Short Notes on Some Gemstone Treatments

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Introduction

The fact that gemstones are treated is probably as old as the fashioning and cutting of gem materials. Because of this, one can consequently find a very large number of literature references. In this short article only a few gemstone species are dealt with, and only a very limited list of references can be given. Articles on common and new treatments are found regularly in gemmological periodicals. Kurt Nassau's book on "Gemstone Enhancement" (1994) widely covers treatments. Their detection, however, is another story, not featured in this book.

A very important point is how the trade releases its knowledge about treatments performed on stones offered for sale. Not only are consumers interested in a clear designation or disclosure of treatments, trade bodies such as the American Gem Trade Association; the International Confederation of Jewellery, Silverware, Diamonds, Pearls and Stones (CIBJO); and the International Colored Gemstone Association have been trying to get the various requirements of the different dealer groups in line. The SSEF Swiss Gemmological Institute is coming out with a catalogue ("SSEF-Standards and their Applications") of standard test reports with explanations for different cases. We have to address the situation of natural gemstones being natural only in part (e.g. colour is artificial), and consider the extent of treatments (how much it affects a given stone).

The objective of gemstone treatments is to improve quality, i.e. to enhance the material. Such a step is taken when the natural beauty does not satisfy the trader or the consumer. Different properties can be affected or improved by the treatment:

Objectives of Gemstone Treatments

1. Change the type or depth of colour.

2. Improve transparency or purity.

3. Increase mechanical stability or durability.

When presenting the treatment issue one can proceed by dealing with a treatment technique (e.g. heating, irradiation, coating etc.) or following the gemstones (e.g. diamond fracture filled, diamond laser drilled, diamond irradiated etc.).

Let us first introduce a few treatment techniques, and later explain the situation for a few gemstones. It is clear that gemstone treatment is a commercial topic, whereas the detection of treatment is a special gemmological task. We are investing a lot of time and money in education about and the identification of gemstone treatments. For a sufficiently safe treatment identification

we need at least some, or better all, of the following analytical instruments: binocular microscope with different light settings, UV-VIS spectrophotometer, FTIR spectrometer, Geiger counter, γ-spectrometer, heat probe, and Raman system.

Treatment Techniques

The most frequently applied methods for gemstone treatments are:

• surface coating (e.g. vapour deposit, hydrothermal overgrowth)

• foilbacking (painting, mirroring or backcovering)

• impregnation with colourless organic substances (e.g. paraffin, epoxy)

• fissure filling with colourless organic substances (e.g. paraffin, epoxy, Bi compounds)

• impregnation with dyes (using natural fissures, or creating new ones)

• laser drilling (and subsequent dissolution of inclusion minerals)

• irradiation (electrons, γ radiation)

• bombardment (neutrons, α-radiation)

• heating (in controlled atmosphere)

• heating with protective or flux-like substances (kryolite, borax)

• diffusion treatment (heating and adding chromophore trace elements)

A few literature references for specific gemstone treatments are Ashbaugh, 1988; Schmetzer, 1987; Themelis, 1992; Nassau, 1994.

Diamonds

From the 4 Cs of a diamond, carat and cut can be changed by repolishing the stone.

Colour and to some extent clarity, however, are intrinsic properties which can only be changed by treatments which are considered as ethically not acceptable, especially when not disclosed properly.

Colour treatment could mean masking colour, e.g. by coating with a coloured substance of the complementary colour. Adding colour to increase a pre-existing tone could be done by irradiation (artificial blue) or bombardment (green), which is frequently followed by annealing (green transforms to yellow or brown). The reaction of a diamond to a specific irradiation depends on the precise type of diamond. Type Ia diamonds turn green first and then yellow after heating, whereas type Ib diamonds turn rose to pink or purple. The situation with artificial colour treatment can be rather complex, and the resulting colour hard to predict when a crystal is composed of zones with different behaviours. The identification of natural or artificial colouration is a delicate matter that requires a thorough study of the VIS-NIR spectrum, taken under liquid nitrogen conditions (usually $-120°C$) and infra-red spectroscopy. In some lucky cases the necessary absorption lines (e.g. 594 nm) are visible in the table spectroscope. Difficulties with green diamonds are due to the fact that the green irradiation colour can occur in nature as well as after artificial irradiation. The effect is the same.

Clarity treatment comprises fissure filling and laser drilling. Fissure filling with highly refractive substances (bismuth or lead compounds) is commercially offered (by Yehuda, Koss, Goldman etc.). The observation is rather easy: colour flashes and

trapped gas bubbles in the fissure planes are visible under the microscope (figure 1). Identification of fillings can also be done with x-ray pictures or chemical tests. Where laser drilling is applied, the straight drill holes are easily visible. They usually end at inclusions or large fissures. Natural narrow channels have also been observed; they are generally angular and do not end with inclusions. As a literature reference, consult Kammerling et. al. (1994)

Ruby Heat Treatment

The main treatments applied to ruby are heat under controlled atmosphere or a protective melt on its surface. Heat alone can transform a stone with purple or brown hues to a more pure red. Where oxidation or reduction of the iron provides the colour transition, temperatures typically between 1,200°C and 1,800°C are involved (Nassau, 1981; Themelis, 1992; Hughes, 1997). Under such high temperature conditions, inclusions are damaged or even dissolved, a fact that allows us to identify thermal treatment by microscopic investigation. With turbid stones the dissolution of rutile silk by heat treatment usually improves the clarity of rubies.

Heat Treatment with Foreign Substances

During the same heat treatment, fissures and fractures can become healed when a flux-like substance is added to the stone. Borates or fluorides, such as borax or cryolite, are used for such measures. The molten compound flows over the surface of the stone and is drawn into the openings by capillarity.

It is important to understand the very important effect such artificial healing has on

Figure 1. Cleavage planes and fissures in this brilliant-cut diamond show a slightly milky appearance together with multicoloured flashes. Tiny gas bubbles are also an indication of the artificial foreign substance used for enhancement. (40x)
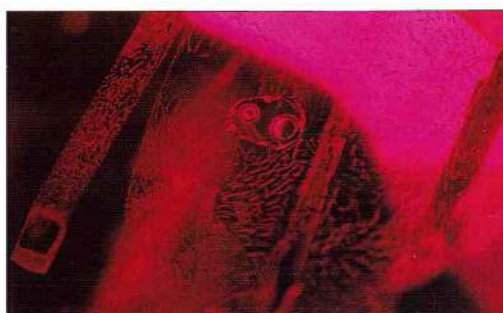

Figure 2. Artificially healed fissures in a Thai ruby. Tubes and droplets of residual melt (usually a boratic glass) define the extension of former fissures. In the larger cavity, several gas bubbles are visible. (60x)

the stones. Whereas formerly, rough stones had been knocked and cleaned and then bruted, today a large volume of rough stones are heated before this process. The result is that the pores and fissures have been soaked by the glassy melt, and the melt remains deep in the former fissures (figure 2). The fissure planes are recrystallised and now show the same "fingerprint" patterns as stones with naturally healed fissures. The newly developed portions of ruby or walls in the fissure plane may be called synthetic ruby since they are produced by human intervention. The dif-

ference, however, is that the artificially healed stones contain foreign residual material from the "flux" used. This material can be called glass or glassy since it has a similar composition to borate glass. It is usually an amorphous borosilicate. It sometimes happens that within the residual glassy droplets in the fissures, crystallisation of radiating fibres takes place. The glass thus partially devitrifies, and in a great deal of heat and glass-treated stones we can recognise whitish arrays of such formations. The centres of the arrays usually contain

a spherical void (figure 3). Diagram 1 explains the progressive steps that a ruby may go through during heat treatment with a glassy melt.

When the glassy substance is on the surface of a stone, it can be dissolved with hydrofluoric acid (HF). It is, however, not possible to remove the glassy substance out of the spaces behind the newly formed ruby walls since HF does not dissolve corundum.
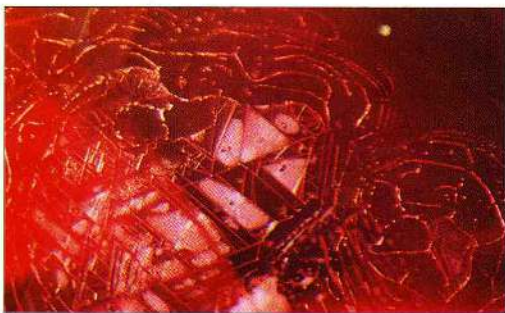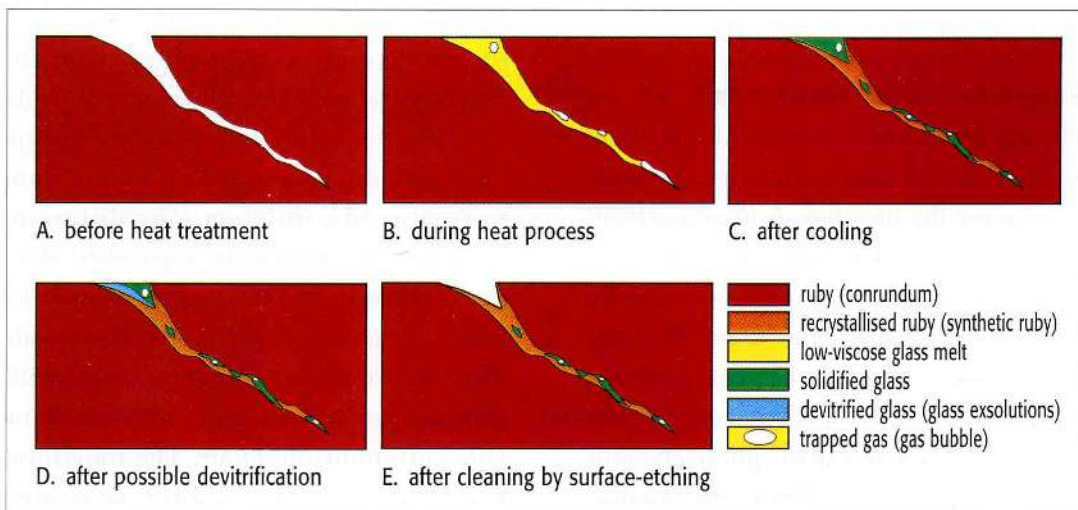
The standards of gemmological laboratories

Figure 3. Artificially healed fissures in a Burmese ruby. The previously glassy substance has been transformed into bunches of radiating fibres (crystals), an effect known as "devitrification". (60x)

Figure 4. Natural corundum with an artificial red colouration. The deposition of red dye follows the irregular fracture planes. (2.5x)

A. before heat treatment

B. during heat process

C. after cooling

D. after possible devitrification

E. after cleaning by surface-etching

ruby (conrundum)
recrystallised ruby (synthetic ruby)
low-viscose glass melt
solidified glass
devitrified glass (glass exsolutions)
trapped gas (gas bubble)

Diagram 1. Artificial fracture filling related to ruby heat treatment.

come into play in how they express the situation where more or less of the foreign material is present in a stone. The most recent standards of SSEF Swiss Gemmological Institute include disclosure of heat treatments and artificial glassy residuals on ruby test reports.

Numerous papers have previously dealt with rubies containing glass-like substances, among them Kane, 1984; Scarratt et al. 1984; Themelis, 1992.

Stained Fissures

Open fractures in light-coloured corundum are sometimes stained red or blue. Necklaces and faceted stones of such material are described e.g. by Schmetzer et al., 1992 (figure 4). Real ruby glows red in ultraviolet (UV) radiation due to its chromium content. We have seen star "rubies" without red UV reaction. Such stones may owe their colour entirely to the infilled dye. They have to be named red-treated corundum, not treated ruby, because they do not contain chromium. Fissures may also be created artificially by quenching, as is sometimes done with quartz (imitations of ruby or emerald), with the dye applied after the quenching.

Sapphire Heat Treatment

The most important treatment carried out on sapphires is heat treatment to produce or increase the blue colour (Nassau, 1981; Emmett et al., 1993). This is possible where the necessary trace elements (Fe and Ti) are already present in the stone. This usually occurs in the form of rutile (TiO_2) as dust or needles. When the needles are dissolved in a reductive atmosphere at a temperature higher than 1,400°C, the titanium is released from the former inclusions and is able to form with divalent iron the necessary Fe/Ti pairs, which are responsible for the blue colour of metamorphic sapphires. The dissolved rutile needles leave traces of dotted lines, and inclusions may decompose and form white "snowballs", as visible in darkfield illumination under the microscope (figure 5).

The short travelling distance of the released titanium is sometimes visible through the internal blue diffusion clouds formed around the former rutile particles.

Other heating conditions are required to create potential asterism, i.e. the formation of rutile. This, of course, goes on at the expense of the blue colour: titanium either in inclusions or as a colour-giving trace element. The heat treatment for creating yellow sapphires is addressed below.

Diffusion Treatment

Where a stone does not contain the necessary chromophore traces, they might be added from outside. Iron and titanium distributed on the surface of a colourless sapphire may travel into the stone when high temperatures are provided for a longer period. The diffusion into the surface of the cut stone gives the sapphire a blue surface colouration. Such diffusion treatments are quite frequently applied to blue corundum, but also performed with chromium to create red corundum. The diffusion-treated stones have to be repolished after the treatment, and this action takes away much of the blue in the facets. The colour distribution is very unhomogeneous and confined to the faceting. Facet edges show concentrations of colour. The unnatural feature is obvious when diffusion-treated corundums are observed under low magni-

fication with transmitted light on a milky glass disc (Figure 6).

Yellow Sapphires

Heat-treated yellow sapphires with stable colour are quite common. The stones exhibit classic heat treatment features such as neo-tension fissures around inclusions, dotted traces along former rutile needles, and "orange skin" on natural surfaces.

Yellow sapphires with irradiated colour are rather rarely encountered. The stability is not guaranteed, and fading under UV radiation or in sunlight is expected. There are, however, various types of yellow sapphires and their identification is not easy (Nassau, 1987).

Emerald Fissure Treatment

The treatment of fissures with organic substances, such as resins, oils or fats, in order to enhance the appearance of the stones has probably been performed for centuries. The infilled substances possess a refractive index similar to that of the stones, and they are able to considerably reduce the visibility of the previously air-filled fissure planes. Today there are a large number of oily to resinous substances, including natural products as well as materials from synthetic production (Hänni, 1992).

Whereas natural resin, oils and waxes were exclusively used in the past, synthetic resins are probably the fillers mostly used today (Themelis, 1990; Kammerling et.al., 1991). They stay longer in the fractures due to their sticky consistence compared to oil which is easily removed with a solvent or detergent. Artificial resins appear under different trade names (e.g. Opticon, Palm

Oil, Epon 828). They may be suspected in an emerald when yellow or purple flashes appear with magnification (Figure 7).

Not everybody from the trade, however, is happy with applications of artificial resins since their durability and optical aspect or possible change upon ageing is not yet clear. Also, the removal of artificial resins from fractures is difficult to almost impossible, in contrast to the traditional oil which is easy to remove or replace.

Among the synthetic resins, bisphenole A resins (sold under trade names such as Epon 828, Opticon, Palma or Palm Oil), styrolised polyisobutylenes (e.g. Emfil) or unsaturated aliphatic polyesters (e.g. LV 15) are encountered as emerald fillers. The application of synthetic resins is frequently called "oiling" the stones, a practice which creates difficulties and should be avoided.

The identification of colourless fillers in fractures is an important task which could prevent a later shock, e.g. when the epoxy turns white after a couple of years. Infrared spectroscopy has been the standard method so far for the identification of organic foreign substances in gemstones. The small amount of substances in the fractures and the relative intransparence of emerald to the infrared radiation is, however, a restriction which frequently inhibits an identification. Another method used as a complementary technique is practiced by a few gemmological laboratories: Raman spectroscopy. The Raman system includes a microscope as a targeting device, a laser source and a special spectrometer system for measuring the Raman signals. The sample spectra are always compared with reference spectra of expected materials.
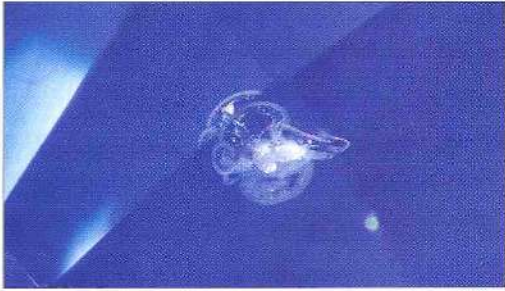
Figure 5. Heat treated sapphire with a decomposed mineral (probably zircon), surrounded by partly healed tension fissures. (60x)
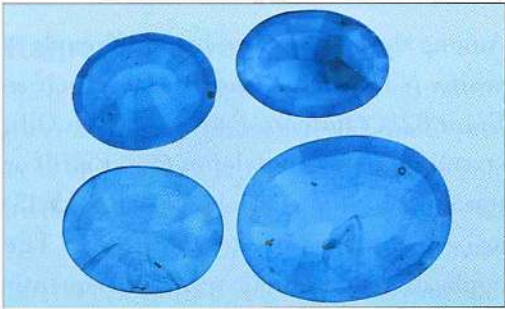

Figure 6. Four diffusion-treated blue sapphires. The artificial colouration along the surface is due to chemical constituents that cause colour when incorporated into the crystal. The effect of the diffusion becomes evident after repolishing: the facets show different grades of blue, and the colour is concentrated in corners and edges.

The characteristic peak areas for organic fillers are found between 1,300 and 1,700 cm^{-1} and 2,800 and 3,200 cm^{-1} (Chalain et al., 1998).

Jade

Jadeite jade is a polycrystalline material, i.e. composed of a multitude of crystals of predominantly the same mineral (mono-mineralic rock). The grain boundaries with fresh material are extremely narrow so that the porosity of the rock is at a minimum. Untreated jadeite is sometimes called A jade. With weathered boulders, however, the outer rim of a jadeite boulder is attacked and the grain boundaries are more

open, leaving space for the introduction of water or iron oxide deposits. Such foreign deposits may ruin the good colour of some material. The cleaning out of iron-spoiled material has been widely performed for several years, followed by a impregnation of the porous material (Figure 8). The filling substances commonly used are colourless epoxy resin and paraffin or wax. The material is then called B jade. Identification with FTIR spectrometry is a routine procedure, and the spectral area of 2700 to 3200 cm^{-1} is analysed in order to show the molecular characteristics of the organic substances.

Figure 7. Orange and purplish flashes indicate the presence of artificial resin in this treated emerald. The identification of this observation needs instrumental confirmation e.g. by FTIR or Raman spectrometry. (60x)
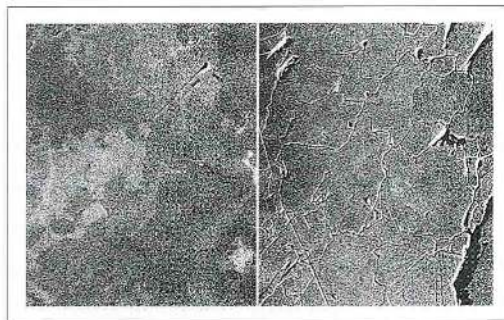

Figure 8. Comparison of compact jadeite (left) and bleached jadeite (right). The granular interlocking in the compact stone is very tight. The looser interlocking in the bleached rock easily allows the introduction of epoxy or wax.

When the filler substance is coloured it may give the stone a better colour. Such treated jades are called C jade. This treatment is usually visible with magnification by the network of colour concentrations along the grain boundaries. Various papers have appeared on the topic of treated jade, among them (Fritsch et al., 1992; Tan et al., 1995).

Topaz

Yellow and orange topaz are probably the better known gemstone varieties among the natural colours. Heating orange material destroys the yellow colour component and ends up as a rose colour. There are, however, natural pink topazes, too.

Colourless topaz is very plentiful but the mineral is only in demand when there is an attractive colour (Figure 9). During the last 10 years an enormous amount of treated blue topaz has reached the market. Light blue material occurs in nature, but darker saturations are produced artificially (Nassau, 1985). Some topazes have potential blue that becomes visible after a γ irradiation (e.g. by a ^{60}Co source) or irradiation with an electron beam (linear accel-

Figure 9. Two natural topaz crystals where the colourless one shows its original colour (left). The blue crystal has a treated colour (right) due to irradiation. Length of the crystals is approximately 2 cm.

erator). Where the potential colour centres are not sufficient for a pleasant blue, bombarding with neutrons creates the colour. The final depth of colour is governed by the strength and duration of the bombarding. The primary brown colour has to be heated gently and turns blue. The depth of blue depends on the dose of treatment. Various treatment routines are commercially applied, producing blue tones with commercial names (e.g. London blue, Swiss blue). Bombarding with neutrons creates radioactivity, and the treated topazes are more or less radioactive. They have to be kept in shielded containers to "cool down". The degree of radioactivity (and thus the time to be kept in a safe) depends on the trace elements, such as ^{46}Sc or ^{182}Ta in the stones, which typically vary from deposit to deposit. In many countries national health authorities give threshold values for radiating materials and customs officers check treated topazes for residual radioactivity.

In the trade and especially in jewellery shops, treated topaz has to be disclosed as does any stone that owes its colour to irradiation or bombardment (see e.g. CIBJO rules 1997). The identification of treated topaz is not easy and not possible without sufficient equipment. The identification methods are γ-spectrometry, thermoluminescence spectrometry or polarised absorption spectrometry. Suggested further reading, e.g. Nassau, 1985; Schmetzer 1987, Hügi 1993. ∎

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