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Color Lightening Chemical Treatments for the Improvement of the Deep Red Colored Ruby Stones' Quality

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Abstract: Corundum mineral species include rubies and sapphires. The mineral corundum is a natural gemstone mined from earth, and is colorless in its purest form. Variations of its color can be caused by trace elements that become part of the mineral crystal structure. Ruby is a crystalline form of aluminum oxide (Al_2O_3) in a closed packed hexagonal structure and is a well-known corundum. Ruby is pink-red to blood red colored gemstone, and its color arises from chromium impurities. The color is determined by three criteria, saturation, tone and hue. The price and quality of the rubies is determined by its clarity, color, size, with the color being the most important factor in determining its grade. The objective of this work is to increase the quality of the red ruby stones by reducing their deep red color after the chemical treatment of the ruby ores. The current treatment involves the usage of hydrofluoric acid, borax, and the heating of the ruby ores at temperatures that exceeded 1300°C. The lead glass treatment of the stones should involve the usage of a stronger lightening agent to minimize the lightening process time, the treatment should also involve the usage of a colorful and suitable metal oxide to increase the stones' quality instead of the white borax, and the heating temperature of the stones should not exceed 900C to prevent the deepening of the color of the stones and to prevent the color from reverting to the original deep red color before the chemical lightening diffusion treatment.

Keywords: Chemical Treatment, Red Rubies, Increase Stone Quality, Lead Glass Treatment, Stone Color Lightening

1. Introduction

Sunil Jewelers, a jewelry store, located in India purchase their rubies by importing them from Bangkok, Thailand, and the mine is located in Tanzania Africa. They are looking to improve the quality of their red rubies by possibly lightening the deep red color of the rubies caused after the chemical treatment of the red ruby ores. Their lead glass chemical treatment included immersing the red ruby ores in 60% hydrofluoric acid for two days, rinsing them with tap water, drying them in an over at 40 C oven for two hours, then mixing 1000g of the treated rubies with 98g borax in 50 ml water and hearing the borax coated red ruby ores for three hours and twenty-five minutes at 650 C oven, then cooling them and mixing with an additional 15g of solid borax and 50 ml of water, and then heating them for eight hours and forty-five minutes at a temperature of 1349°C.

Corundum mineral species include rubies and sapphires. The mineral corundum is a natural gemstone mined from earth, and is colorless in its purest form. Variations of its color can be caused by trace elements that become part of the mineral crystal structure. Rubies red color arise from chromium trace elements, and its color ranges from orange red to violet red. The greater the amount of chromium results in the deeper red color of the rubies. [1]

Ruby is a crystalline form of aluminum oxide (Al_2O_3) in a closed packed hexagonal structure, a rock forming mineral, and is a well-known corundum. Corundum can contain traces of metals, titanium, vanadium, iron, and /or chromium. Ruby is pink-red to blood red colored gemstone, and its color arises from chromium impurities. [2]

The price and quality of the rubies is determined by its clarity, color, size, with the color being the most important

factor in determining its grade. The color is determined by three criteria, saturation, tone and hue. Saturation is the distribution and the evenness of the color: are there lighter and darker patches visible or is it even throughout. The depth of the color is the tone: is it light or dark or in between. The physical color of the rubies is hue: is it pink, red or in between. The biggest price factor for the rubies is its color. The price for the very light and the very dark rubies can be similar. The price of the rubies is determined by all three factors, saturation, tone and hue. The color and the visibility of the rubies is affected by inclusions and fractions formed during the natural growth process of the stones and under years of pressure. Rubies will look dull in color and sparkle if they contain many inclusions, and they will look pinkish or whitish. The color of the rubies become deeper, more even, and brighter as the extent and number of inclusions decrease. The rubies become more valuable when they contain color combinations and when the stones have higher clarity. Standard and basic treatments are used to improve the quality of the rubies. Treatments include oiling, glass filling, dying, bleaching, laser drilling, waxing, irradiating, and heating. Lead filled or glass rubies are temporarily treated to mask inclusions, and it would create structural defects in the long term. Permanent treatment includes heating the rubies to deepen its faded red color. [3]

Many techniques can be used to embellish and enhanced gemstones. The gemstones' worth can increase by using some enhancement techniques. Many methods can be used to enhance the clarity and the color of the gemstones: diffusion treatments, heating, dying and oiling, fracture filling, irradiation, lead glass treatment and bleaching. Diffusion treatments is commonly used for corundum, and it includes heating the stone with the addition of a coloring agent. The added coloring agents diffuse into the stone, they usually enter only a fraction of a millimeter, effectively color the stone, and it's a new treatment that keeps being developed. When the material is heated at high temperatures, the chemicals are allowed to enter the stone as the molecular structure of the material loosens. The chemicals penetrate the surface and near the surface. The diffusion process affects only a shallow layer of the material and is a slow process. Asterism on corundum can be created by diffusion of added titanium creating star rubies and sapphires. The color enhancement by diffusion treatment is permanent as long as the stone isn't scratched away its exterior and as long the color isn't removed by physically polishing the stone. The diffusion treatment must be reported to the consumer under the FTC, Federal Trade Commission guidelines. Some gemstones are permeable as they allow fluids such as waxes, oils and dyes to penetrate and flow through them using the oiling, dying and impregnation technique, opal, turquoise, and emeralds are examples of such gemstones. This oiling and dying process allow the substance, the wax to enter into the pores filling the cracks, make the stone have a glossy finish, enhancing the stone's appearance by reducing effects of cracks scattering the light, and overall makes the stone look more valuable. Dying involves the deepening of the color of the gemstone. Non-porous gemstones must have fissures created within the stone before dying in order to accept the dye using a process called "quench cracking". Naturally porous gemstones don't require this process. Resins, both plastics and natural resins, and oils, cedar oil, palm oil, olive oil and canola oil have been used, and the stones need to be reoiled every 5-10 years because of its drying. It's not recommended washing dishes when wearing rings with porous stones, as dirt can enter the stone and contaminate it changing its color reducing its quality. Fracture filling involves the filling of the fractures with substance with similar optical density as that of the gemstone being enhanced. Fractures in ruby and diamond can be filled using resins, plastics or lead glass. This process increases the value of the gemstone. Changing the color of the gemstone can be done by irradiation, where the stones are irradiated with radioactive substance, nuclear reactors or particles accelerators. Diamonds can be colored by exposing them to radium, a radioactive element. Gemstones such as corundum (sapphire, ruby), pearls, and quartz can change color by using particle accelerator, such as postal mail sterilizer, according to geological institute of America. Not all color changes are permanent, but some stones' color remain permanent. Heating is used to enhance the clarity and the color of most corundum, ruby and sapphire. The elements in the corundum is redistributed by heating the stone, rutile needles (TiO_2) may start to dissolve, and the color of the stone may become more evenly distributed and more intense. The inclusions remain unaltered and recognized if the stone aren't heated. Heat treatment is commonly used to improve the ruby's color, and to remove blue patches, purple tingle, and silk. Heat occurs at temperatures of 1800°C. Lead glass filling became more frequent in recent years, and it includes filling the fractures inside the stone with lead glass to improve its transparency. Lead glass filling treatment includes, pre-polishing the rough stones, cleaning the rough stones with hydrofluoric acid, heating the stones with no fillers at temperatures as high as 1400°C to eradicate the impurities inside the stone, it can be heated at 900°C as the silk would still be intact, and heating the stones a second time in an oven with different chemical additives, solutions and mixtures. The second heating includes dipping the stone into oil and covering it with powder, and heated to temperature of 900°C-1400°C for an hour in an oxidizing atmosphere. The powder transforms into a paste upon heating and fills the fractures. The paste becomes completely transparent after cooling and it improves the stones transparency. The second heating can be repeated several times with different mixtures. [4-7]

Corundum contains thin long crystals rutile inclusions called "silk". These inclusions melt at a temperature below that of the surrounding corundum. Heating the corundum at proper temperatures causes the rutile to be absorbed into the crystal lattice increasing the stones' clarity and hence increasing its quality. [8]

The stones of ruby are heated between 800-2000°C from several minutes to several days in the heat treatment of the stones to enhance and deepen the color of the stones. It's a permanent treatment to reduce inclusions, heal fractures, remove brown tint and for different color zoning. The flux

heat treatment includes adding flux such as borax to the stones while heating to heal fractures and to improve the stones clarity, and it works with reduced heat temperature. It seals the cracks, and increases the stability of the stones. [9]

Bleaching can be used to lighten the color of the gemstone. It can be done using sunlight or bleach. Prolonged exposure to sunlight and/ or the use of bleach causes the color of the gemstone to be lighter. [10, 11]

The lead glass treatment includes, rinsing and clearing the outer surface of the stones to remove impurities that would disturb the treatment, heat treatment of the stones at temperatures 900-1400Cto remove impurities in the fissures and to improve the stones' color, and the stones are then mixed with powder metal oxides and heated to form the glass composition. The powder may contain silica, lead, and metal oxides which also enter the glass composition. There are two well-known types of glass composition, the basic formula, and the popular formula. The basic formula includes the lead rich transparent glass with a heat treatment temperature of 900C, whereas the popular formula includes some metal oxides to optimize the color of the stones and to add the glass composition, the treatment temperature is 1000C, and oil is added to stone before mixing with the powder to completely cover the stones. In both processes the powder coated stones are placed in a crucible and placed in a furnace set at the appropriate temperature at a controlled atmosphere. Precautions have to be used due to the use of lead compounds at high temperatures. The stones can be heated several times with several oxides to attain the desired results achieved. [5]

2. Experimental

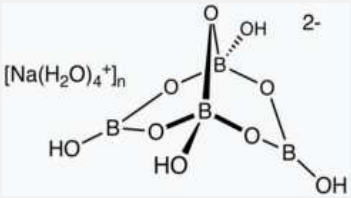
Chemical compounds used in the current lead glass treatment of the ruby ores are listed in table 1. Structures, physical properties, and common uses in various industries are also listed.

Hydrofluoric acid, a chemical compound with formula HF. It is a weak corrosive acid in aqueous medium. It's commonly used in the making of refrigerants, herbicides, aluminium, pharmaceuticals, and plastics.

Borax, a chemical compound with the formula $Na_2H_20B_4O_{17}$. It's a colorless water soluble solid that has applications in chemical laboratories, households, and it has some industrial applications as a buffering agent, pharmaceutical alkalizer, preservative against wood fungus and in artificial aging of wood. It is also used as an ingredient in beauty products, lotions, toothpastes, acne products, mouthwashes.

Ruby, is a deep red solid stone made of trigonal crystals of repeating Units of Al_2O_3:Cr. It's used in the jewellery industry, and it is also used in the making of watches and some medical instruments.

Table 1. *Chemical Compounds used in the current chemical treatment of the ruby ores.*

Chemical Name	Molecular Formula	Structure	Physical Properties	Common Uses
Hydrofluoric Acid [12-17]	HF	H-F	Colorless, highly corrosive liquid, and a weak acid in aqueous solutions.	Synthesis of Inorganic and organofluoride compounds, semiconductor industry, and oil refinery. It's also used in the making of herbicides, refrigerants, aluminium, plastics, and pharmaceuticals.
Borax [18-21]	Na2H20B4O17		Colorless water soluble solid.	Has household, chemical laboratory, and some industrial applications; artificial aging of wood, pharmaceutical alkalizer, buffering agent, pesticide, preservative against wood fungus. Borax is also used as an ingredient in lotions, toothpastes, acne products, mouthwashes, herbicides, ceramic glaze, and paints.
Ruby [2, 22, 23]		Trigonal crystals of repeating Units of Al2O3:Cr	Pink red to deep red solid stones.	Used in the jewelery industry, and it is also used in the making of medical instruments, and watches.

3. Discussion

The current lead glass treatment includes two steps, after the rinsing and the drying of the stones in a 40C furnace. The two-step process are a chemical diffusion treatment and a fracture filling glass flux treatment with borax. The chemical diffusion treatment is a very long process that requires labor, it involves immersing the rinsed dried stones in a 60% solution of hydrofluoric acid for two days. It's also a process of lightening of the deep red color and the degrading of the ruby stones into smaller stones. It's recommended the use of a stronger lightening agent such as bleach or a stronger acid to minimize the time consumed in this chemical diffusion lightening treatment of the stones. The amount of time for the diffusion treatment is dependent on the color shade desired.

The fracture filling of the glass flux treatment involved the mixing of the stones with water moistened borax, heating the mixture in a crucible for three hours and twenty-five minutes at 650 C oven, the cooling followed by adding additional water moistened borax and then heating them for eight hours and forty-five minutes at a temperature of 1349c°. Borax is a white solid and doesn't add any color to the pale outer surface of the stone after the lightening chemical treatment of the

stones. It's recommended the use of a colorful metal oxide: pale yellow potassium oxide or heavy yellow bismuth oxide or yellow-orange cesium oxide, in the flux treatment of the stones to add color to its pale outer surface to improve the quality of the treated stones. Bismuth oxide is a well-known chemical compound used in glass, ceramics and porcelain pigment. Also, it's not recommended heating the stones at temperature over 900C as it only deepens the color of the chemically treated stones, and it reverts the lightening diffusion treatment results of the first diffusion treatment step. Heating the stones at a temperature that doesn't exceed 900C would suffice to break the silk, causing the stones to be clearer, and increasing its quality without the deepening its color.

4. Conclusion

The lead glass treatment of the stones should involve the usage of a stronger lightening agent to minimize the lightening process time, it should involve the usage of a colorful and suitable metal oxide to increase the stones' quality, and the heating temperature of the stones should not exceed 900C to prevent the deepening of the color of the stones and to prevent the color from reverting to the original deep red color before the chemical lightening diffusion treatment.

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Conflicts of Interest

The authors declare no conflicts of interest.

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