ALTERING THE APPEARANCE OF CORUNDUM CRYSTALS

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2,488,507 11/1949 Burdick et al. 106/42
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ABSTRACT

The appearance of a corundum crystal is altered by subjecting the crystal to an elevated temperature while the crystal is embedded in a powder comprising a major amount of alumina, and a minor amount of titanium oxide with or without a metal oxide colorant.

5 Claims, 7 Drawing Figures
ALTERING THE APPEARANCE OF CORUNDUM CRYSTALS

This application is a continuation-in-part of application Ser. No. 210,140, filed Dec. 20, 1971 now abandoned.

The invention relates to a process for altering the appearance of corundum crystals and to crystals treated by the process. The process is useful as a means for changing the color of natural or synthetic corundum crystals, and as a means for correcting or masking certain color defects that are most frequently encountered in synthetic corundum crystals. An understanding of the manner by which such defects may arise will be enhanced by a brief review of certain of the known methods for producing synthetic corundum crystals.

Synthetic corundum crystals of gem quality are produced commercially by the Verneuil or oxyhydrogen-flame process. In a typical Verneuil process, alumina powder is fed from a hopper with a fine mesh screen bottom into an oxygen stream. The oxygen flows downwardly through the central tube of an oxyhydrogen burner. Hydrogen is fed to the flame through an annular passage surrounding the central tube. The flame from the burner is discharged into a furnace containing a ceramic pedestal. The pedestal is centered in the furnace below the bottom tip of the central tube of the burner, and at a predetermined vertical distance below said tip.

The powder is fed intermittently through the central tube by tapping the hopper with a hammer. The powder falling through the flame builds up as a mass, either on the pedestal or on the tip of a thin corundum crystal supported on the pedestal. As the powder builds up on the upper surface of this mass, the pedestal is lowered in order to maintain a constant distance between the bottom tip of the central tube and the top of the growing crystal. The powder feed rate is adjusted at first so that the diameter of the growing crystal increases. When the diameter has attained the desired dimension, the powder feed rate is adjusted to maintain this diameter. When the flame temperature, powder feed rate, and pedestal withdrawal rate are properly coordinated, a cylindrical monocrystalline mass of corundum, i.e., alpha alumina, known as a boule, is grown. The boule is then heat-treated or annealed at about 1900°-1950°C in a controlled atmosphere, oxidizing or reducing, for one to two days to help relieve stresses in the boule.

The alumina powder that is employed as the feed is produced by calcining pure alum (hydrated ammonium aluminum sulfate). When alumalone is used, the alumina powder obtained therefrom is used to produce water-white or colorless sapphire. The production of colored sapphires and rubies is attained by adding various metallic salts to the alum. The metal salts are ultimately converted to oxides in the finished corundum crystals. The metal oxide colorant additives are called “dopants.”

Fuller descriptions of the oxyhydrogenflame or Verneuil process for growing synthetic corundum crystals may be found in U.S. Pat. Nos. 988,230 and 1,004,505, and in Volume 7, pages 157 et seq., of the Kirk-Othmer “Encyclopedia of Chemical Technology” (The Interscience Encyclopedia, Inc.: New York).

A number of processes for producing synthetic asteriated corundum crystals are known. The basic process, described in U.S. Pat. No. 2,488,507, is a modification of the Verneuil process wherein a titanium-doped alumina powder is employed for growing the boule. The resultant boule, which comprises an alumina crystal having a titanium oxide dissolved therein, is subjected to a heat treatment to precipitate fine, needle-like crystals of a titanium compound along prominent crystallographic planes of the alumina crystal. The asterism is caused by these needle-like crystals.

In U.S. Pat. No. 2,690,630 a process is described in which a crystal is heated while in contact with a titanium compound to introduce the compound into the crystal surface. The titanium compound may be mixed with alumina. Subsequent heat treatment produces asterism.

In the so-called “flux process,” of U.S. Pat. No. 2,690,062 the temperature at the surface of a growing boule is fluctuated. The crystal grows in a series of thin, longitudinally distributed upwardly convex transverse layers. Alternate layers have the titania distributed across the full widths thereof, whereas the rest of the layers have titania concentrated adjacent the periphery. In cutting a gem stone en cabochon from a boule grown by this flux process, the rounded upper surface or “crown” of the cabochon coincides approximately with the contours of said layers.

The Verneuil process and its modifications described above, are critical to carry out. The process requires the successful coordination of several parameters. To name just a few, the rate of powder feed, the flame temperature at the surface of the growing crystal and the rate at which the supporting pedestal for the growing crystal is lowered, must all be coordinated within narrow limits. Even a temporary lack of coordination can cause a defective area in the growing crystal. For this reason, there is a significant proportion of gemstones produced from Verneuil process boules that have color defects. Such defects include the following:

1. Non-uniform color. First, a gemstone can have a clear or a dark area as a result of some of the dopant being non-uniformly distributed in that area. Frequently these defects appear at the center of the stone. Second, distinct bands can sometimes be seen in a gemstone cut from a boule grown by the flux method. Such boules normally contain alternating dark (TiO₂-rich) and light (TiO₂-poor) layers. Banding is normally not visible to the naked eye because the layers are impalpably thin. However, if a layer is thicker than usual, it can be seen by the naked eye where it intersects the surface of the gemstone. Such thicker layers can occur as a result of the temperature falling to fluctuate for one or more cycles, a temporary increase in the alumina powder flow, a variation in the withdrawal rate of the pedestal, or the like.

2. Undesired color. By “undesired color” is meant a color differing in hue, brilliance, or saturation from a desired color. Synthetic corundum can have undesired color for a variety of reasons. For instance, the wrong atmosphere during the annealing step can cause the color to be off-specification. To illustrate, when producing ruby-colored corundum, if the atmosphere is sufficiently oxidizing, the corundum will have a bluish tinge. This defect is usually not apparent until a gemstone has been cut and ground from the boule. Another cause of undesired color in synthetic corundum is the wrong quantity of dopant. Too much dopant causes the color saturation to be too high, and too little dopant causes low saturation. Of course, natural sapphires can, and frequently do, have undesired color.
3, "White feet". In this type of defect a white area occurs adjacent to the base of the stone. It is caused by fabricating stones too near the edge of the blank, the blank usually having a white skin. This type of defect does occur in natural stones.

It is an object of the invention to provide a process for altering the appearance characteristics of corundum crystals.

It is another object of the invention to provide a process for altering the color of corundum crystals.

A further object of the invention is to provide a process for producing corundum crystals having uniform color from asteriated corundum crystals having non-uniform color.

Another object is the production of a cabochoon-cut asteriated corundum crystal of gem stone quality from a crystal suffering appearance defects.

Briefly, the process of the invention by means of which these objects are attained comprises embedding a corundum crystal having undesired appearance characteristics in a powder containing about 1 to 25% titania and up to 20% of a metal oxide colorant, the remainder alumina and heating it to an elevated temperature below the fusion temperature of the powder for a time sufficient to impart to at least the surface portions of said crystal desired appearance characteristics sufficient to mask such undesired appearance characteristics.

In the accompanying drawing:

FIG. 1 is a side elevation, partly in section of a crucible containing a number of cabochoon-cut corundum crystals to be treated in accordance with the invention;

FIG. 2 A through E represent in top view and side elevation cabochoon-cut asteriated crystals having visible defects of the type suitable for treatment by the process of the invention color variations being shown by stippling; and

FIG. 3 is an enlarged vertical partial section of a cabochoon-cut asteriated crystal after treatment in accordance with the invention.

In a first important aspect, the invention provides a process for correcting non-uniform color in a corundum crystal. Thus, corundum crystals having clear areas and corundum crystals exhibiting banding can be subjected to the process of the invention to produce thereby corundum crystals whose color appears uniform. In a second important aspect, the invention provides a process for changing the color of corundum crystals. Thus, corundum crystals of one color are subjected to the process to produce thereby corundum crystals having another color whose hue, brilliance, or saturation is different from said one color.

The process is carried out by heating a cabochoon-cut corundum crystal while its surface portions are in contact with a powder comprising alumina and titania with or without a minor proportion of a metal oxide colorant for a period of time sufficient to effect the desired color change of the crystal or to correct color defects. Referring to FIG. 1, a convenient way of practicing the process is to pack a plurality of crystals 10 in powder 12, which is contained in a crucible 14, care being taken to prevent the crystals from making direct contact with each other.

The crucible containing the crystals is heated in an oven suitably filled by natural gas. The elevated temperature employed will normally be within the range of from about 1600°C to about 1850°C. A preferred temperature range is from about 1700° to about 1800°C. At temperatures below 1600°C., the process becomes uneconomically slow, and if the temperature becomes too high, surface damage of the corundum crystal can occur. Of course the temperature must be below the fusion point of the crystal. Generally temperatures much above 1800°C. should be avoided for the reason that the titanium oxide lowers the melting point of the powder. If fusion of the powder occurs, the surface of the corundum crystal will be damaged.

The crystals are maintained at the treating temperature for a period of time sufficient to alter the appearance of the crystals. To illustrate, the times can vary from about 2 to about 200 hours, depending upon the exact nature of the crystal being treated. For instance, highly polished gemstones require longer treatment time and natural stones shorter treatment time. The atmosphere in the treating oven is normally an oxidizing atmosphere, although in some cases a reducing atmosphere is employed, especially when treating blue sapphires, as is more fully discussed below. To obtain an oxidizing atmosphere, natural gas, which is predominantly methane but usually contains some higher gaseous hydrocarbons, is burned in the oven in a natural gas-to-oxygen volume ratio of about 1 to 2.5. To obtain a reducing atmosphere, the natural gas to oxygen ratio can be about 1 to 1.5.

In the event that a corundum crystal treated by the process of the invention has not been satisfactorily asteriated, the crystal can be subjected subsequently to a conventional asteriating heat treatment at about 1100°C to 1500°C. Such conventional asteriating heat treatments are disclosed in U.S. Pat. Nos. 2,690,062 and 2,690,630.

The powder employed in the process of the invention comprises a mixture of alumina and titania with or without metal oxide colorant. Such colorants are oxides of metals such as iron, chromium, vanadium, and nickel, which impart color to corundum. The alumina of the mixture is inert to the stones, merely serving as a support and as a separator between them. Titania tends to aid diffusion of color throughout the affected surfaces of the stone and, for example, tends to cause diffusion of the bands producing the form of defect illustrated by FIG. 2A. The quantity of titania needed depends on the severity of the defect. Titania itself produces no significant color in corundum but tends to diminish the color intensity. Accordingly for white or light colored stones no colorant oxide need be present in the alumina-titania powder.

If stones of strong colors such as blue, red or purple are desired, the powder should also contain dopants or colorants appropriate to the desired colors. For blue coloration iron oxide is used, for red chromium oxide is used. Nickel oxide produces a grayish green. For certain colors, combinations of oxides are used, for example, purple is obtained by using both chromium and iron oxides. The powder used in the process of the invention contains about 1 to 30% by weight of titania. The remainder is alumina and colorant. The quantity of colorant oxides varies with the specific materials and the desired density of color. Generally a total quantity of up to about 20% by weight of colorant may be used. In the case of iron oxide usually not more than about 1% by weight is needed to produce a desirable blue stone. In any case, to avoid fusion of the powder it is
desirable to use as little colorant as possible to attain good color.

The powder can be produced by calcining alum containing a compound of the appropriate metal or metals which will produce the desired oxide or oxides on calcining. Mechanical mixing of the alum and the metal compound is unnecessary since the alum goes through a liquid phase during the calcining. Thorough mixing is achieved automatically as the alum passes through this liquid phase. The calcined powder is of extremely fine particle size generally being not greater than about 1 micron. Examples of metal compounds that can be added to the alum in order to incorporate therein a metal oxide colorant include ammonium dichromate, ferric ammonium sulfate, nickel sulfate, and ammonium metavanadate. Titanium tetrachloride is a convenient and satisfactory source of titanium in the powder.

The calcining conditions for the production of the powder can vary from a temperature of from about 1850°F to about 2050°F for a period of from about 2 to about 5 hours. For instance, calcining at a temperature of about 1920°F for about 3 hours is useful. The calcinable is carried out in any suitable oven or furnace, such as a natural gas fired oven using an air:natural gas volume ratio of about 10:1.

Referring now to FIG. 2A through E of the drawing, typical defects treatable by the process of the invention are represented in top and side elevation views. Such defects are banded stones (FIG. 2A), clear centers (FIG. 2B), dark spots (FIG. 2C) off color (FIG. 2D) and white feet (FIG. 2E). In these representations as above indicated stippling is used to indicate color variations but it should be understood that the stones although varying from translucence to opacity do not contain discrete particles visible to the naked eye. Their asterism is represented by lines extending from crown to base. In FIG. 3 a treated stone 10 is represented in section showing the treated area 16, the base 18 and the internal portion or core 20 of the stone.

Referring particularly to FIG. 3 the treated area 16 of a treated stone generally is about 0.001 to 0.020 inch in thickness after polishing. This thickness is determined primarily by the time and temperature of treatment as above discussed and to some extent by the atmosphere in the furnace. Generally in a reducing atmosphere deeper penetration is obtained in shorter time than in an oxidizing atmosphere. To achieve the benefits of the process of the invention the thickness of the zone affected by the process need not be great, but since polishing is required, it should of course be sufficient not to be removed in the polishing step.

A stone embodying the invention thus is a cabochon cut coronadum crystal having an internal portion or core of nonuniform or undesirable appearance characteristics and an external zone at least in the crown portion of the stone of uniform desirable appearance, the thickness of such zone being sufficient to impart to the stone uniform, desirable appearance characteristics of gemstone quality. Generally the thickness of the treated zone as above stated is about 0.001 to 0.024 inch and for optimum results is about 0.002 to 0.020 inch. In the treated zone the chemical composition of the stone may be somewhat different from that of the core of the stone for instance containing somewhat more dopant. For example in some stones the TiO₂ content at the surface was about 0.2% while at the core the TiO₂ content was about 0.08%. Similar differences have been noted in iron oxide content of treated stones. These differences in composition are of no consequence for the invention is concerned with correcting visual defects in stones as distinct from chemical, crystallographic, or physical defects such as cracks or chips.

In the production of man-made asteriated gem stones of cabochon cut it is customary in the industry to produce on the base of the stone some identifying indicium of the manufacturer. To do so in some instances requires sandblasting. Such operation of course removes some of the surface of the stone, and in the case of stones embodying the invention this may be a treated surface.

The following specific Examples illustrate the practice of the invention and serve as a guide to attaining its objectives.

**EXAMPLE 1**

**Production of Powder**

A charge of 1.75 pounds of crystalline hydrated ammonium aluminum sulfate is provided in an alumina crucible. The crucible is placed in a natural gas-fired oven along with other crucibles containing the same charge, and rapidly (within 15 to 20 minutes) heated from room temperature up to 1920°F. The crucibles are held at that temperature for 3 hours, and then cooled. The contents of the crucibles are then poured through a screen into a suitable container. The yield is about 0.2 pound of alumina powder per crucible.

Various metal oxide colorants are incorporated in the powder by adding aqueous solutions of metal compounds to the hydrated ammonium aluminum sulfate prior to the calcining step. Table I, below, displays the quantity in milliliters of representative aqueous metal compound solutions of the indicated concentration by weight required to achieve the indicated concentration of metal oxide in the alumina powder, the per cent concentration being based upon total weight of powder.

**TABLE I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. in Soln.</th>
<th>Ml. Added</th>
<th>% Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium tetrachloride</td>
<td>35</td>
<td>100</td>
<td>22, TiO₂</td>
</tr>
<tr>
<td>TICl</td>
<td>11.6</td>
<td>22</td>
<td>0.5, Fe₂O₅</td>
</tr>
<tr>
<td>Ferric ammonium sulfate</td>
<td>12.05</td>
<td>100</td>
<td>6, Cr₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃ · NH₄H₂SO₄ · 2H₂O</td>
<td>19.5</td>
<td>100</td>
<td>6, NiO</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

Deep blue sapphire crystals having nonuniform surface color (banding or clear areas such as shown in FIG. 2A and 2C), and/or having too low color saturation (such as shown in FIG. 2E) are subjected to a temperature of 1750°C. In a reducing atmosphere for 30 hours, embedded in powder containing 0.25 weight percent ferric oxide and 13 weight percent titanium dioxide, the remaining alumina. After this treatment, the crystals have a uniform, deep blue color.

When iron oxide is included in the alumina powder, the powdered tends to sinter. However, good results have been achieved in correcting defective deep blue sapphire by using alumina powder containing from about 0.1 to about 0.5 weight percent ferric oxide, and from
12 to about 18 weight percent titanium dioxide. Within these ranges of metal oxide colorants, at most only moderate sintering is encountered while the process is at least 90 percent successful in correcting defects.

**EXAMPLE 3**

Purple sapphire crystals having a reddish tinge, and red sapphire (i.e., ruby) crystals having non-uniform color or too low color saturation, are subjected to a temperature of 1750°C. for 96 hours in an oxidizing atmosphere, while being embedded in powder containing 6 weight percent chromia, 22% titania, the remainder alumina. The crystals so treated have a uniform ruby-red appearance.

**EXAMPLE 4**

Yellow sapphire crystals having nonuniform color or off-specification color saturation (i.e., either too high or too low color saturation), are subjected to a temperature of 1750°C. for 48 hours in an oxidizing atmosphere, while being embedded in powder containing from 3 to 6 weight percent chromia, 24 weight percent titanium oxide, the remainder alumina. The crystals so treated have a uniform salmon pink color.

**EXAMPLE 5**

Yellow sapphire crystals having nonuniform color or whose color saturation is too low are subjected to a temperature of 1750°C. for 96 hours in an oxidizing atmosphere, while embedded in powder containing 2.5 weight percent nickel oxide, 3.5 weight percent chromia, and 15 weight percent titanium dioxide, the remainder alumina. After this treatment, the color of the crystals is a uniform light gray-green.

**EXAMPLE 6**

Pink sapphire crystals whose color is non-uniform, black sapphire crystals whose color is non-uniform, and milky white sapphire crystals having non-uniform color, are subjected to a temperature of 1750°C. for 96 hours in an oxidizing atmosphere while embedded in powder containing 22 weight percent titanium oxide, the remainder alumina, no colorant being present. The crystals are uniform in color (pink, black, or white, respectively) after this treatment.

**EXAMPLE 7**

Milky white sapphire crystals having nonuniform color or undesired color (such as a grayish tinge), are subjected to a temperature of 1750°C. for 96 hours in an oxidizing atmosphere while being embedded in powder containing 6 weight percent chromia, and 22 weight percent titanium dioxide, the remainder being alumina. After this treatment, the crystals have a uniform pink appearance.

**EXAMPLE 8**

Pale blue sapphire crystals having nonuniform color are subjected to a temperature of 1750°C. for 96 hours in a reducing atmosphere while embedded in powder containing 10–15 weight percent titanium oxide the remainder alumina, no colorant being present. After this treatment, the crystals are a uniform pale blue (azure) in color.

It will be seen from the foregoing discussion and examples that the invention makes possible the production of visually acceptable asteriated corundum crystals of gem stone quality from crystals which while otherwise acceptable have appearance defects. Since the value of a gem stone of a given size depends almost entirely on appearance, the invention is of real commercial significance. It makes possible the salvage of man-made crystals which otherwise would be rejected and also makes possible the upgrading of natural crystals which frequently suffer from appearance defects. It must be emphasized that stones treated in accordance with the invention are not of inferior quality as gem stones as compared with stones not requiring treatment. Because of the great durability of corundum the treated zone is permanent. It is in no sense of the word a laminate but is an integral portion of the stone.

A further advantage of the invention derives from the ability to change the color of stones. By the invention a manufacturer could produce boules of all one color, for instance white, and change the color of cabochon-cut stones prepared from them to suit the demand for other colors.

What is claimed is:

1. A process for altering the appearance of corundum crystals so as to produce crystals having uniform color appearance comprising the steps:
   a. preparing a powder comprising a major proportion of alumina and a minor proportion of an oxide of titanium and iron oxide in an amount ranging from about 0.1 to about 1 weight percent;
   b. contacting the surface of a corundum crystal having undesirable appearance characteristics with the powder of step (a); and
   c. heating said crystal in contact with said powder in a reducing atmosphere at an elevated temperature within the range of about 1600°C. to about 1850°C. for a time sufficient to alter the appearance of said crystal so as to produce a crystal having a surface of uniform color.

2. The process of claim 1 wherein the powder contains from about 0.1 to about 0.5 weight percent iron oxide, from about 12 to about 18 weight percent titanium oxide and remainder alumina.

3. A process of claim 2 wherein the further step of heating said crystal to an asteriating temperature of 1100°C. to 1500°C. is added.

4. A process for altering the appearance of corundum crystals so as to produce crystals having uniform color appearance comprising the steps:
   a. preparing a powder comprising a major proportion of alumina, an oxide of titanium and at least one metal oxide colorant selected from the group of chromium, nickel and vanadium sufficient to effect a desired color change of the crystal;
   b. contacting the surface of a corundum crystal having undesirable appearance characteristics with the powder of step (a); and
   c. heating said crystal in contact with said powder in an oxidizing atmosphere at an elevated temperature within the range of about 1600°C. to about 1850°C. for a time period sufficient to alter the appearance of said crystal so as to produce a crystal having a surface of uniform color.

5. The process of claim 4 wherein the further step of heating said crystal to an asteriating temperature of 1100°C. to 1500°C. is added.