Emerald Treatments

Their Effects and How to Recognize Them

Lore Kiefert discusses an age-old gemstone topic

A gemstone's clarity, and therefore, its value, is reduced by the presence of fractures or inclusions. Because of the volatile environments in which emerald forms, they tend to have plenty of both. The crushing forces and fluid actions of metamorphic processes endured by the surrounding rocks have led understandably to fissures in the gem crystals. Should growth continue after damage to the crystals, fractures can be at least partially healed. In cases in which fractures form after the growth phase of the crystal or during mining, these defects no longer have the opportunity to heal naturally.

Treated Since Antiquity

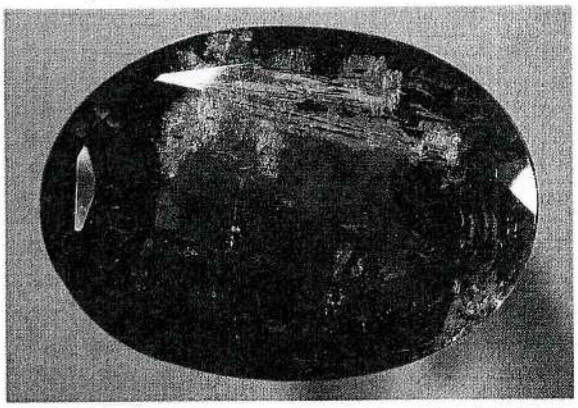
To improve the clarity of emeralds, open fissures may be disguised by impregnating the stones with some more or less permanent substance. The tradition of treating emeralds to improve their clarity has its roots in ancient times when rough and polished emeralds were treated with colorless or green-colored oils. Numerous recipes have been found, such as those by Pliny and in the Stockholm Papyrus, supposedly written in Egypt around 400 B.C.

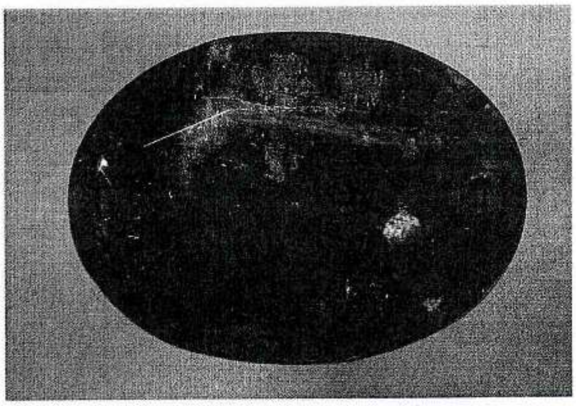
As a rule, emerald treatments are limited to filling fissures with an organic substance whose refractive index is close to that of emerald, making fissures less visible. The use of a colored substance can enhance a pale stone. Because of emerald's chemical composition, heat and irradiation do not improve its color and these techniques are not employed.

For the last twenty years, special equipment has been in use to inject fillers into cracks in stones under vacuum or under vacuous pressure and heat. In this way, even fissures in large stones can be completely filled. In addition to traditional oils, artificial products such as epoxy resins that have no natural counterpart are employed. The refractive properties of these products are much closer than oil to the refractive properties of emerald.

Over the last ten years, the use of these new substances has led to uncertainty in the emerald gemstone market and exports have declined dramatically, especially those from Colombia. In 1995 exports of Colombian emeralds brought 458 million US dollars into the Colombian economy, but by 1997 exports had shrunk to 130 million US dollars (Michelou, 1998). Although the reduction in exports was partially caused by the ongoing recession in Japan, the emerald industry was jolted into dealing with the treatment issue. Today, emeralds treated with epoxy resin are virtually unsalable.

Treatment of fissures with colorless organic substances is regarded by many gemstone dealers as an acceptable practice and according to international commerce rules, does not need to be specifically declared. The trade, however, is becoming more and more desirous of identification of the specific treatment products used. According to the rules of the *Confédération Internationale de la Bijouterie, Joaillerie, Orfèvrerie des Diamants, Perles et Pierres* (CIBJO), emeralds treated with green-colored substances must be la-





Untreated emeralds show pale patches caused by reflection of light from air filled fissures and fractures (above). After treatment with oil these reflections are significantly diminished (below). Photos by H. A. Hänni

Literature for Further Study

"Identification of Filler Substances in Emeralds" a detailed study by Kiefert, Hänni, Chalain and Weber appeared in the Journal of Gemmology 1999 26: 8, 501-520 and is well worth reading.

beled "treated emerald" (CIBJO, 1997).

Emerald Treatments Today

In 1983, Ron Ringsrud first described the process used in Colombia for filling fissures. Ideally it occurs in five steps:

1. Rough stones that have already been oiled are soaked in alcohol or another solvent to remove the oil. For cut stones, abrasives that may have entered open fissures during cutting are also removed at this point.
2. The stones are then cooked in acids (a mixture of HCl and HNO_3) at low temperature in pressurized vessels. Under either pressure or vacuum, the acid bath dissolves the remaining iron oxide in the fissures along with any remnants of chromium oxide from the abrasive. After this step, only acid is left in the cracks.
3. Next, the stones are rinsed with either water or a solvent to remove the acid.
4. They are then put into an oil bath, and after soaking for some time, the oil is emplaced in the cracks under vacuum or a combination of vacuum, pressure and heat.
5. Lastly, excess oil is removed, and the stone is wiped with a cloth.

According to Ringsrud (1983), cedar wood oil and Canada balsam were the impregnating oils of choice in Colombia. They are more viscous than mineral oil or linseed oil and, therefore, are retained better in the fissures. Their refractive indices are 1.515 and 1.520 respectively, close to the refractive index of emerald (1.57-1.58). The light reflected from the fissures almost disappears, and the transparency of the stones is improved.

Epoxy resins, silicone oils, UV-hardening resins and mixtures of various substances are now available. These new substances have refractive indices that are even closer to those of emerald, making cracks less visible than through the use of traditional oils.

A significant problem, however, came to light in the early 1990's, when a substance called *Palm Oil* or *Palm,* actually the epoxy resin *Araldite 6010*, came into use. With a refractive index of 1.57, Palma hides fissures much better than oil, but the resin decomposes over time. In one out of five treated stones, within a few months after application, the dried Palma becomes visible to the unaided eye as a white, milky substance in the fissures. Another epoxy resin with similar properties is manufactured by Shell under the name *Opticon* (*Epon 828*).

If cracks reappear after using oil, the gemstones are cleaned with a solvent and the oil treatment repeated; with artificial products, however, it is difficult to clean and re-treat the stones. Gemological laboratories have been, thus, forced to learn more about the products being used to treat emeralds and to identify the type, composition and quantity of those fillers.

Identification of Fillers

• **Visual:** Observation under a microscope is usually enough to detect filler substances. Even the extent of the treatment and the type of substance used can be, in some cases, detected visually. An important precondition for the observation of filler substances is that the fissure reaches the stone's surface. Light reflected from the surface of a stone often reveals the starting point of a fissure which can be followed into the interior of the stone by transmitted light.

Green oils and artificial resins are sometimes used on very pale stones. Magnified by a microscope or loupe, concentrations of color on fracture surfaces are easily recognizable; colored substances are not, therefore, difficult to identify.

Air bubbles and dendritically dried zones can form on the fracture surfaces of treated stones; these are sure signs of fracture filling with foreign substances. Epoxy resins with refractive indices close to those of emerald often show *flash effects* as the stone is rotated and appear orange, pink or blue. Air bubbles in the resin and flash effects aid in precisely determining the size and position of an artificially filled fissure, this information is important if the stone is to be spectroscopically examined.

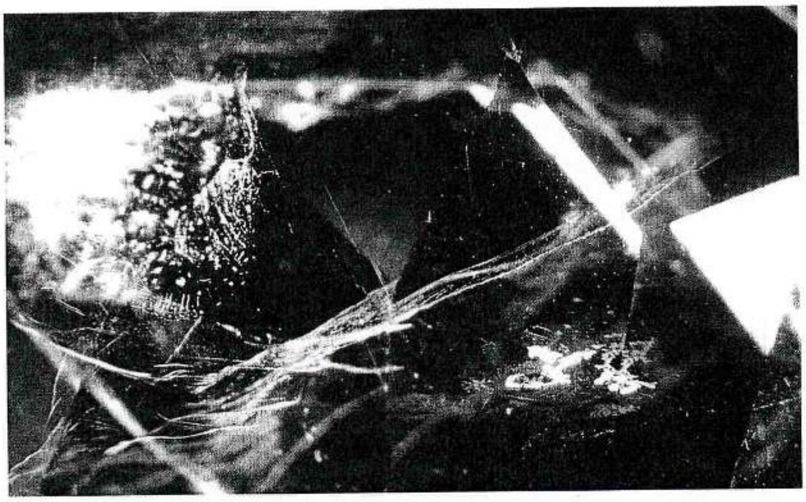
• **UV:** A practical instrument for determining the position and quantity of fissure fillings is a long-wave UV lamp (365 nm). Whereas the emerald itself, depending on its chromium and iron contents, is either inert or fluoresces weakly reddish under long-wave UV light, fillings may fluoresce more or less strongly yellow or white. Unfortunately, not all fissure fillers fluoresce. Ringsrud warns that cedar wood oil from Merck, which is used in Colombia, is inert, while Canada balsam fluoresces yellow. Mineral oil and Johnson's Baby Oil, as used in Sandawana, Zimbabwe, fluoresce weakly yellow. Epoxy resins such as Palma or Opticon fluoresce bright white.

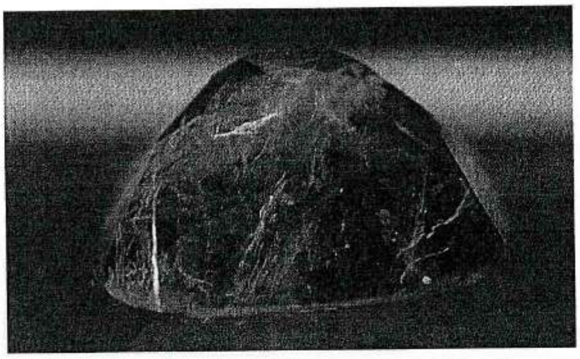
• **Spectroscopy:** The bonds of organic substances vibrate under infrared or Raman wavelengths and can be characterized by spectroscopy. To date, all of the organic substances used on emeralds are commercially available, and their spectra are published. All show characteristic peaks between 400 and 3200 cm^{-1} in their infrared as well as in their Raman spectra. Since the emerald spectrum overlaps that of the fillings, the diagnostic segments are the 2800 to 3200 cm^{-1} region in the infrared and the 1200 to 1800 cm^{-1} region in the Raman spectra. These regions do not suffer interference from emerald absorption; thus, any bands that appear can be assigned to filler substances.

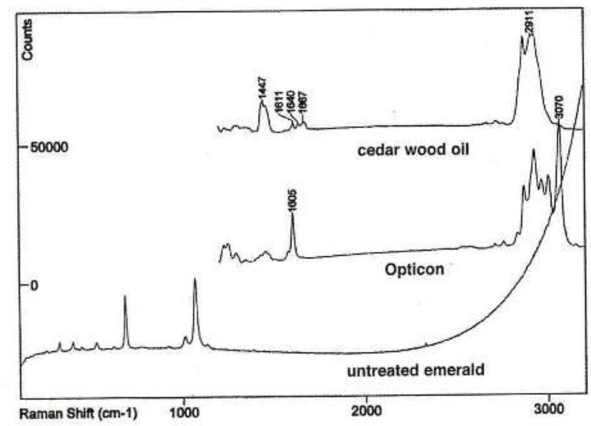
• **FTIR:** Examination by Fourier Transform Infrared Spectrometry is generally not oriented. The position of the fissures is not normally considered and the entire stone is investigated. The advantage to this method is that even internal regions of the stone contribute to verification. The disadvantage is, when only a few filled fissures are present and they lie outside the analyzed region, no signal is received from the substance and fillers remain undetected.

• **Raman Spectrometry with Microscopy:** Raman spectrometers, used in state-of-the-art laboratories, are outfitted with a microscope to precisely locate fissures. A laser beam is directed through the microscope onto the substance used to fill the fracture. Unfortunately when the analyzed substances lie deep in the stone, the results cannot be interpreted with certainty; furthermore, easily altered substances, especially oils, emit bright fluorescence without showing characteristic peaks. The diagram on the right shows the Raman spectra of cedar wood oil (upper curve), Opticon (middle) and the surface of an untreated emerald (lower).

Both FTIR and Raman spectrometry enable differentiation between the most frequently used fillers: oil, cedar wood oil, Canada balsam and epoxy resin. These methods cannot, however, differentiate between Johnson's Baby Oil and sewing machine oil; between Opticon and Palma; or between natural and synthetic cedar oils. As each possesses similar properties (refractive index, solubility, viscosity, etc.), distinguishing between them is usually commercially unnecessary.







Upper:
Orange and pink "flashes" are typical for emeralds filled with epoxy resin, (magnification x20).

Left:
Emeralds with fracture-fillings sometimes exhibit a whitish fluorescence along the fissures under long wave UV. Both photos by Hänni

Diagram:
Raman spectra of cedar wood oil (upper curve), Opticon (middle) and an untreated emerald (lower).

The Outlook

The shock felt by the emerald trade, especially in Colombia, due to the new fracture filling techniques has spurred the development of methods for distinguishing between filler substances.
New filler substances, more permanent than other artificial resins, are currently being tested. *Permasafe*, for example, came on the market in 1998. Particularly interesting are those fillers that can be easily removed. The maker of a filler called *Gematrat*, a mixture of oil and artificial resin, makes this claim. Other companies are focusing on finding methods for dissolving artificial resins like Opticon or Palma.