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PROCESS FOR COATING GEM STONES

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ABSTRACT OF THE DISCLOSURE

Improved processes for applying a hard protective coating to natural or synthetic gems involving the deposition of a thin layer of aluminum oxide on the surface thereof. The coated gem stone is subsequently heat treated at temperatures between about 800° to 1400° C. to harden the coating and to interdiffuse the coating film and the surface of the gem stone. A pretreatment of the gem stone to form a silica layer may be employed to promote rapid interdiffusion.

SPECIFICATION

This invention relates to an improved method for coating natural or synthetic gem stones. More particularly, the invention pertains to processes for applying a hard protective coating to natural or synthetic gems without detracting from their appearance, and to the novel coated gem stones produced thereby.

Many gem stones of high refractive index are relatively soft which naturally limits their utility. Previous attempts to impart hardness to such soft natural or synthetic gem stones as rutile, strontium titanate, zircon, topaz and the like by coating have not been generally successful. Often the desired improvement in hardness has not been achieved, and discoloration of the gem stones has been encountered after prolonged exposure to the elevated temperatures used in the coating operations. Moreover, the difference in the refractive indices of the coating and the natural or synthetic gem substrate is obviously highly undesirable.

One object of the present invention is to provide improved methods for coating natural or synthetic gems which avoid the difficulties encountered in the prior art methods.

Another object of the present invention is to provide improved processes wherein a hard protective coating can be readily applied to natural or synthetic gems.

A further object of the present invention is to provide improved processes for coating natural or synthetic gems with a hard protective coating while avoiding discoloration and other characteristics which are deleterious to the appearance of such gem stones.

A still further object of the present invention is to provide novel gem stones characterized by a markedly improved hardness and satisfactory appearance such as coloration and light refraction.

These and other objects of the present invention will be readily apparent from the ensuing description and illustrative embodiments.

In accordance with the present invention it has now been found that if soft natural or synthetic gem stones of high refractive indices such as rutile, strontium titanate, zircon, topaz and the like are coated with a thin film or layer of aluminum oxide, i.e., synthetic sapphire, a marked improvement in hardness, as measured by scratch tests with a diamond point, and a marked resistance to chipping are attained. The size of the gem stones which may be treated by the processes of this invention can vary widely, and individual natural or synthetic gem stones ranging in size from about 0.03 to 0.5 inch or more in

diameter, may be satisfactorily employed. Generally the processes of this invention comprise the uniform deposition of an aluminum oxide film or layer on the exposed surfaces or on a portion of the surface of the soft gem stones. This deposition of a substantially uniform film or layer of aluminum oxide is accomplished by the pyrolysis or decomposition of a vaporized aluminum composition in a treating chamber wherein one or more of the soft natural or synthetic gem stones are positioned.

More particularly, a gas which is inert to the soft gem stone is passed through a liquid aluminum composition in such a manner as to permit generation of a gas stream containing the inert gas and the vaporized aluminum composition. The inert gas which may be employed in the practice of this invention include such gases as oxygen, nitrogen, hydrogen, air, argon, helium, and the like. The aluminum composition through which the inert gas is passed in order to generate said gaseous feed stream is preferably a vaporizable substituted hydroxy-containing aluminum compound, and preferably an aluminum alcoholate, which will provide a final vapor pressure to the aluminum composition-containing vapors of from about 2.0 mm. to about 10.0 mm. at 150° C., and preferably from about 2.0 mm. to about 5.0 mm. at 150° C. The preferred aluminum alcoholate substances which may be employed in the practice of this invention include such aluminum alcoholates as aluminum isopropylate or isopropoxide, aluminum ethylate, aluminum butylate, aluminum methylate, and the like. These alcoholates may be employed either in monomeric or polymeric form. During the vaporization step, the alumium alcoholate substance is held at an elevated temperature of from about 100° C. to about 200° C., depending upon the alcoholate used, while the inert gas is passed therethrough. For example, temperatures of from 150° to 170° C. are used with aluminum isopropoxide. The aluminum alcoholate can be stabilized as by the addition thereto of a stabilizing agent, for example, aluminum n-butylate, when the aluminum composition chosen to be employed in the practice of this invention is the trimeric form of aluminum isopropoxide, in order to prevent polymerization either at the vaporization temperature or during prolonged storage at lower temperature. In practice, it has been found that when the trimeric form of aluminum isopropoxide is employed in this vaporization process, the resulting aluminum isopropoxide vapors are in the dimeric form.

The resulting aluminum composition-containing gaseous mixture is introduced into a treatment chamber containing the soft gem stones and subjected to an elevated temperature sufficient to effect pyrolysis or decomposition of the aluminum composition.

Upon contact of the aforementioned aluminum composition-containing vapors with the soft natural or synthetic gem stones at a temperature of from about 250° C. to about 1000° C., and preferably from about 400° C. to about 600° C., a deposition of an aluminum oxide film or coating takes place on the surface of the gem stones. The deposition of this film is preferably allowed to continue until a uniform film of a thickness of from about 0.1 to about 10.0 microns is obtained, and most preferably a thickness of from about 1.0 to about 3.0 microns. The speed with which the film or layer is deposited should be such to allow the formation of a uniform film to take place without impairing its color characteristics, and generally should be greater than about 0.1 micron per minute. It is important to avoid undue or prolonged exposure of the gem stones to elevated deposition temperatures which would tend to cause deterioration, i.e. discoloration.

The deposition step is followed by a heat treatment wherein the coated gem stones are subjected to an elevated temperature of from about 800° to 1400° C., and pref-

erably from about 900 to 1000° C., for about 30 to 200 minutes to destroy any residual hydroxide groups. The film or layer of aluminum oxide is thereby hardened sufficiently as determined by scratch tests with a diamond point. This heat treatment converts the aluminum oxide film to an essentially crystalline form but does not render the film opaque.

The coated gem stones are then cooled to ambient temperature. In some instances such as in the case of a synthetic gem stone composed of strontium titanate it has been found advantageous to cool the coated gem stones slowly until a temperature of about 400° C. has been reached. This type of cooling involves gradual reduction of the temperature at a rate of about 5° C. per minute. Alternatively, the cooled, coated gem stones may be reheated to a temperature between about 400° to 600° C. in order to eliminate any discoloration caused by the high temperature treatment.

In accordance with another aspect of the present invention it has now been found that the film or layer of aluminum oxide, deposited as described above, can be interdiffused with the surface of the gem stone. The interdiffusion step can be important because of the considerable difference between the refractive indices of the coating and the substrate. With interdiffusion the reflection of light from the interface is reduced to such an extent that under normal conditions of illumination, i.e., by the human eye unaided by instruments, the film or layer of aluminum oxide is rendered invisible. The reflection at low angles of incidence is reduced to such an extent that no interference colors can be seen; whereas at high angles of incidence sufficient reflection takes place so as not to reduce the sparkle of the gem stone so that it appears to be composed wholly of the relatively low refractive index of the coating, i.e., aluminum oxide (sapphire). Interdiffusion is carried out after the initial coating procedure as described hereinabove, and prior to cooling. Thus, after the desired amount of protective coating has been applied, the coated gem stones are heated to an elevated temperature ranging from about 800° to 1400° C., preferably from about 900° to 1200° C., for a period of from about 30 to 180 minutes, and preferably from about 60 to 120 minutes. Coated strontium titanate, for example, is effectively treated by heat treatment at 1000° C. for 60 minutes.

A further feature of this invention resides in the discovery that the interdiffusion treatment can be promoted by initially predepositing on the surface of the gem stone being treated, a thin film or layer of a diffusion promoter such as silica. This thin silica film, which is deposited on the surface of the gem stone prior to the application thereto of the aluminum oxide protective film, is formed by the decomposition of a silicon-containing compound which may be accomplished in the same manner as heretofore described for the aluminum oxide film, except that a silicon containing compound, for example, substituted silanes and polysilanes, is employed in the gaseous mixture introduced into the treatment chamber. The silica film, which may be satisfactorily employed, should have a thickness less than about 10 percent, and preferably about 1 percent of the thickness of the aluminum oxide film which is to be subsequently applied. Tetraethylsilicate is one of the preferred materials but other silicon-containing compounds as ethyltriethoxysilane, methyltriethoxysilane, tetramethoxysilane, and the like may also be satisfactorily employed. The promotion of rapid interdiffusion being important to prevent undesirable discoloration of the natural or synthetic gem stones, excessively long exposure to high temperatures should be avoided.

Conventional apparatus may be employed in the practice of the processes of this invention. Thus, for example, the deposition or predeposition steps may be accomplished by the use of an electric field or by use of high temperature electric furnace type heating chambers.

In addition to the foregoing, the general process of the instant invention may also be employed to apply a thin protective coating of aluminum oxide on high quality optical components, for example, lenses, prisms and the like, thereby protecting these components from mechanical damage without affecting the optical properties thereof.

This invention will be more fully understood by reference to the following illustrative embodiments.

EXAMPLE 1

A brilliant, cut stone of strontium titanate having a diameter of about 0.3 inch, is positioned in a depression in a carbon block and placed in the treatment chamber so that only the top section of the stone protrudes above the surface of the block. The treatment chamber is then heated to and maintained at 500° C. A stream of nitrogen gas is passed through a saturator containing trimeric aluminum isopropoxide held at 145° C. and then is passed over the surface of the heated treatment chamber. The resulting heated nitrogen gas vapor is then introduced into the treatment chamber for a period of thirty minutes at a gas velocity of 100 cubic centimeters per minute. Thereafter, the strontium titanate gem stone is removed from the treatment chamber, placed in a separate furnace, and heated at a temperature of 1100° C. for sixty minutes. The gem is then cooled and maintained at a temperature of 500° C. for a period of 240 minutes, and is then allowed to cool to room temperature. The resulting aluminum oxide film coating on the gem stone is measured and found to be 1 micron in thickness. The hardness of the coating is tested by moving a diamond point over the surface of the stone under a load such that the scratch depth is less than the coating thickness, and the depth of the resulting scratch is measured in comparison to materials of known hardness. The coated strontium titanate stone has a rating of 8.8 on the Mohs' scale. The coated stone is visually examined and the presence of the coating is not detectable to the naked eye.

EXAMPLE 2

A brilliant cut stone of rutile is positioned in a carbon block so that only the top portion of the stone protrudes above the surface, and is placed in the treatment chamber. Nitrogen gas is saturated with tetraethylsilicate by being passed through a saturator containing the material and maintained at a temperaure of 100° C. The tetraethylsilicate saturated nitrogen is then introduced into the treatment chamber having a temperature of 650° C. for a period of five minutes. The temperature of the chamber was then reduced to 500° C. and nitrogen gas saturated with aluminum isopropoxide at 145° C. is introduced for a period of 60 minutes. Thereafter the gem stone was heated at a temperature of 950° C. for a period of 60 minutes and then held at 500° C. for an additional 240 minutes before being allowed to cool to room temperature. The coating on the gem stone had a thickness of 2 microns, was not visible to the naked eye and had a hardness value of 8.8 on the Mohs' scale.

EXAMPLE 3

A topaz is positioned in a carbon holder so that only the top section of the stone protrudes above the surface and is placed in the treatment chamber. The carbon block is grounded and an electrode is placed above the block. Nitrogen gas, saturated with aluminum isopropoxide at 145° C. is allowed to flow through the chamber between the electrode and the carbon block at a pressure of 0.1 torr. An electric field of 3000 v./cm. at 60 Hz. is then applied between the grounded block and the electrode for a period of 60 minutes. Thereafter the gem stone is removed from the chamber and is found to have a coating of 5 microns in thickness with a hardness value of 8.0 on the Mohs' scale.

While the particular embodiments of this invention are shown above, it will be understood that the invention is

obviously subject to variations and modifications without departing from its broader aspects.

What is claimed is:

1. A method for uniformly applying a hard protective coating to a natural or synthetic gem stone which comprises:
   (a) generating a gas inert to said natural or synthetic gem stone, which gas contains substantial amounts of a vaporizable substituted hydroxy-containing aluminum compound;
   (b) contacting the surface of said natural or synthetic gem stones with said gas at a temperature of from 250° to about 1000° C. for a period sufficient to form a coating on said gem stone of from 0.1 to about 10.0 microns in thickness;
   (c) heating said coated gem stone at a temperature of from 800° to about 1400° C. for a period of from 30 to about 200 minutes; and
   (d) cooling said coated gem stone to room temperature.

2. The method of claim 1 wherein said gem stone is rutile.

3. The method of claim 1 wherein said gem stone is strontium titanate.

4. The method of claim 1 wherein said gem stone is topaz.

5. The method of claim 1 wherein said aluminum compound is an aluminum alcoholate.

6. The method of claim 5 wherein said aluminum alcoholate is aluminum isopropylate.

7. The method of claim 5 wherein said aluminum alcoholate is aluminum ethylate.

8. The method of claim 5 wherein said aluminum alcoholate is aluminum n-butylate.

9. The method of claim 5 wherein said coated gem stone is cooled slowly to about 400° C.

10. The method of applying a hard protective coating to a natural or synthetic gem stone which comprises:
   (a) generating a gas inert to said gem stone, which gas contains a substantial amount of a decomposible silicon containing compound;

   (b) contacting the surface of said gem stone with said gas at a temperature of from 250° to about 1000° C. for a period sufficient to form a silica coating on said gem stone of from about 0.001 to about 1.0 microns in thickness;
   (c) contacting the surface of said coated gem stone at a temperature of from 250° to about 1000° C. with a gas inert to said gem stone, which gas contains substantial amounts of a vaporizable aluminum alcoholate for a period sufficient to form a coating on said gem stone of from about 0.1 to about 10.0 microns in thickness;
   (d) heating said coated gem stone at a temperature of from 800° to about 1400° C. for a period of from 30 to about 200 minutes; and
   (e) cooling said coated gem stone to room temperature.

11. The method of claim 10 wherein said gem stone is strontium titanate.

12. The method of claim 10 wherein said gem stone is rutile.

13. The method of claim 10 wherein said gem stone is topaz.

14. The method of claim 10 wherein said silicon-containing compound is tetraethylsilicate.

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