The emerald fillers

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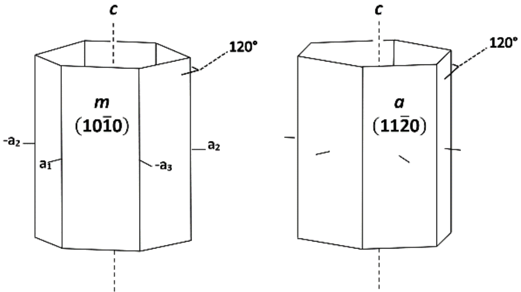
Introduction

Emeralds very frequently show cracks or fractures, in addition to healing glazes and other internal defects. The causes of these fractures are multiple: relaxation of internal stresses (deformations, etc.), and/or pressure and temperature conditions of their geological environment during and after growth, and/or extraction processes (use of explosives, percussion by hand tools, etc.).

The fractures are conchoidal and the emerald shows a difficult and imperfect cleavage along to [0001] (pinacoid, *c*), and more rarely along [$10\bar{1}0$] and [$11\bar{2}0$] (prism faces 1st and 2nd order) (Fig. 1) (Sinkankas, 1981; Adewoye, 1986). These fractures and cleavages are also described as "disbonds" along the faces of the prism, as well as basal fractures in the literature (Chalain *et al.*, 1998). In a cut stone, depending on their size, arrangement and orientation, these cracks will be more or less observable.



1st order prism 2nd order prism

Fig. 1: Diagrams of the 1st and 2nd prism orders. Modified after Sinkankas, 1981.

History

With an (attested) beginning of their extraction, in Egypt (Jebel Zabarah, Wadi Sikait, etc.) at the end of the Ptolemaic[1] period (Harrell, 2004), for almost twenty centuries, people have been trying to hide the frosts and cracks in emeralds (as far as they reach the surface) by impregnating them with various liquids, or at least to reduce their visibility. At the same time, people have also tried to artificially intensify the colour of emeralds by using tinted liquids.

There are a number of old reports describing techniques for improving transparency (Poirot, 1998). Among the best known are the following in the *Naturalis Historia* of Pline the Elder, 73-77 BC, about the Median[2] emeralds "*Those* [the emeralds, NOA] *which are not entirely green at first become more beautiful by the use of wine and oil*" (Littré, 1877), or this rather

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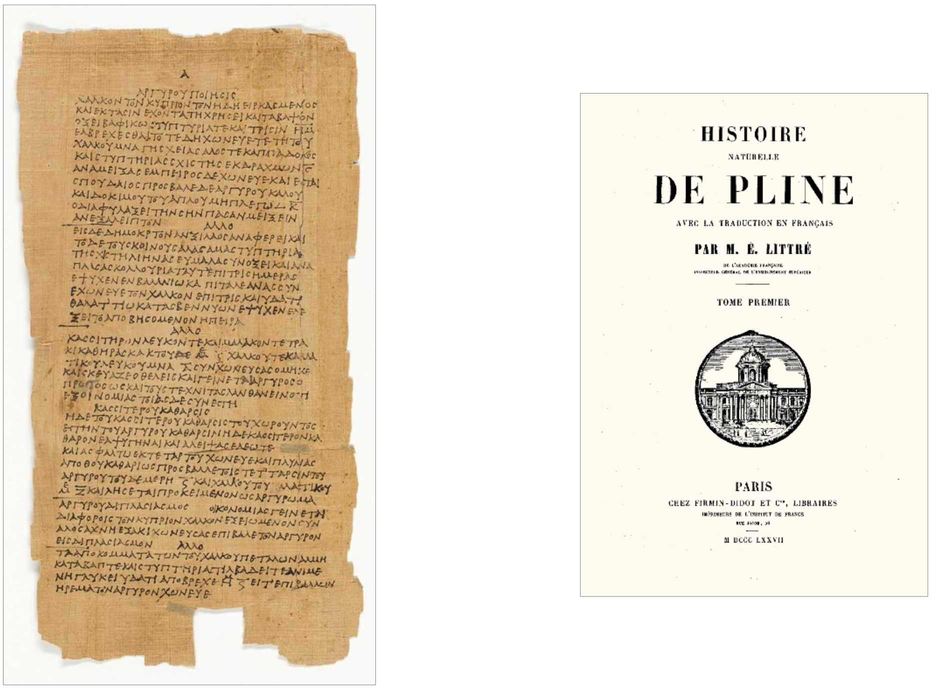
[1] First century BC.

[2] Media: Mede Empire (Mādai), which at its culmination would have extended approximately from the Strait of Hormuz to the Caspian Sea and from northern Afghanistan to the southern Black Sea (controversial).

detailed description in the Stockholm Papyrus[3] (Fig. 2) end IIIrd - middle IVth century BC, "…/ *Take some leeks, squeeze out the juice, mix with the leek juice an equal amount of oil, put in a new jug with the stones* (the emeralds, NOA) *and cook for three days, until they become pleasant to you. Let the stones be in a basket so as not to touch the bottom of the jug.*" (Halleux, 1981).



HISTOIRE
NATURELLE
DE PLINE
AVEC LA TRADUCTION EN FRANÇAIS
PAR M. É. LITTRÉ
DE L'ACADÉMIE FRANÇAISE
INSPECTEUR GÉNÉRAL DE L'ENSEIGNEMENT SUPÉRIEUR

TOME PREMIER

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Fig. 2: On the left, the first page of the Stockholm Papyrus, Source: National Library of Sweden, Shelfmark: Acc 2013/75, olim Dep.45. Right, title page of the first volume of the *Naturalis Historia* by Pliny the Elder, translated in 1877 by E. Littré. Source Gallica, National Library of France.

The aim of filling

A fissure causes an optical discontinuity in a material and can be considered here as a film of air in the gem's mass. However, air has different optical properties from those of emerald, notably a refractive index[4] average of $n = 1.00$, whereas emerald has a variable refractive index of $n = \approx 1.56$ to ≈ 1.60 ($n = 1.560$ to 1.596 and $n = 1.566$ à 1.602) (cf box 1). In gemmology, it is the iron and alkali ion content that has the greatest noticeable influence on the variation of indices (Deer *et al.*, 1992). This difference of index n between air and emerald is the main cause of the visibility of the cracks because it allows a mirror effect on the two faces of the crack.

The filling of cracks with a liquid reduces the refractive index difference in the stone. The closer the index of the liquid is to the index of the stone, the less visible the crack will be, depending on its size, position and orientation. The experiment can be done empirically with water, which easily fills the cracks even if they are thin. Water (^1H_2O), having a refractive index of 1.333 (Weber *et al.*, 2002), reduces the index difference with respect to air sufficiently for an improvement to be observed.

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[3] The quotation is sometimes mistakenly mentioned as being from the Leyden Papyrus. It does appear in the Stockholm Papyrus (*Papyrus Graecus Holmiensis*, end IIIrd century), which would have been discovered in Thebes, probably in the early XIXth century.

[4] All indices shown are collected at 589nm (589.3nm, corresponding to the D_1 et D_2 lines of the sodium spectrum), at room temperature.

BOX 1

Air *n* index

n = 1 (± ≈ 0.0003), depending on the gas mixture (content in CO_2, etc.), pressure, temperature and relative humidity (Stone *et al.*, 2004).

Emerald *n* index variation

The variation in the *n* index of emeralds depends on the nature and amount of trace element substitution present, *id est* Si^{4+} by P^{5+} et B^{3+} in tetrahedral coordination, Al^{3+} par Fe^{3+}, Cr^{3+}, V^{3+}, Sc^{3+}, Ti in octahedral coordination and Be^{2+} by Li^{+} en tetrahedral coordination, compensated by alkali metals (Cerny *et al.*, 1976).

The used substances

As water evaporates quickly, oils were used first, as they had relatively good stability and a higher *n* index than water. The classic organic vegetable oils (peanut, coconut, sesame, etc.), with an index between *n* ≈1.46 and ≈1.48 (Alimentarius, 2009), seem appropriate, but in the end, in the context of the use of emeralds on jewellery, their stability is not sufficient either, as they degrade and their masking effect disappears in a few weeks to months.

Today, cedar oil is preferred because, in its fluid state, has a high average index of $n > 1.50$ (ISO International norm, 2004). It is this last point that made it an immersion liquid in microscopy to improve resolution at high magnifications, until its replacement by synthetic oils.

As far as emeralds are concerned, natural cedar oil has another interest, it exists in a very viscous form[5], which can be situated around $\approx 1.5 \cdot 10^3$ Pa·s at room temperature (≈ 20°C) [6], which substantially increases its stability over time (less evaporation and little leakage).

But this high viscosity makes it difficult to fill cracks, which measure from approximately ≈ 1 to 10 nm thick and of variable length (Célarié, 2004). Moreover, the cracks in the emerald are not straight, sometimes exhibiting very complex morphologies and being interconnected. To compensate for this difficulty, this very viscous oil is used hot (typically ≈ 60-70 °C) to increase its fluidity and is infiltrated with presses at pressures ranging from 0.2 to 1 pascal (200 to 1000 atmospheres). Atmospheric vacuum/pressure systems do not work with viscous oils.

There are several types of cedar oil, from different "cedars"[7], obtained at first by harvesting exudates, scarification of trunks, today by hydrodistillation of wood, sawdust, chips and other wood waste, etc. (Aberchane, 2001). It is commonly said that the most commonly used for filling emerald cracks comes from "Virginia cedar". (*Juniperus virginiana*, Linné, 1753) (Fig. 3). In fact, the genus *Juniperus* contains several taxa and the oils said of *Juniperus virginiana* marketed are often mixtures of several species native to the USA, *Juniperus ashei*, Buchholz, 1930; *Juniperus osteosperma*, (Torr.) Little, 1948; etc., at least for parts.

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[5] The increase in viscosity is accompanied by a slight decrease in refractive index, typically *n* ≈ 1.49.

[6] Pa·s = Pascal.second, or Poiseuille (1 Pa·s = 1 Pl).

[7] The use of the name "cedar" is inappropriate, it is in fact a juniper of the genus *Juniperus*. Its use is a literal translation of the English term "cedar", as English speakers use the same term for many different conifers.

Fig.3 : At left: *Juniperus virginiana*, Linné, 1753 ; at right: *Picea glauca,* (Moenc; Voss), Hélardot, 2020,
Photo credit: U.S. Fish and Wildlife Service.

More recently, another natural organic substance has also been used, the Canada Balsam (Ringsrud, 1983). It is a turpentine-like oleoresin extracted from a North American conifer known as *Abies balsamea*; (Fig. 3) (Linné) Miller, 1768, synonym of *Picea glauca* (Moench) Voss 1907.

Among other applications, this substance was initially used in optics for the assembly of lenses, the preparation of thin slides, etc. Its interest lies in its very high transparency in thin layers, its refractive index being relatively high: $n \approx 1.53$ (Kužel, 2001) and the ability of gases to diffuse into its mass without forming observable bubbles when it is in a thin layer. This last feature is interesting, not only because the absence of bubbles creates a better optical continuity, but also because the absence of gas volumes (bubbles) makes the substance more stable over time. Although it is said not to crystallise, this is not always the case in the cracks of emeralds, probably due to the interactions it has with a highly variable environment. Its viscosity at 20° is high, around 3 Pa·s (at room temperature: 20 °C) (Merck, 2017); to infiltrate the emeralds, it is fluidized by heating.

On the other hand, Canada Balsam of optical quality is a relatively expensive substance, which is probably why it has been and remains little used today.

Finally, there are mineral oils (saturated hydrocarbons derived from petroleum), which are typically paraffin oil, which comes in three forms: liquid (most common), solid and intermediate forms of highly variable average viscosity.

Liquid paraffin has a lower refractive index than cedar oil, $n \approx 1.46 - 1.47$, and a viscosity of 25 à 80 mPa·s (at room temperature: 20 °C) (Roth, 2020; Mezger, 2011), this low viscosity makes it easy to use for filling.

At high viscosities (solid state as wax), paraffin is used with varying degrees of success, the wax is frequently found in the form of "plugs" at the opening of cracks without it being possible to say whether this is intentional or whether it is used as a "finishing" substance (polishing). It is sometimes found as a filler as such. Although it is a non-transparent but translucent material, it will appear transparent in very thin films in a fissure. On the other hand, when the stone contains cavities accessible from the surface and fills them, it will form white masses which will then have the opposite effect to that intended. Although it is a solid, it can nevertheless be infiltrated under pressure when heated to temperatures of around 70 °C, where it becomes a liquid with a viscosity of around > 10 Pa·s (Rossetti *et al.*, 1999).

With paraffin, it is necessary to evoke the white of whale (spermaceti[8]) sometimes mentioned in the past as a filler. As the infrared spectrum of spermaceti is indistinguishable from that of fatty substances, and knowing that paraffin wax was often mixed with it, this does not allow us to confirm analytically that this substance was indeed used. Finally, since the hunting of sperm whales has fortunately been banned since 1982, their use will remain an unverified historical record and, in any case, anecdotal (Wellendorf, 1963; Rice, 2009).

In recent decades (≈ 1980, mainly in Colombia), oil has gradually been replaced by epoxy resins for the treatment of emeralds (cf box 2). Today, the majority of emeralds that are traded in Europe do contain this material, with a preferential distribution by geographical origin. It is mainly Colombian and Brazilian emeralds that are usually processed in this way. Zambian emeralds contain, for example, predominantly mineral oil. Finally, those from other world deposits have a wide range of substances, including (like the Colombian and Brazilian ones) a wide range of different epoxy resins.

BOX 2

History of epoxides

The discovery of the epoxy function is attributed to a Russian chemist N. A. Prileschajewun in 1909. The first syntheses began to be produced in the early 1930s with a first patent filed in 1934 by the German chemist Paul Schlack, then around 1940, the development of the epoxides we are interested in, based on bisphenol A (DiGlycidylEther of Bisphenol A, or DGEBA) (Fig. 4) has generated several patents filed thanks to the work of chemists Pierre Castan (Switzerland) and Sylvan Greenlee (USA).
In the list of the first industrial applications, it should be noted that they were used as early as the 1930s in aeronautics, notably by Aero Research Ltd.
There are today five major families of epoxies, with several thousand variants, developed for a large number of often very specific applications (mechanical strength, electrical conductivity, temperature resistance, etc.), with an annual world production of several million tonnes (Global Industry Analysts, Inc., 2011).

In their usual use, epoxy resins (polyepoxies) are synthetic materials of varying degrees of hardness, produced by the reaction of an epoxy precursor (base) to which a hardening agent has been added. These precursors are compounds with two or more terminal epoxide functions that can polymerise via two processes: chain (anionic) or step (cationic). The epoxies used in the treatment of emeralds are anionics.
Polymerisation is accompanied by a cross-linking process which binds the macromolecules of the product together by covalent bonds, creating intermediate bridges between the linear chains (anionic precursors), ultimately creating three-dimensional molecules. After cross-linking, the polymers formed are considered insoluble (Flory, 1953; Lee, 1967; Marmet, 2013). They are mainly used for the production of so-called organic matrix composites (OMC).

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[8] Spermaceti, a substance composed of fats and waxes, present in the melon (an important organ located in the head) of cetaceans, particularly sperm whales (*Physeter macrocephalus*; Linné, 1758).

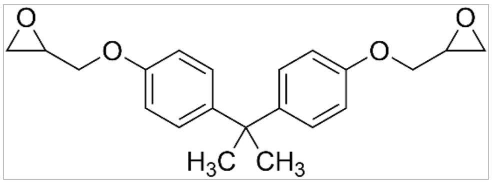

Fig. 4: The Bisphenol A Diglycidyl ether, formula $C_{21}H_{24}O_4$. Credit Emeldir, Wikipedia

In most cases, the epoxies found in emeralds are not hardened (no hardener is added), only the base (precursor) is infiltrated. Some attempts have been made with a hardener but without success, the best known being marketed under the suggestive name of "Permasafe" in 1998 (Fritsch *et al.*, 1999). This epoxide, when polymerised, produced a very transparent, but brittle solid that yellowed very quickly (Chalain, 1999).

When epoxydes fillings are cured, which is relatively common, it is usually fortuitous. These are often photo-polymerisation processes initiated by inadvertently present precursor agents. The polymerised state of the resin is not really detectable with the analytical methods used for their identification. In infrared spectrometry, in the window available in emeralds, polymerisation generally only manifests itself by a change in the intensities of the bands used for their identification, which is not really exploitable (Rekik, 2009). The polymerised state of epoxides in emeralds is only observed during tests of the extraction of these substances for the cleaning of the stones, as it is generally almost impossible to dissolve them at the temperatures tolerated by the emeralds.

It should be noted that the epoxides we are interested in for the treatment of emeralds are in fact glues, the best known of which, marketed since 1946, bears the name "Araldite" (a DGEBA, box 2). It is sometimes said that the primary interest of epoxies is that they allow the rough to be consolidated before shaping, which would reduce the loss of weight during cutting, making it possible to obtain more and/or larger stones than would have been possible to cut in a given rough. So much so that it is sometimes impossible to clean certain stones because one or more fragments can come off (Fig. 11) once the glue has dissolved.

For emeralds, from an optical point of view, epoxies have a definite advantage over oils, as there are some that have refractive indexes that correlate well with those of emeralds. Indeed, their indexes are globally between $n \approx 1.49$ (UL, 2020) and $n \approx 1.65$ (Speight, 2005), and often with excellent transmission in the visible range (UL, 2020).

Thus, several epoxides are used, with or without hardener, under different brand names which are for the most known: Opticon, Gematrat, Palm Oil, Epikote, Epon, etc. The best known of these being Opticon 224 which has a refractive index of 1.545 (Kammerling *et al.*, 1991).

These epoxides and oils can be coloured to intensify the colour of pale stones. Coloured substances are generally applied to stones of a fairly low quality with a relatively high number of fractures, which homogenises the added colour. Their very simple detection (immersion microscopy) will not be discussed here.

Finally, a certain number of more or less exotic substances have been encountered occasionally in emeralds. Such as clove oil, cyanoacrylates, various essences, industrial liquids for pneumatic systems, etc.

Stability

The notion of stability of fillers should not be considered solely in terms of time, which is only the framework on which other conditions will have a more or less significant impact. The nature of the environment is a crucial element, whether in the context of " normal " use (that of a particular client): temperature and humidity variations, exposure to various cleaning products (soapy water, alcohol, etc.), use of small ultrasound systems, exposure to artificial or natural light; or in the framework of "professional" conditions (traders, jewellery workshops): solvents, steam, direct exposure under intense lights, metal polishing products, use of powerful ultrasonic systems and various manipulations (see box 3).

In addition, to consider the stability of the substances, they must be divided into two groups, the first including cedar oil, unmixed Canada balsam, mineral oils, unhardened epoxides; and the second including hardened epoxides.

BOX 3

The conditions of use of emeralds

"Regular" conditions (private individuals):

Using soapy water or alcohol to clean the jewellery can empty the cracks (much faster with alcohol). Small ultrasonic baths alter the majority of unhardened substances and can create new cracks or expand existing ones; their use should be avoided and the customer should be informed. Variations in humidity and possible contact with cosmetic products can lead to chemical changes in the substances.

Professional conditions:

Paradoxically, the effects are much more severe than regular conditions, especially in the workshop. Indeed, setting requires the craftsmen to clean the jewellery once completed to remove all deposits (wax, metal polishing paste, etc.).

Although ultrasonic baths or steam cleaning are obviously to be avoided for the reasons mentioned above, they are sometimes used for convenience, or in a hurry, which is a well-known constraint in the profession. There is a risk of partial or total emptying of the cracks. The same applies to solvents such as alcohol, acetone, toluene, etc. Ideally, the jewellery should be cleaned dry (cloth, soft wood tip, etc.), and/or briefly with soapy water at room temperature.

For dealers, the main constraint is the change in environmental conditions, especially when the stones travel, and when they are exhibited in trade shows or in shops. This induces variations in pressure and temperature (particularly brutal when the stones are shipped by air) and hygrometry, which will induce contraction and expansion movements that will empty the cracks, at least at their openings, in a very variable manner.

Exposure to intense light sources alternating with periods of darkness (display cases, safes) will induce the same effects on mounted or unmounted emeralds, with the addition of intense lighting accelerating the natural ageing process of cedar oil, which will be more reactive to these effects, depending on its viscosity, than mineral oils.

Stability

First group: cedar oil, Canada balsam, mineral oil and unhardened epoxides

Unmixed cedar oils are stable for up to ten years in the best cases. Over time, they change autonomously and to a greater or lesser extent depending on their nature. The degradation mechanisms are spontaneous and start with an oxidation reaction that generates free radicals; this is followed by a number of evolutionary, irreversible processes that are stimulated simply by temperature, white light and UV radiation (Adams, 1991).

In the most important fissures, the oils reduce in volume to a greater or lesser extent, become opaque and turn yellow through the formation of carbonyl groups. In addition, some oils are subject to a siccative process which can lead to partial cross-linking. With time, they end up retracting substantially, no longer adhering to the faces of the crack and taking on a granular or dendritic appearance, coloured from very pale yellow to brown, passing through ochre, which then makes the cracks that contain them very visible.

For small (very thin) cracks, the process is less visible, as the thickness of the film is thinner and the opacification and colouring are less noticeable. The other organic oils show generally the same ageing characteristics.

Canada balsams will show more or less similar signs of ageing, with many variations due to the many possibilities of mixing with other substances, including cedar oil. In fact, it is difficult to describe more or less constant principles of ageing. Globally, they can take on a cracked and less frequently dendritic appearance, often have a strong tendency to yellow and even darken, and they can detach from the crack faces (Rudloff, 1967).

In addition to intrinsic ageing due to time, cedar (and organic) oils and Canada balsams are sensitive to UV radiation, exposure to intense white light, variations in humidity (for cedar oil) and temperature and are very sensitive to solvents (toluene, xylene, acetone, alcohols, etc.). Finally, they are also sensitive to ultrasonic cleaning and to a lesser extent to steam cleaning systems (Johnson, 2007).

The mineral oil (paraffins)[9].

Liquid, semi-liquid (*paraffinum subliquidum*) and waxy (*paraffinum solidum*) paraffins are intrinsically relatively stable over time. The main degradation factor is oxidation. In theory, in paraffin oil the degradation produced by oxidation will first generate soluble products, then produce insoluble deposits by polymerisation, all accompanied by an increase in acidity. This oxidation leads to the appearance of a yellowish colour. However, at room temperature this process is extremely slow for emerald fissure fillers. To date, very few deposits that may result from this process have been microscopically observed (Johnson, 2007).

Liquid forms have a particular sensitivity to direct UV radiation (which is very moderate in emeralds), which sensitivity is proportional to their viscosity (Schnurmann, 1954). They do not tend to yellow as quickly as epoxides because they are purified and do not contain aromatic rings.

They are very sensitive to solvents (toluene, xylene, acetone, alcohols, etc.), sensitive to ultrasound and steam cleaning like organic oils, and to a lesser extent to temperature variations; being immiscible in water, they are very little sensitive to hygrometric variations.

The evolution of oils over time is now something we know well, as they have been used for a very long time. After degradation, emeralds need to be cleaned and re-oiled, which is now a relatively simple operation for cedar oil, a little more complex for mineral oils.

<u>Second group:</u> The hardened epoxy resins

For hardened epoxy resins, the intrinsic ageing phenomenon is a glass transition phenomenon which starts as soon as the bases are mixed with a hardener, or when a photo-polymerisation is induced. It corresponds to an evolution of the nature of the macromolecular chains formed which is a thermodynamic equilibrium problem. These will reorganise to a configuration close to equilibrium.

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[9] The term "mineral oil" includes many different hydrocarbons. We will only consider here paraffin oil, which is regularly mentioned in the literature. This oil exists in several forms, the "purest" being that for cosmetic or medicinal use which is treated to eliminate all traces of some polycyclic aromatic hydrocarbons harmful to humans (benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[e] pyrene, etc.).

From a practical point of view, this will manifest itself, among other things, in a decrease in volume. This decrease in volume will be in addition to the initial contraction that occurs immediately after polymerisation and reticulation (Fig. 5). In the medium term, this may result in resin detachment from one side of the crack or in increased stresses, the long-term effects of which on the gemstone are not yet well known.

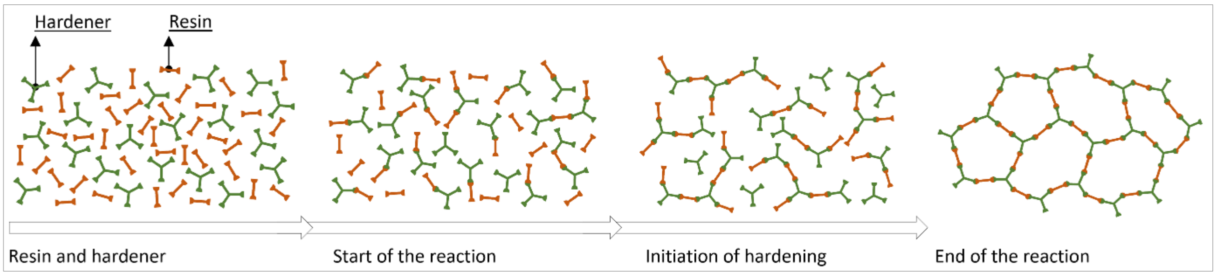

Fig. 5: Simplified scheme of a cross-linking reaction. F. Notari, 2021, after CERN, 2019

Deterioration also occurs through the absorption of free water molecules through nanoscale pores and the incorporation of water into polymer chains through the hydrogen or dipolar bonding of hydrophilic sites. Most of these bonds are very strong and the water molecules will literally be trapped in the network. This incorporation can cause multiple points of expansion, particularly at the opening of cracks on the surface of the gem, which complicate (by opposing) the tension effects due to other shrinkage mechanisms. The presence of water can also accelerate the photo-oxidation process. In the long term, an oxidation process of the aromatic rings colours the epoxies from yellow to brown and a more or less important opacification can appear (Nguyen, 2013; Maggana *et al.*, 1999; Bellenger *et al.*, 1983; Down, 1984).

It is not objectively possible to predict how polymerised resins will evolve in the long term, as the number of possible modifications is so large, and because their use as fillers for emeralds is relatively recent.

The causes of environmental changes are, paradoxically, certain solvents, but also variations in humidity and temperature, exposure to intense light and cleaning processes (ultrasound and steam) (Johnson, 2007).

Finally, some lapidaries have complained of sudden alterations of epoxy resin in cracks (during re-cutting or repairing emeralds) when the cracks containing them were in contact with the disc.

The extent of induced improvement and its estimation

Quantifying the importance of improved emerald transparency is a very sensitive subject, which has been (and still is) much talked about and controversial (McClure, 1999), which is understandable, as its impact on the appearance of the gem can be very important and will therefore affect the value of the emerald in the same way. This improvement is defined by several grades, which vary between laboratories in terms of terminology and number (Fig. 6). These grades are (for example), *minor, moderate, medium, significant, very significant*, some laboratories also use the *insignificant* grade, which is an often-controversial concept.

Fig.6: Colombian emeralds from ≈ 6 to > 10 carats, before and after oiling, with colourless oil. Here, the transparency improvement grades are for all: very important. Photos E. Disner.

Concerning the grades, one can consult for example the LMHC (Laboratory Manual Harmonisation Committee) information sheet N°5 on the internet, which is an interesting attempt to normalise and standardise grading.

While it has the merit of proposing two well-explained scales of grades, for cracks and cavities, it remains somewhat summary and comes up against the complexity of cases encountered in reality. It does not mention the orientation of the cracks, which is a major factor, and the representations of cracks in the diagrams in the document do not show *a priori* any apparent variations in orientation, but give the impression that all the cracks are parallel to the direction of observation, in this case apical or "*face-up*".

As we have written above, these grades are not defined by the nature or quantity of the substances present (all things considered), but by the combined size, position and orientation of the filled cracks. Always bearing in mind that this is an improvement in transparency and therefore refers to normal conditions of observation by the consumer or the gemmologist, *id est* with the naked eye and in the final set stone. When looking at an un-set stone with a given grade, one may sometimes get the impression that the grade is a bit "optimistic", but it should be understood that once the stone is set, its internal characteristics will be much less visible (Fig. 7 et 8).

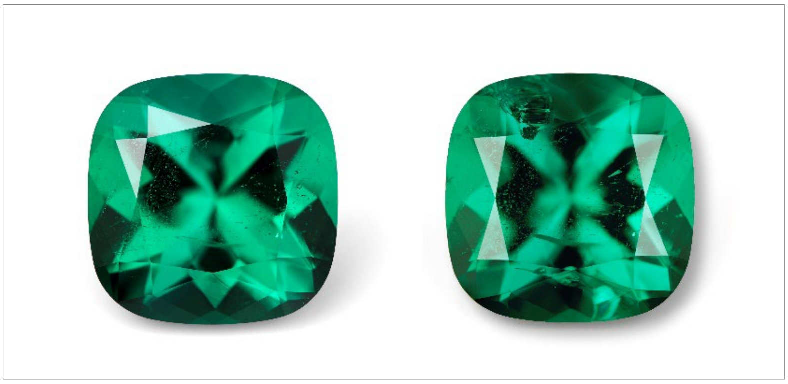

Fig.7: Colombian Emerald, weighing > 8 carats, before and after cleaning. Here, the grade of transparency improvement would be *low to moderate*. Photos C. Nacht.

Fig. 8: Colombian emerald, weighing > 6 carats, before and after cleaning. Here, the grade of transparency improvement would be *significant*. Note that cracks perpendicular to the table (parallel to the direction of observation) remain visible although attenuated, while cracks more or less parallel to the table (perpendicular to the direction of observation) are better masked. Photos C. Nacht.

On the other hand, certificates sometimes mention the presence of a substance that is only present in infinitesimal quantities in a stone, when the quantity detected is well below what the eye can perceive (often detected by micro-Raman). This is frequently the case when a stone has been cleaned and retains some remnants of the substance at the bottom of the cracks. In such a situation the notion of improving transparency becomes obsolete.

Indeed, the theoretical separating power (resolution) of human eyesight has its limits, and it varies between individuals. If we assume that the eye is a simple optical system, it can be expressed as a minimum angle of separation, which is generally one minute of arc ($10/10^e$ equivalent) but may not in principle be less than 30 seconds of arc ($20/10^e$). That is, an acuity that would allow at best to see objects from ≈ 0.3 mm to 1 metre, under optimal conditions of contrast and luminance, the latter conditions being paramount (Gatinel, 2015). Due to the internal conditions of the emeralds (low luminance, hue, birefringence, etc.), residual traces of substances with a size of ≈ 50 to 100 µm (which is usually the case after cleaning) cannot induce a perceptible improvement in transparency.

In theory, it would be the observation, with the naked eye, of the stone with empty cracks and then filled cracks that would ideally allow a grade to be objectively attributed. However, as it is rare to be able to proceed in this way (empty/filled fissures comparison), laboratory gemmologists must estimate this improvement on emeralds with filled fissures, which is not necessarily easy.

Observing the nature of the filled cracks is not always a simple matter. The microscope with a circular illumination around the stone on a black background is a good way to detect all the cracks present. Indeed, with a circular illumination around the stone, there will always be a reflection, even partial, of the light on the walls of the cracks, allowing to see them, as long as there is a minimum of incidence with respect to the direction of observation. Filled cracks, perpendicular to this direction, are not always easy to observe.

The luminescence microscopy

Finally, luminescence microscopy is probably the most effective method for quantifying induced enhancement. It consists of luminescing the fillers (Fig. 9). Indeed, most of them luminesce when excited with (for example) a blue-violet exciter[10] and the observation of the filled cracks is then easy. The identity of the substance present can then be determined, as

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[10] *Id est* with an exciter centred at around 450 nm.

organic oils and epoxides (Fig. 10) luminescent in hues ranging from yellow to green and from green to turquoise-blue or whitish (schematically), respectively, while emerald, depending on its iron content[11], will luminesce more or less intensely in red due to the chromium (Cr^{3+}) present. When the luminescence (Fig. 11 to 13) of the fillers is weak (intrinsically or very small and thin cracks), the sometimes very intense chromium luminescence can be avoided by filtration, which allows the observation of very small filled cracks, undetectable by traditional microscopy, (down to < 20 µm) which then appear on a black background (Notari *et al.*, 2002; Hainschwang *et al.*, 2015).

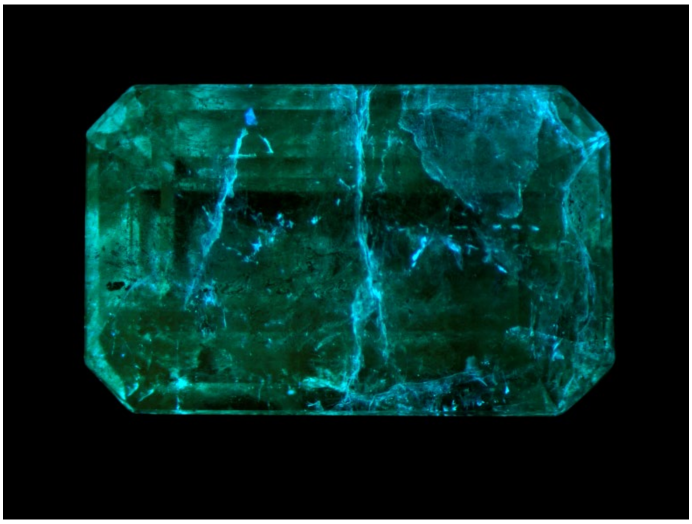

Fig.9: Brazilian emerald of < 2 carats, with a large number of cracks filled with resin (blue luminescence). The grade here is "*significant*", mainly because of the crack at the top right, parallel to the table, and which would induce a significant mirror effect. Micrograph F. Notari.

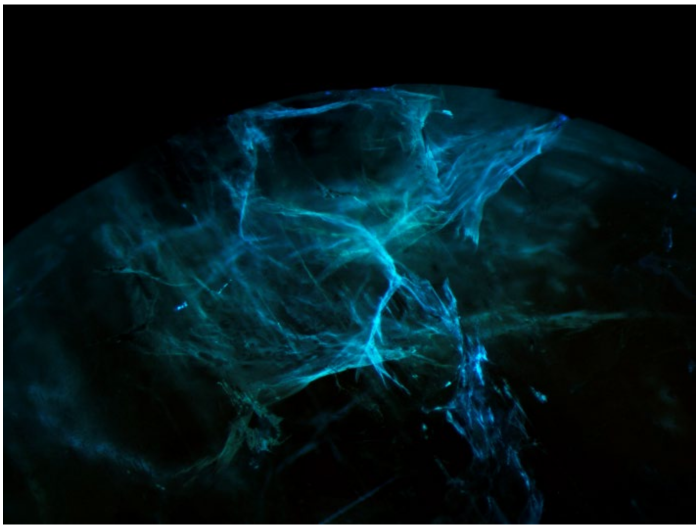

Fig. 10: Luminescence micrograph of a > 35 carat emerald cabochon from Colombia, whose fissures contain epoxy resin in the foreground (blue) and a mixture of oil and epoxy in the background (bluish green). The identity of the two substances present is confirmed by infrared spectroscopy. The red luminescence of Cr^{3+} is here attenuated by filtration. Field width ≈ 15 mm. Micrograph F. Notari.

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[11] Iron is a luminescence poison.

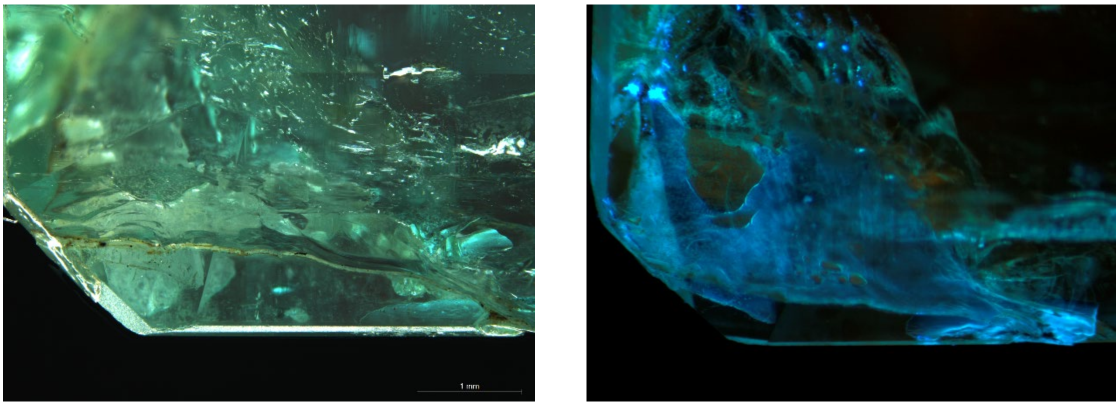

Fig. 11: On the left, the corner of this Colombian emerald is held in place only by the epoxy resin. On the right, the extent of the resin film holding the piece glued can be seen in luminescence. On the left, the scale bar is 1000 µm, darkfield illumination. Micrographs by F. Notari.

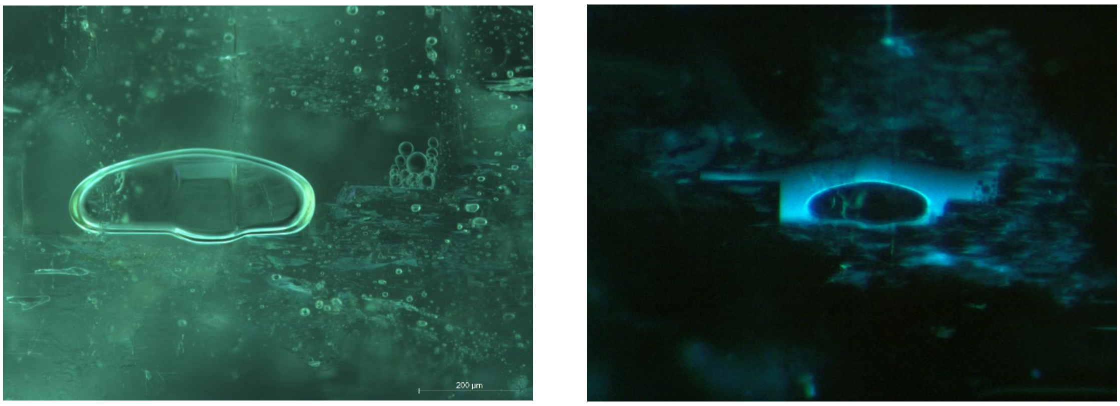

Fig. 12: On the left, a kidney-shaped bubble accompanied by a group of smaller round bubbles in a Colombian emerald. The morphology of the large bubble, together with this cluster of smaller bubbles, makes us think of resin, which is confirmed by the hue of the same inclusion in luminescence. On the left, the scale bar is 200 µm, darkfield illumination. Micrographs by F. Notari.

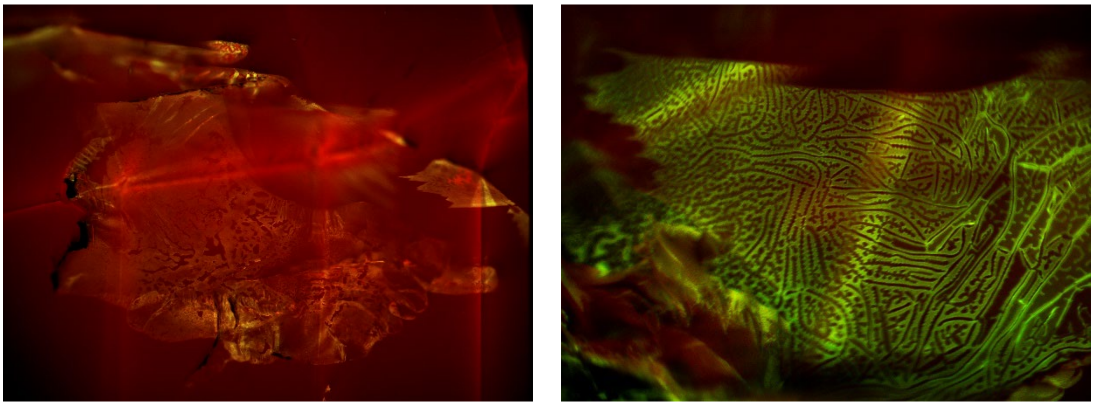

Fig.13: On the left, fissures containing degraded oil, slightly dendritic, field width ≈ 15 mm. On the right, spectacular dendrites in an epoxy resin filling, field width ≈ 10 mm. Micrographs F. Notari.

Precautions to be taken in luminescence

Regarding luminescence, it is important to choose an exciter that is not too energetic, rather towards the blue (≈ 490-450 nm), which will be of lower energy than the UV often used. This is to limit the risk of inducing photo-polymerisation, or cold polymerisation. This photo-polymerisation, which is well known to industry, has long been practised on various materials to modify their mechanical properties. It can sometimes, in the case of epoxy resins, and depending on the chemical impurities present (photo initiators), be induced by UV irradiation with the classic gemmological wavelengths (*id est* 365 nm), even if the lamps used are of relatively low power.

In the context of laboratory analysis, this point is of real importance because the epoxy bases used must remain fluid in order to maintain their adhesion properties to the walls of the crack, and be able to play the optical role expected of them. As we have said above, the polymerisation of epoxides generates a certain number of changes in the state of the substance which, in the medium or long term, can more or less seriously harm the appearance of the gem and, moreover, make it impossible to clean.

The use of UV radiation will also accelerate the ageing of organic oils.

The other advantage of using an exciter in the visible range is that it will not, or hardly, induce luminescence of any organic compounds present in the emerald (*id est* in the brines).

The gemmological reports

For emeralds, in all cases, in addition to the usual information, description, identification, eventually likely geographical origin, a gemmological report must mention the nature of the filling substances present, as well as the importance of the improvement in apparent transparency (and therefore colour) brought about by the filling of the fissures. The latter information is the most important with regard to the treatment. Indeed, while some jewellers tolerate the presence of epoxides, most are attentive to the extent of the improvement induced, which must be indicated and quantified. This is important information to pay attention to, because for a given appearance, the amount of enhancement can vary the value of an emerald by a substantial factor.

Reliability of reports over time

Finally, there is the question of the validity of the certificate over time. Several cases of post-certification treatments have been reported, and laboratories are familiar with this problem. This may be the case of an emerald containing cedar oil, which has been replaced by epoxy resin which masks cracks better because of its higher refractive index. Or an emerald with no improvement in transparency where a small unpleasant fissure has been masked by some kind of filler.

These subsequent treatments can be carried out by professionals or at the request of the customer who has purchased the stone, which in the latter case is acceptable since it will have been done with full knowledge of the facts and will not be part of a transaction referring to a gemmological report.

For these reasons, laboratories now mention the possibility of post-certification treatment, either in the reserves or explicitly on the main page of the report. It is not uncommon for an emerald to be accompanied by several reports, or for a new report to be requested when a transaction is finalised.

Conclusion

Two main families of substances, oils (in the broadest sense) and synthetic resins (typically epoxides) are used to fill cracks (and sometimes "frost") in emeralds to mask them. Each family has its defenders and detractors, and it is not for the laboratories to take a position in this debate. Their role is to identify the substances present and to quantify the improvement in transparency.

This role is essential, as it allows the true nature of the product to be known and allows it to be traded with peace of mind. There are sometimes small differences in this gradation from one laboratory to another. But globally all laboratories with experience in this field now provide quality work and reliable reports for the benefit of the consumer.

Generally speaking, the partisans of epoxy resins point out their stability (which, for hardened resins, is highly debatable), and a higher refractive index than oils, which allows cracks to be better hidden. This last point is curiously taken up by the detractors of epoxies as being a problem in the sense that certain defects would no longer be observable by traders with conventional means (magnifying glass, small binocular).

The defenders of oils point out the traditional aspect (a so-called customary treatment) and the fact that it is nowadays quite simple to clean an emerald that has been oiled for a long time and to oil it again. Finally, and this is in the air of time, that it is a natural product. They attack synthetic resins as being glues.

In the end, the identity of the substance satisfies the "personal" choices of the traders as well as the jewellery companies. The only problem lies in the polymerisation of epoxy resins, which will start an ageing process whose consequences are unpredictable and irreversible.

On the other hand, the information concerning the importance of the improvement of the induced transparency is part of the code of good conduct towards the consumer.

This is fundamental, because it is the consumer who is at the end of this long chain which, from the depths of the mines via the purchasers of the rough, the cutters, the traders and the jewellers, will enable him to acquire in full knowledge this remarkable gem with its rare colour.

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