic radii of tetravalent titanium is reported to be 0.68 Angstrom unit. It has been found that cationic elements having ionic radii less than about 0.60 Angstrom unit and greater than about 0.75 Angstrom unit, and which are nonvolatile at the temperature of the boule formation, should not be present in the TiO_2 starting material in amounts substantially greater than a mere trace detectable only as such by spectrographic analysis. Elements which have ionic radii between about 0.60 and 0.75 Angstrom unit may be present in somewhat more than spectrographically detectable traces. These enter the crystal lattice structure of the rutile single crystal to form solid solutions, whereas elements which have ionic radii outside the range specified, inhibit the formation of the rutile single crystal.

Furthermore, the starting material should be free, or at least substantially free from elements which react with titanium or titanium dioxide to form chemical compounds. Elements which react with titanium or titanium dioxide to form chemical compounds also inhibit the formation of rutile single crystals, regardless of whether such elements have ionic radii within the proper range. Thus, magnesium which has an ionic radius within the specified range cannot be used because it reacts with TiO_2 to form magnesium titanate. The compounds formed from such reactive elements crystallize in their own distinctive patterns and inhibit the formation of a rutile single crystal.

Impurities which commonly occur in titanium dioxide but which are incompatible with the rutile crystal lattice are silicon, magnesium and lead. With the techniques and equipment available when the present invention was

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made, these impurities, in general, could not be tolerated in amounts substantially greater than 0.15% silicon, calculated as SiO_2 ; 0.005% magnesium, calculated as MgO ; and, 0.002% lead, calculated as PbO . In this connection, however, it should be pointed out that small amounts of other elements which may be present in the TiO_2 starting material as tolerated impurities, or added to impart a desired color to the final rutile single crystal, may act as solvents for elements which are undesirable, thereby raising the minimum amount of such undesirable impurities which may be present without preventing formation of the rutile single crystal boule. Thus, elements of the iron family such as cobalt and nickel, which impart to the final rutile crystal definite colorations, will tend to raise the tolerance for silicon. It will be appreciated that a maximum upper limit for the content of incompatible impurities cannot be precisely given, but for the production of a rutile single crystal boule having maximum purity and a minimum of internal stresses, the TiO_2 starting material should be free, or at least substantially free from incompatible impurities, as explained above. A satisfactory TiO_2 starting material for the practice of the present invention should not contain more than about three-tenths per cent total incompatible impurities. With improved techniques and equipment, larger percentages of impurities may possibly be tolerated.

Some elements which may be added to the TiO_2 starting material for a particular purpose may be undesired impurities under other conditions. For example, when a water-white crystal is desired, alumina is added to eliminate the straw-white tone of pure rutile. Even a trace of coloring oxide would be an undesirable impurity in such a case. Likewise, when a colored crystal is desired, alumina, which tends to lighten the color, may be undesirable.

It is, therefore, preferable that the TiO_2 starting material be as pure as is practically possible and all impurities should be eliminated or held to a minimum regardless of the ionic radius or chemical or physical effect of the impurity. When the TiO_2 starting material is free or substantially free of impurities, the operations employed in producing the crystal can be standardized and the resulting crystals will be substantially uniform as to color and structure.

Patent No. 2,521,392, issued September 5, 1950, discloses a suitable form of TiO_2 starting material together with methods for its preparation.

For the most efficient results, the TiO_2 starting material should be very fine, fairly uniform and possess an open structure with units capable of being rapidly melted. A TiO_2 starting material 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 0.5 micron should be avoided because such particles do not satisfactorily fuse under the conditions of the invention. Additives such as coloring oxides should be used in powdered form and have about the same particle size as the TiO_2 .

Another factor which the successful achievement of the present invention depends is the nature of the flame in which the particles of starting material are fused. Verneuil processes employ a flame resulting from the combustion of hydrogen and oxygen and in the prior art the ratio of hydrogen to oxygen was such that the flame was reducing in varying degrees of intensity.

At elevated temperatures titanium dioxide gives up oxygen and unless oxygen loss is prevented, all or part of the TiO_2 is converted to lower or sub-oxides of titanium, e. g. Ti_2O_3 . This loss of oxygen proceeds with considerable rapidity under the conditions produced by an oxyhydrogen flame wherein the TiO_2 is fused and the loss is accelerated when, as is the case using a typical Verneuil process, the flame is a reducing one. Under such conditions, the formation of lower or sub-oxides of

titanium is such that mixtures of small crystals of various oxides of titanium are produced rather than a single crystal boule.

The small particle size of the starting material and the prevention of reduction during crystallization in accordance with our invention results in single crystal, i. e. massive non-granular boules. In the growing of single crystals, it seems to be important that the crystal be grown from a single nucleus, as a plurality of nuclei apparently result in a multicrystalline rather than a monocrystalline structure. When the particle size of the starting material is very small, the material is probably fully melted under the conditions of the present process and recrystallizes in the plane of the nucleus. Should the particles be too large to be fully melted, the unmelted portion might form a new crystal nucleus so that a multicrystalline structure would result. The same is probably true if conditions are such that some Ti_2O_3 or TiO is formed. These compounds would break up the orderly formation of monocrystalline TiO_2 so that new crystal nuclei would form and a multicrystalline mass would result.

It has been found according to the present invention that for the production of a rutile single crystal boule an excess of oxygen, over that required completely to react with the hydrogen, should be fed to the flame at all times. Preferably, the ratio of oxygen to hydrogen by volume should be about 1:1 and should not be less than about 8.5 parts of oxygen to 9.5 parts hydrogen by volume. Preferably, also, a part and generally a major part of the oxygen should be fed to the flame as an outer cover or envelope.

The preferred form of apparatus for carrying out the present invention is a modified Verneuil burner as illustrated in Figure 2 and the method of carrying out the invention in its most effective embodiment will now be described.

The starting material 13, which may be substantially pure TiO_2 with or without a suitable additive, is placed in the hopper 14, which is provided with a screen, preferably about 100 mesh, of wire mesh or silk cloth 15. The hopper 14 is mounted within a housing 14a and there is a free space between the hopper and the wall of the housing. The housing is provided with an inlet 16 for the introduction of oxygen, a cover 17 and a knocker 18 connected with suitable electrical or mechanical means, for instance, for causing the knocker 19 periodically to rise and to fall, striking the cover 18. From the conical bottom 19 of the housing 14a below the hopper 14, a long tube 20 extends downward and forms at the bottom, the inner concentric ring of the burner. This burner 21 is formed of the central tube 20, a jacket 22 forming a middle, or intermediate, concentric ring of the burner, provided with an inlet 23 for the introduction of gas, and a jacket 24 forming an outer concentric ring of the burner provided with a gas inlet 25. Generally we prefer to introduce oxygen through the center tube 20 and outer ring 24 and to admit hydrogen through the intermediate ring 22, but the burner may be operated by admitting oxygen through the center tube and intermediate ring and the hydrogen through the outer ring. If desired, one or more cooling jackets may be provided, for instance between the gas introduction jacket and around the outside of the burner.

The burner opens into a chamber 26, which is preferably formed of suitable fire resistant material, such as firebrick, 27, conveniently formed of two substantially semi-cylindrical halves. In the chamber 26 there is positioned a rod 28 made of fire resistant material, e. g. firebrick or zirconia, upon which the flame impinges when the apparatus is operating and upon which the boule forms. The rod 28 is supported on platform 29 provided with means, for example a threaded screw with handle 30, for lowering the platform 29 and rod 28 as the boule grows vertically in size.

In operating the apparatus, oxygen is admitted to the burner through inlets 16 and 25, inlet 16 taking a minor portion of the oxygen, e. g. about one-quarter of total oxygen and inlet 25 the major portion, e. g. about three-quarters. Hydrogen is admitted through inlet 23. It will be understood that the quantity of the respective gases and the rate of flow will be controlled by manometers and reducing valves, as necessary, and in known manner. The flame is then lit and the knocker 18 set in motion. With each blow of the knocker, a small amount of starting material is sifted through the screen 15 and entrained in the stream of oxygen coming into the housing 14a through inlet 16 and carried through the tube 20 into the flame. The quantity of oxygen and hydrogen and the range of flow will be regulated during the formation of the boule to produce a flame having a temperature somewhat higher than the melting point of titanium dioxide which is about $1820^{\circ}C$. The flame should be kept at a temperature between about $1825^{\circ}C$. and $1900^{\circ}C$., preferably at about $1850^{\circ}C$. and should not exceed $1900^{\circ}C$. because at this temperature the boule melts and flows over.

At the onset of preparing a boule, the flame is adjusted to a temperature slightly below the melting point of TiO_2 . The particles of TiO_2 are heated as they enter the flame and fall upon the top of the rod 28 and form a fused sintered mass in the shape of a cone. The flame temperature is then increased to above the melting point of TiO_2 and the top of the sintered cone becomes fused and forms a single crystal seed or bud which grows into a small sphere as additional heated TiO_2 particles strike it and are fused. The top of this sphere is molten to slight depth, the molten portions being meniscus shaped as shown in Figure 5. The heated TiO_2 particles melt and form this molten meniscus. The single crystal or sphere grows upward vertically and horizontally through the solidification of the bottom of the molten mass. The spherical shape is lost and the single crystal begins to assume the typical shape of a boule. When the single crystal grows to its maximum diameter, which is a function of the size of the flame, which is, in turn, a function of the dimensions of the burner, the growth of the boule is substantially all vertically upward. As the boule grows upward, the rod 28 and the platform 29 are gradually lowered by adjusting means 30 so that the molten meniscus of the boule occupies the same position in the flame. While growing, the boule has a molten meniscus at the top and temperature zones substantially as shown in Figure 5.

The operation may be carried on to obtain boules of any desired length within the maximum permitted by the dimensions of the apparatus. It has been found that with increasing diameter of the boule, the internal strains and stresses tend to increase. With a burner of the character described with a nozzle of three-quarters inch wide, it has been found entirely practicable to produce boules having diameters between about one-half to three-quarters inch. The length of the boule appears to have no effect on internal strains, but the longer the boule becomes, the greater is the strain on its tip or seed end 9, and if the boule becomes too long, it will snap off from the rod 28. With boules having diameters between one-half and three-quarter inch, it has been found possible to make boules of from one and one-half to two inches in length. It will be understood that the invention is not limited to boules of any particular diameter and length, but may be operated, if necessary, with suitably modified apparatus to produce boules of any varying dimensions.

After a boule of desired size is formed, the flame is shut off and the boule and apparatus are allowed to cool after which the boule is broken away from the rod 28.

As pointed out above, crystals of substantially pure rutile may vary from deep blue-black to light straw or

nearly water-white color depending upon the degree of

oxygen deficiency. As produced, the boule usually has a more or less frosted outer surface, and when split the interior surfaces of the pieces are vitreous and shiny and may even possess a metallic luster. When formed, regardless of whether it is of substantially pure rutile or whether it contains a coloring oxide, the boule is usually oxygen deficient and is characterized by a deep blue-black metallic color.

In the present invention, the oxygen deficient rutile single crystal is heated at elevated temperatures in an oxidizing atmosphere until a sufficient amount of oxygen has been incorporated into the crystal lattice to produce a predetermined desired color. As the crystal lattice becomes more nearly satisfied with respect to oxygen, the blue color becomes lighter and the transparency of the crystal increases until the blue color disappears entirely and the crystal is a straw white.

As hereinafter described, the invention also contemplates and includes a second heating in a reducing atmosphere in the event that the crystal contains an excess of oxygen over that desired for a particular color or other property. For example, if the oxidizing treatment is carried so far that the crystal is of too light a color, the color may be darkened by reduction.

As measured on a Beckman spectrophotometer, the color of an oxygen deficient rutile crystal has a dominant wave length between about 480 millimicrons and about 575 millimicrons, the dominant wave length of darker crystals being near the lower end of the range and the dominant wave length of the lighter, more fully oxidized crystals being nearer the upper end of the range. As the crystals are oxidized, the transparency also increases. For example, a blue crystal 2.5 millimeters thick has a light transmission of about 25% while the same crystal when fully oxidized has a light transmission of about 70% measured on a Beckman spectrophotometer.

The temperature at which the initial oxidizing heating should be carried out should be within the range from about 650° C. to about 1500° C. It has been found that at temperatures much below 650° C., oxygen will not be appreciably incorporated into the rutile single crystal. It has also been found that there is a decided loss in brilliance, luster and fire in the rutile crystals when oxidized above 1500° C. and at that temperature, the rate of oxygen incorporation into the rutile crystal is excessively rapid and difficult to control. Preferably the oxidizing heating should be carried out at about 1100° C. to 1300° C.

The oxidizing atmosphere is supplied by means of an oxygen-containing gas, for example air, in which the rutile single crystal is heated. Preferably, the heating should be carried out in a stream of oxygen or air enriched with respect to oxygen.

The heating should be continued for the length of time required to produce the desired degree of oxidation as evidenced most conveniently by the color of the crystal. After a slight amount of oxygen has been taken up by the oxygen deficient crystal of substantially pure rutile, its color changes from the original blue-black to a deep blue. Further heating results in increased oxygen absorption by the crystal, the color correspondingly changing to lighter shades until finally the crystal is fully oxidized as evidenced by loss of all blue tone and substantially pure rutile exhibits a straw-white color. The color of the fully oxidized crystal of substantially pure rutile is not water-white but may be described as white with a straw tone or termed for convenience, straw-white.

It is not always possible when practicing the invention to achieve exactly the desired blue color. At the elevated temperature, the color may differ from that when the crystal is cold. The oxidation is progressive and slight differences in size of the crystals causes changes in degree of oxidation with time. Minor impurities also may affect the oxidation rate, e. g. rutile boules con-

taining the maximum tolerable amount of SiO₂ apparently reoxidize much more slowly than boules having low SiO₂ content.

It may be found that a slight excess of oxygen has been incorporated into the crystal over that desired to obtain a certain color or property. This excess may be removed by subjecting the crystal to a second, reducing heating. This second heating should be carried out at temperatures between about 500° C. and 1000° C., preferably 600° C. to 800° C., in a reducing atmosphere, preferably a stream of hydrogen or a mixture of hydrogen and an inert gas. Carbon monoxide may be employed, but it is not as effective as hydrogen. Below about 500° C., the crystal will not give up oxygen while above about 1000° C. the liberation of oxygen is too rapid for satisfactory close control.

When the rutile contains a coloring oxide, as for example alumina or oxides of cobalt and nickel, the oxidizing treatment causes the blue-black color to disappear so that characteristic color due to the coloring oxide becomes apparent. By controlling the amount of oxidation, crystals can be produced in which the color due to the coloring oxide is combined with the blue shades due to oxygen deficiency.

In order to achieve the best results, care should be exercised to avoid as much as possible alternating oxidizing and reducing treatments because repeated heating and cooling produces internal strains within the crystal so that it becomes brittle and will tend to shatter when an attempt is made to cut or shape it into some desired form. With the scope of the invention, those skilled in the art will quickly learn how to control the initial oxidizing treatment with a minimum of required subsequent reducing treatment.

If desired, the whole boule as originally formed may be treated according to the present invention but so to do will require considerable prolongation of the treatment because of the relatively large size of the boule. It may, therefore, be desirable to cut the boule into a desired shape, for instance, a plate, or cube, or prism, prior to the initial oxidizing treatment. If the boule is suspected of containing fractures, the presence of which cannot be readily detected when the color is deep blue-black, it may be found expedient to carry out the first oxidizing heating until the boule is fully oxidized and at which time, its light color will readily permit detection of fracture, then to cut the boule into the desired shape with reference to any fractures found and to then subject such shapes to the second reducing heating.

It was found that the hardness of substantially pure rutile single crystals prepared according to the present invention is greater than that previously reported for rutile, viz. 6.5 on the Moh scale. The following table shows representative hardness values on the Moh scale obtained for rutile crystals prepared according to the present invention.

Type of Crystal	Hardness Moh Scale	
	Parallel to "C" Axis	Perpendicular to "C" Axis
White (Straw tone).....	7.5-8.0	7.0-7.5
Light blue.....	6.5	7.0-7.5
Deep blue.....	6.0	7.0-7.5

It is interesting to note that the hardness values remain constant along planes perpendicular to the "C" axis while the hardness values decrease with an increase of oxygen deficiency along the planes parallel to the "C" axis.

From the foregoing, it will be apparent that we are able to attain the objects of the invention and provide large single crystals of rutile having predetermined color and characteristics and to provide a method of producing such crystals and controlling the color and other properties thereof. The foregoing description is illustrative and

various changes and modifications can be made without departing from the spirit of the invention or the scope of the appended claims.

What is claimed is:

1. A method for the preparation of a rutile single crystal boule which comprises progressively fusing a finely divided, substantially pure TiO_2 in an oxidizing flame produced by the combustion of hydrogen and oxygen wherein a minor portion of said oxygen is introduced into the core of the flame and a major portion of said oxygen, constituting with the minor portion an excess over that required for the combustion of the hydrogen, is introduced into the flame at the outer surface thereof forming an enveloping oxidizing atmosphere around said flame.

2. A method according to claim 1 in which the finely divided substantially pure TiO_2 is introduced into the core of the flame entrained in the minor portion of the oxygen.

3. A method for the preparation of a rutile single crystal boule which comprises progressively fusing a finely divided substantially pure TiO_2 in an oxidizing flame produced by the combustion of hydrogen and oxygen wherein a minor portion of said oxygen insufficient for the complete combustion of the hydrogen is introduced into the core of the flame and a major portion of said oxygen, constituting with the minor portion an excess over that required for the complete combustion of the hydrogen, is introduced into the flame substantially concentrically with said core to complete the combustion of the hydrogen and provide an oxidizing atmosphere.

4. A method according to claim 3 in which at least 8.5 parts of oxygen are added for 9.5 parts of hydrogen by volume.

5. A method according to claim 3 in which the ratio of oxygen to hydrogen by volume is substantially 1 to 1.

6. A method for making a single crystal of rutile capable of having a light transmission for a 2.5 millimeter section of at least 25% when subjected to a subsequent oxidizing heat treatment, comprising periodically passing axially through a flame and melting therein powdered titania, accumulating and crystallizing the titania so melted as a single crystal on a support aligned axially with such flame, moving such flame and support apart axially of such flame, and maintaining an oxidizing atmosphere about said titania during fusing and crystallizing.

7. A method for making a single crystal of rutile having a light transmission for a 2.5 millimeter section of at least 25%, comprising periodically passing axially through a flame and melting therein powdered titania, accumulating and crystallizing the titania so melted as a single crystal of rutile on a support aligned axially with such flame, moving such flame and support apart axially of

such flame, maintaining an oxidizing atmosphere about said titania during fusing and crystallizing, and subsequently heating the rutile crystal in an oxidizing atmosphere at a temperature between 650°C . and 1500°C .

8. A process for lightening the color of a dark single crystal of synthetic rutile to render it suitable for use as a gemstone, which process comprises heating such a crystal at a temperature between about 650°C . and about 1500°C . in an atmosphere of oxygen, and arresting such heating when the desired lighter color is obtained.

9. A process for correcting overoxidation of a single crystal of synthetic rutile which comprises heating said crystal in an atmosphere of a reducing gas at a temperature between about 500°C . and 1000°C .

10. A process for making a single crystal of synthetic rutile of gem quality comprising periodically passing small amounts of powder consisting essentially of titania axially down through an oxy-hydrogen flame onto a support to melt such powder; causing the powder so melted to crystalline on said support as a substantially black and opaque single crystal of rutile; and then converting said single crystal to a lighter color by heating said crystal at a temperature above 650°C . and below 1500°C . in an oxidizing atmosphere of oxygen, and arresting such heating when the desired lighter color is obtained.

11. As an article of manufacture a highly refractive, flame-formed monocrystalline mass of rutile adaptable for the preparation of gems and optically useful objects having a color characterized by a dominant wave length of about 480 millimicrons with a light transmission of about 25% to a dominant wave length of about 575 millimicrons with a light transmission of about 70%, said light transmission being measured by a spectrophotometer at the dominant wave length through a section 2.5 millimeters thick.

12. As an article of manufacture a highly refractive, flame-formed, monocrystalline mass of rutile adaptable for the preparation of gems and optically useful objects having a color characterized by a dominant wave length of about 575 millimicrons and a light transmission of about 70% through a section 2.5 millimeters thick as measured by a spectrophotometer.

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