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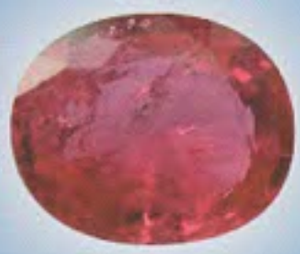

GLASS-FILLED RUBY FROM BANGKOK

- MEASURING DISPERSION ON THE REFRACTOMETER
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GLASS-FILLED RUBIES

CLARITY-ENHANCED RUBIES WITH GLASS-FORMING ADDITIVES

Ted Themelis, Bangkok
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ABSTRACT

This paper described the filling of fractured rubies with lead, bismuth, tantalum and other oxides-additives including chromophores. In December 2004 a series of experiments were performed at the author's gem treatment lab in Bangkok, using various methodologies practiced commercially in Thailand. The experiments showed that certain combination of metal oxides can effectively fill surface-reaching cavities in rubies at relatively low to mid range temperatures of 900-1300 °C. Starting material consisted of rubies with surface-reaching cracks. After treatment, the cracks were filled with the clarity and overall appearance of these rubies being considerably improved. The structure of most of these fillers is amorphous, thus these rubies may be referred to as *glass-filled rubies*. In Thailand these treated rubies are known as ruby-star or by their alternative name *pao-mai*, meaning *new burn* in the Thai language. This treatment is easily identified with a gemmological microscope; where characteristic inclusions such as the 'flash-effect', irregular-shaped reflective platelets/voids, 'frosted' areas, gas 'bubbles' and other features are observed. Stability and durability of the glass-filled rubies may be somewhat affected due to recutting and polishing and jewellery repairs. Disclosure of this treatment is mandatory, and their selling price in the market is relatively low.

BACKGROUND

Successful filling of surface-reaching fractures and other surface-related clarity imperfections in diamonds was first reported by Zvi Yehuda, an Israeli diamond cutter, in 1982. The exact nature of the filler is unknown and the process is often used following laser drilling. In the late 1980's and early 1990's several firms started providing similar service to the diamond industry, and they continue to do so today. These filled diamonds are marketed as *clarity enhanced diamonds*.

Several international patents have been issued. For example, US patent No. 2.853.393 of 23rd September 1957, titled 'High-index glass elements', which is assigned to the Minnesota Mining & Manufacturing Company, described the composition of glassy fillers that consisted of bismuth oxide, lead oxide and many other compounds. European patent EP 1 069 087 A1, titled 'Glass composition and method for filling microcavities in natural minerals' that was awarded to Rene De Keyzer of Belgium) on 17th January 2001 is the most important reference for it outlines the various compounds used in the glass infilling process for gem materials.

The glass-filled rubies were first encountered in Chanthaburi (Thailand) in the late-1990s. The filling process, which incorporated fluxes and other additives, was applied mostly to M?ng-Hsu rubies. Limited quantities of these glass-filled rubies have since appeared sporadically in the market and have originated from Thailand. In 2002 more glass-filled rubies appeared in the market. Since mid-2004, considerable quantities of large and better quality glass-filled rubies have flooded the international gem markets. In March 2004, a lab alert was issued by the Gemmological Association of All Japan (GAAJ), followed by similar alerts from other labs, including the Asian Institute of Gemmological Sciences (AIGS). Today, nearly all glass-filled rubies in the market are processed by the Thais treaters. In Thailand, the glass-filling process is known as *pao-mai* (meaning new-burn in the Thai language) or by its alternative name *ruby-star*.

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Fig. 1. Glass filled ruby of 1.24 ct processed by the author in December 2004.

THE PRODUCT (Figs. 1 & 2).

Currently, the filling process is applied mostly to low-medium commercial grades of rubies with surface-reaching fractures and cavities. The process aims to replace the liquid and air residing in the fissures and microcavities of the untreated rubies with metal oxides in order to reduce their visibility and so improve the clarity of the stone. Glass-filled rubies are currently available in the market in any shape, and various sizes, some of them weighing more than 120 carats.

TECHNIQUE OF TREATMENT

Step 1: Selection of the starting material

Many types rubies with surface-reaching fractures are suitable for treatment. At this time the most cost-effective treatment is performed on rubies from Antilamena (Madagascar) (Fig. 3). *Mica-type* and *junk-type* rubies from Tanzania, Kenya and elsewhere are also suitable for the process, although the results vary considerably.

Fig. 3. Rubies from Antilamena (Madagascar) are most suitable for this treatment.

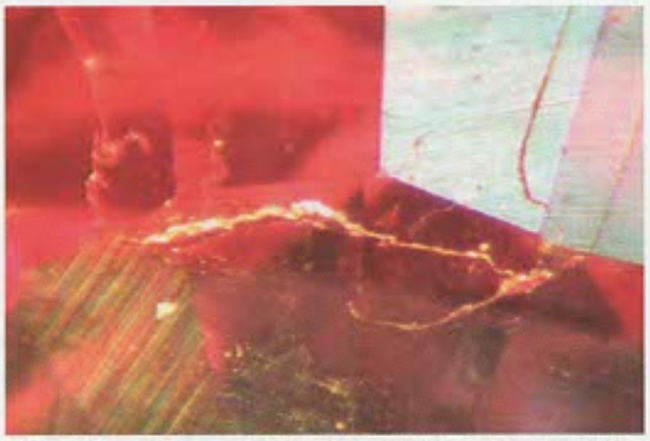

Fig. 2. Surface-reaching fractures in a ruby filled with a glass of lead oxide and other additives. 15x.

Step 2: Preparation of the rubies prior to treatment

Suitable rough rubies are trimmed and performed to yield the most suitable shape in order to remove unwanted foreign substances that could interfere with the subsequent heat treatment process.

Step 3: Selection of additives

Selected metal oxides such as lead oxide (PbO), bismuth oxide (Bi_2O_3), tantalum oxide (Ta_2O_5), totalling at least 90% wt. may be used in the process (Fig. 4). In addition, glass-forming oxides, such as boric oxide (B_2O_3), phosphorous pentoxide (P_2O_5) and others may be also used. Often, copper oxide (Cu_2O) and other oxides also may be added in the final mixture. It is noted that an optimal combination of PbO, Bi_2O_3, Ta_2O_5 and other metal oxides, even with the absence of other additives, is capable of forming a glass without divitrification. In Thailand, most commonly used additives are various combinations of lead oxide, silica and borax.

Fig. 4. Lead oxide, tantalum oxide and bismuth oxide are just a few of the chemicals used in this treatment process.

The selected additives are mixed with ionized water to form a slurry solution and applied to the rubies to be treated. These rubies are then placed into ceramic crucibles. As each gem treater possesses their own 'cooking' recipe, quite rightly, further details of the methodology used cannot be revealed. Thus, the chemical composition of the fracture fillers found in the glass-filled rubies varied widely.

Step 4: Selection of heating parameters.

At this time, only electric furnaces are used in this treatment. The heating process is performed, usually in air, or preferably in an oxygen-rich atmosphere. The soaking temperature ranges from 900 °C (M.P. of PbO = 888 °C) to 1250 ° (M.P. of Cu_2O =1230 °C), or even higher to 1500°C if silica is used (M.P. of certain impure SiO_2 = 1525 °C).

The different steps in a typical heat treatment process for glass infilling rubies are illustrated in figure 5.

Step 5: Load the crucibles and perform the heating process.

The crucibles together with their rubies are loaded in an electric resistance box-type, front-door furnace of about one cubic foot heating chambers (See figure 6).

Fig. 6. The author loading a crucible into an electric furnace at Chanthaburi, Thailand.

Typically, four crucibles containing 7,000-8,000 ct in total may be treated in one process. Larger capacity and/or different furnace types are also used capable to treat 4+ kilograms of ruby in one single run.

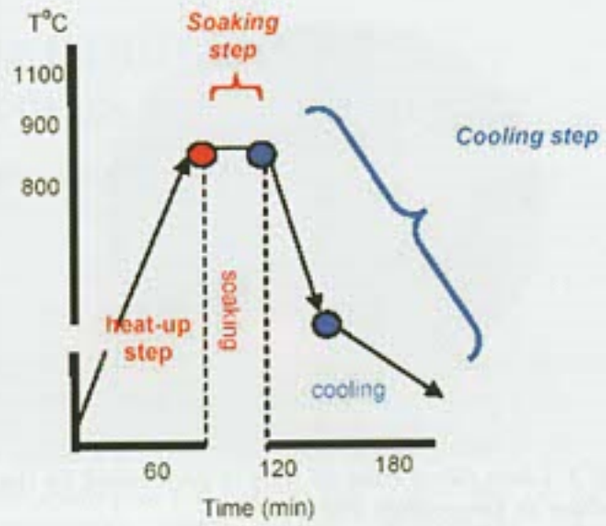

Fig. 5. Typical heat treatment process for glass infilling ruby includes a heat-up step of 60 plus minutes, a soaking step of 15 minutes, and a cooling step of variable length as the crucible may be removed from the furnace at any time after the soaking step.

Pre-treatment & post-treatment features & observations

Figure 7 illustrates rubies before (LHS) and after this (RHS) treatment.

Fig. 7. Glass filled rubies before (LHS) and after (RHS) treatment.

The ceramic crucibles in which the rubies were treated were often discoloured (Fig. 8), but not seriously damaged by the additives used in the heat treatment process.

Fig. 8. Glass filled rubies stuck to the walls of crucibles that have been stained yellow due to diffusion of lead oxide and pink due to diffusion of copper oxide used in the process.

Treated rubies (Fig. 9) were coated with a glassy residue that is always removed in during subsequent faceting and polishing process and, as a consequence, is never observed on the external surface of the treated ruby.

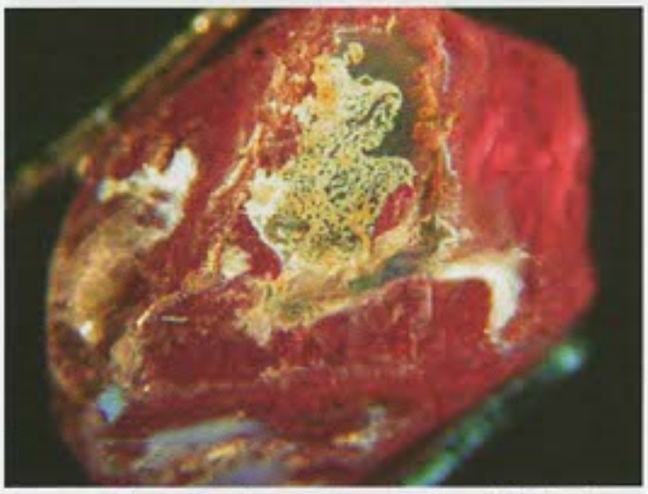

Fig. 9. Glossy residue coating a glass-filled ruby.

Identifying features

Inclusions found in glass-filled rubies (see over pages) that can be used to identify this treatment include:

Characteristic features

- A 'flash' effect from fissures when these are examined in dark-field illumination near parallel to the surface of the glass filled fracture (Fig. 10A). NOTE: The "flash" effect is not always present in the glass filled rubies, due to different type of additives used.
- Reflective platelets and patches within glass filled fractures (Fig. 10B)
- Distinct differences in lustre as the glass exits facets (Fig. 10C)
- 'Tubules', often filled with coloured additives (Fig. 10D)
- Gas 'bubbles' within glass filled fissures (Fig. 10E)
- "Frosted" areas within glass-filled fractures (Fig. 10F)

Other features

- Undistorted "silk" and rutile crystals (Fig. 10G) observed, if the maximum temperature in the heating process was below ~ 1,250 ?C.
- Undistorted solid crystals and mineral inclusions that have a melting point greater than the maximum temperature used in the heating process.
- Colour zoning
- Parting
- Lamellar twinning
- Former 'liquid' inclusions that have been distorted due to heat
- Features that generally characterise heat-treated ruby

Cautionary words

In this paper, use of the term glass does not refer only to glasses formed from silicon oxide (SiO_2). This is a misconception. Although rare, some Thai treaters do not use silica in the glass-filling process. In this paper the term glass refers to any compound that has an amorphous structure that has to be proven by its X-Ray Diffraction pattern or by other means of analytical instrumentation. In this study the amorphous nature of the additives reported has not been verified.

In glass-filled rubies, the 'healing' of the surface-reaching fractures must be further investigated. It is known that when borax-based additives are used in heating M?ng-Hsu rubies at high-temperatures, the so-called solvation process is taken place. In layman's terms, the solvation process simply means that the induced borax-based additives are thermo-chemically reacted with the nutrient emanated from the host corundum and re-crystallized in situ, thus 'closing' the void in the fracture that results in 'healing' of the fracture. Technically, these rubies are considered to be 'partially-synthetic', due to partial re-crystallization of corundum in their 'healed' fractures. However, when 'healing' is observed in the glass-filled rubies, it is not clear whether this 'healing' is due to the solvation process - if, indeed the solvation process takes place at such low temperatures - or to other causes. More research is needed before the answer to this question will be known.

Potential health hazards

The glass-filling process in rubies may pose some potential health hazards to the treater. As a consequence, in all stages of this process, protective gear (suit, eye gear, gloves, respirator mask and other devices) must be used as per US Occupation Safety Health Administration (OSHA) recommendations. No health hazards are pose to the end user and consumer by glass-filled rubies.

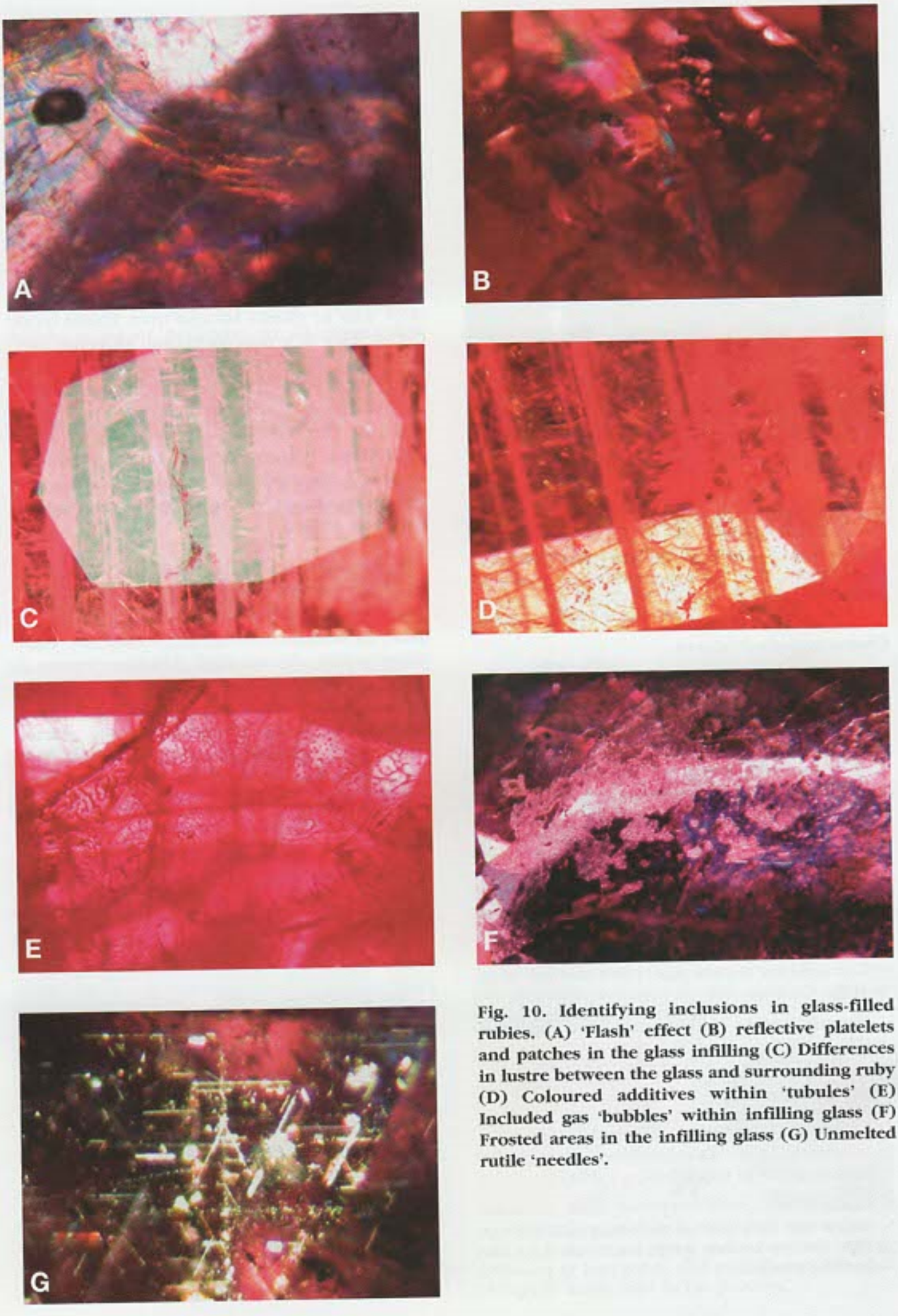

Fig. 10. Identifying inclusions in glass-filled rubies. (A) 'Flash' effect (B) reflective platelets and patches in the glass infilling (C) Differences in lustre between the glass and surrounding ruby (D) Coloured additives within 'tubules' (E) Included gas 'bubbles' within infilling glass (F) Frosted areas in the infilling glass (G) Unmelted rutile 'needles'.

Stability & Durability

The author has conducted several stability-durability tests on glass-filled rubies. These tests revealed:

- No visual damage after the glass-filled rubies were exposed to a 250W mercury lamp for 48 hours.
- No alterations in colour and/or clarity were noted when glass-filled rubies were exposed for several minutes in direct flame of a BIC cigarette lighter.
- No damage was noted when the glass-filled stones were cleaned in an ultrasonic bath.
- Some portion of the surface of the glass-filled rubies may be damaged if the stones are in contact with hydrofluoric acid (HF).
- Glass-filled rubies may be damaged during jewellery repair with a jeweller's torch.
- The surfaces of glass-filled rubies may be damaged by recutting and repolished.

Disclosure

Due to the influence of man, all glass-filled rubies should be disclosed at every level of gem merchandising. Such disclosure must comply with the US-Federal Trade Commission rules or the equivalent in other countries.

These rubies may be disclosed based using the author's general gem classification system of N for Natural and T for Treated. Appropriate prefix/statement, which identifies this specific treatment, also may be included. For example:

Natural ruby, treated (with glass-filled additives), or, Natural ruby, enhanced with glass-filled additives

A blanket statement, such as "All gemstones assumed treated, otherwise stated", should accompany all sales documents.

Conclusions

Glass-filled rubies are a welcome addition in the gem and jewellery industry as long as they are accurately identified and clearly disclosed. The attractive appearance, relatively good stability-durability and low price of these glass-filled rubies offer yet another choice for the consumer. In summary, comparative data for fracture filled gemstones is presented below.

Acknowledgements

My personal thanks to Mr. Mahiton "Kob" Thongdeesuk, Mr.Tamm and other treaters in Chanthaburi who contributed specimens and verified the facts of this article.

Comparative data on fracture-filled gemstones

	Flux-filled rubies	Glass-filled rubies	Glass-filled diamonds	Emerald
Basic composition	Borax + silica + other	Lead + bismuth+ other	Unknown compounds; also lead + bismuth + other	Oil, resin, oleoresin
Treatment	High-temp (to 1800oC)	Low-temp (900-1250oC)	Low-temp (>1000oC)	Low-temp (>150oC)
"Healing crack" feature	Excellent*	To be investigated	NO 'healing	NO 'healing
Stability and durability	Very stable	Somewhat stable	Somewhat stable	Unstable
Identification (10X visual)	Detectable	Detectable	Detectable	Detectable
Disclosure in the market	Treated-rubies	Glass-filled-rubies	Clarity enhanced diamonds	Enhanced emeralds
Price *	US$500-$600/ct*	US$150-200/ct*	30%-40% below RAPPAPORT pricelist	OPEN

*Prices stated above are indicative for comparison purposes only. It means that if a flux-treated ruby costs US$500-$600/ct the same ruby could have cost US$150-$200/ct if is treated with lead additives.

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