Colombian Emeralds

Clarity-Enhancement of Emeralds

Q2 2019





Introduction

All emeralds contain inclusions and tiny fractures as a result of their process of formation. These are one of the most important microscopic characteristics of emeralds and they are a strong indication of natural origin. The characteristic "Jardin" - (French for "garden" - is not considered a flaw unless there is an abundance of imperfections.

However, human nature strives for perfection and since ancient times, the oiling of emeralds to improve their appearance has been a common and therefore widely accepted practice. One of the first descriptions of the use of oil as a filling material for fissures, especially for emeralds, was given by C. Plinius Secundus (55 AD) in his 37th book of natural history. Other historic information are the Papyrus Graecus Holminensis (400 AD), as well as Arabian writings from the 14th century. Since the 1980s, the use of resins has become increasingly common in the clarity enhancement of emeralds.

Nearly all emeralds are treated to improve their appearance. "Oiling", fracture-filling or clarity enhancement are the terms used to describe this process. In the oiling process, involving heat and pressure, surface reaching fractures are filled with a colourless liquid that enables light to pass through the emerald unhindered, thereby improving its appearance. In ancient times, cedar wood oil and other oils were used for this purpose, but today a wide range of substances are actually employed, depending on the origin of the emerald. Artificial resins have become the common filler substances for the clarity treatment of emeralds today.

It is the abuse of some less honourable market operators during the 1980s and 1990s that has brought a whole industry in disrepute and led to a sharp drop in emerald sales during the 1990s. While these abusive and fraudulent practices have largely been stopped, many, in particular the consumers, are still suspicious and wrongly view emeralds as a risky purchase or a complicated gemstone.

This Monteverde Emeralds Report on emerald treatments tries to shed light on common practices and issues regarding the clarity enhancement of emeralds.

The Oiling Process

The fracture filling of emeralds is commonly referred to as "oiling", although it is not necessary oil that is used in the process. It is possible and not uncommon that emeralds receive their first oiling in their rough state, before they are even cut to facetted emeralds.



Emeralds being cleaned in acetone

Before oiling, the emerald should have been thoroughly cleaned and any residues from polishing or any leftovers from previous fillers should have been removed.

In the oiling process, emeralds are placed into a pressure chamber. In a more sophisticated oiling apparatus, a vacuum is first induced and all air removed from the chamber. This will improve the oiling result, because the presence of air in fissures could create tiny bubbles in the liquid that is used as a filler. Then, the chamber is filled with the liquid clarity enhancer, completely submerging the emeralds. Subsequently, pressure is normalised and excess pressure is then applied to push the liquid into the fractures. To reduce its viscosity (resistance to flow), the filler is thinned by heating it to around 80 degrees Celsius while under pressure. The filler is then allowed to cool and its viscosity level rises high enough to prevent seepage.

In slightly less sophisticated and more compact machines, the emeralds are placed straight into a pressure chamber and submerged in the clarity enhancing substance. The container is then closed and heated to about 80 degrees celsius. Due to the heat, most air still present in fissures escapes from the fractures and pressure rises, thereby forcing the liquid into the fractures. The oiling process lasts 2-3 hours, after which the machine is switched off and the container is allowed to cool down. Once pressure is normalised, the emeralds are removed from the container and they are wiped clean of any remaining liquid with a cloth.

The success of the "oiling" process depends on the ability of the chosen filler

to be induced into the surface-reaching fissures of the emerald and remain there. The more fissures and inclusions are present, the more the gemstone's appearance will be improved by the oiling process.

Some emerald dealers then apply hardeners to the surface of the emerald, sealing the surface-reaching fractures, or the filler is hardened using UV light. In some treatments, hardeners are mixed into the clarity enhancement liquid, making the whole treatment very durable. This practice has advantages and drawbacks which will be discussed further down.

All filling materials will deteriorate over time, making a renewed oiling necessary. However, there is the risk of breakage during this oiling process, as a result of pressure and heat. Therefore, it is best to avoid frequent oiling.



Emerald oiling apparatus

Note: Emeralds are actually not as complicated as it is often thought: oiling is the only possible treatment. Because of the emerald's chemical composition, heat and radiation do not change its colour and as a result, these techniques are not employed. Emeralds cannot be filled permanently with glass, because the heat would make the gemstone break in the process. Oiling does not alter the natural gemstone itself: the emerald can subsequently be cleaned, which will completely remove the clarity enhancement liquid.



Heavily treated gemstones may appear of deceptively high quality, which is why it is recommended to have valuable emeralds certified by a reputable laboratory. A laboratory report will identify the gemstone as a "natural emerald" (as opposed to a synthetic or a composite emerald, see page 20), it will state whether there is evidence of clarity enhancement and to which degree the emerald has been improved by this treatment. This will tell the buyer, how much the emerald's appearance could worsen with time, if the filler were to deteriorate.

Since all emeralds have inclusions and fractures - and all emeralds are usually clarity enhanced - it is accepted that a normal or average typical emerald could be expected to display evidence of "moderate" clarity enhancement.

Finer qualities of emeralds would achieve a classification of "minor" or by a few laboratories even "insignificant" clarity enhancement. An emerald that exhibits no evidence of clarity enhancement is also commonly called a "no-oil emerald". Provided that the quality of the actual gemstone is good, these are extremely rare and valuable. However, leaving an emerald un-oiled will not by itself enhance the value of the gemstone, if the emerald is of low quality and little beauty.

The extent of clarity enhancement is only one part of the value equation, which also includes colour, weight, origin and the presence of other inclusions, so the degree of treatment does not by itself equate to an emerald's value. "Significant enhancement" does not necessarily mean low value, just as "minor enhancement" or "no evidence of enhancement" does not necessarily mean high value, if the stone has a weak colour or many internal inclusions that are not surface-reaching. The value of a low-quality emerald that is heavily included will not be improved at all by a report that says it has only minor enhancement.

Colour is the single most important factor in determining the value of an emerald. Clarity enhancement does not change the inherent colour of the stone, but it can change the appearance of an emerald's colour by masking the fissures and reducing the amount of light scattered by those fissures. Therefore, the colour of the stone may appear better than it was before. Comparing two eye-clean emeralds of the same colour and beauty, the stone with less treatment will be more valuable, and the price increases exponentially the less treatment is present.

All clarity enhancements will deteriorate over time, therefore, having an

emerald that requires little treatment is definitely a good investment. It requires less frequent re-oiling and even when the filler has decomposed, the piece of jewels might still look beautiful. As a result, emeralds with insignificant treatment command a sometimes significant premium over moderately treated emeralds.

Top tier brands around Old Bond Street in London or Place Vendome in Paris will mostly only display jewellery with emeralds that have little or no treatment and these brands rarely compromise on quality. What these emeralds also have in common is that their gemstones display a superior colour and brilliance. Untreated emeralds of top colour are extremely rare, constituting less than 1% of the market of facetted emeralds. As a result these emeralds command very high prices.

Emeralds with moderate clarity enhancement can be a good and more affordable alternative. Whether you have an emerald with minor or moderate clarity enhancement, you would probably choose to re-oil it either way, once the clarity enhancement starts displaying signs of age. Therefore, whether you would want to pay a premium for a finer gemstone is a personal decision.

Care should be taken when purchasing emeralds with "significant"



Emerald before and after clarity enhancement

clarity enhancement, as their appearance could be expected to deteriorate significantly over time. In addition, they might be less stable gemstones and even re-oiling could pose a risk of damage to the gemstone. It might be preferable opting for an emerald with a lighter colour and less treatment over one that has a better colour, but has been significantly treated.

Surface-reaching fractures on the table of the emerald are a value-reducing feature, as any deterioration in the filler would immediately be visible to the naked eye.

At Monteverde Emeralds we only work with fine quality emeralds, from nooil up to moderate clarity enhancement.

Commonly Used Fillers

There exists a lot of misinformation, confusion and apprehension about emerald treatments. The question which filler to use has become a hotly contested subject of discussion. Before discussing the topic in more detail here and in the following chapter, let's take a step back and recall why we treat emeralds and what we expect from the clarity enhancement:

The oiling process is intended to mask fractures and imperfections. The **refractive index** is a measure of the bending of a ray of light when passing from one medium into another. We perceive the fractures inside the emerald, because light - on its path through the emerald and the air in its fractures - is broken several times and partially or totally reflected, so that we see grey or intransparent marks. If the fracture is filled with a liquid, this will improve the appearance of the gemstone, as the light can now pass unimpeded through the gemstone. The closer the refractive index of the filler is to that of the emerald, the better this works. Ideally, they would be identical.

Therefore, the first desirable property of a clarity enhancement is that its **refractive index is close to that of the emerald**. Secondly, all clarity enhancements decompose or deteriorate over time. Therefore, **durability** is the second important factor in judging a clarity enhancement (and the ease of removing the filler from the emerald during the process of cleaning). Best suited are high-viscosity fillers that are thick and sticky in their natural state at room temperature, but which are thin and liquid at higher temperatures during oiling.

Thirdly, the filling **liquid should be clear and colourless**.

With this in mind, we will try to give an overview of commonly used substances in oiling emeralds. Depending on availability of alternatives and geographical location, Johnson's baby oil, bees wax, olive oil, palm oil, sewing machine oil and many more could be encountered. Often, one will also find a mix of different fillers. This may be intentional, or a result of re-oiling a previously oiled emerald with a different clarity enhancement. Here, we discuss only the most commonly used clarity enhancements, dividing them into three groups:

- * Oils (natural or synthetic)
- Liquid Resins/Pre-Polymers (natural or synthetic)
- * Manufactured Polymers

Oils (natural or synthetic)

The term "oil" means different things to different people. It could refer to mineral oils, vegetable oils, or essential oils, all of which have in the past been used for the oiling of emeralds. In terms of the three criteria established above (refractive index. durability, colourless), the problem with oils is that they do not perform particularly well in any of the categories. For most oils, the refractive index is under 1.50 and as a result, their effectiveness in masking imperfections is not ideal. More importantly, oils tend to have a low viscosity, which means that they are still relatively liquid at room temperature. Consequently, they dry out quickly or seep out from the emerald over time, which means the treatment has a short longevity. Many organic oils are not colourless, but yellow/brown/green to start with, or they change colour over time as they decompose.

Today, cedarwood oil (or cedar oil) is the most common and most important oil being used for clarity enhancement of emeralds. Cedar oil has a refractive index of 1.495-1.510, which is not ideal, but close enough to that of the emerald (~1.56-1.60). In terms of durability, cedarwood oil is somewhat viscous at room temperature, but sensitive to temperature changes (turning liquid or vaporising) and light exposure. It is insoluble in water. Its main advantage is its relative ease of removal during the cleaning process by, for instance, ether, acetone or pure alcohol. Natural cedarwood oil is transparent, but has a light yellow to brown colour, a strong smell and is therefore not ideal for oiling emeralds. The main components of many essential oils, including cedarwood oil, can nowadays be synthesised and commercial essential oils may be partially or wholly synthetic. The cedar oil used for oiling emeralds - and most people are unaware of that (!) - is actually a synthetically produced oil and by no means natural. It is clear and colourless and was originally destined for use in microscopy. This synthetic cedar oil contains the same main components as natural cedarwood oil cedrene and cedrol, usually mixed with another oil. For completeness sake it is worth mentioning that most of the time, natural cedarwood oil is actually not produced from true cedar trees either, but from conifers, such as pine and fir trees, junipers or cypresses.

Liqui<u>d Resins / Pre-Polymers (natural or synthetic)</u>

Resins are traditionally mixtures of organic compounds, such as amber, frankincense, myrrh and balsam. The word resin is today applied to many substances that will set into a hard lacquer or enamellike finish, for example nail polish. Certain "casting resins" and synthetic resins (such as epoxy resin) have also been given the name "resin". In polymer chemistry and materials science, a resin is a solid or highly viscous substance of plant or synthetic origin that is typically convertible into polymers (hence also called prepolymers). Unhardened pre-polymers are the building blocks that can be used to make manufactured polymers.

<u>Oleoresins</u>

Some plant-based resins when soft are known as 'oleoresins', and when containing benzoic acid or cinnamic acid they are called balsams. Oleoresins are <u>naturally occurring</u> mixtures of an oil and a resin; they can be extracted from various plants. Natural resins can harden (polymerise) over time (e.g., amber, copal).

In the context of oiling emeralds, Canada balsam is one of the most commonly used oleoresins. It is extracted from the North American balsam fir tree and it is a popular filler for treating emeralds. Canada balsam is transparent, yellowish to slightly greenish, viscous, slightly fluorescent, sensitive to both light and temperature, insoluble in water, but soluble in acetone, ether, oil turpentine and alcohol (making all of these good cleaning agents for stones filled with this oleoresin). The specific gravity is about 0.980-0.994 gr./cm³ with a refractive index between 1.52 to 1.54. Like cedarwood oil, Canada balsam used in emerald oiling is nowadays also often synthetically produced.

Synthetic resins

These are synthetically produced unhardened prepolymers, such as epoxy prepolymers and other prepolymers (including UV-setting adhesives). An important example is bisphenol A diglycidyl ether, an organic compound used as constituent of epoxy resins (prepolymers used as ingredient in adhesives). The compound is a colourless solid that melts slightly above room temperature. Epoxy resins are liquid, but can be crosslinked with other substances to harden into polymers. These substances are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing or polymerisation. If the resin is used without hardener, it remains soft/liquid.

Since the 1980s the use of synthetic resins has steadily increased and replaced traditional oils and oleoresins for the clarity enhancement of emeralds. 90% of emeralds are today treated with synthetic resins.

The most popular clarity enhancement in Colombia is a synthetic resin that is - somewhat misleadingly called "<u>Palma</u>". It has, however nothing to do with palm oil, but is a general purpose, unmodified, colourless epoxy resin based on bisphenol A with medium viscosity better known as <u>Araldite</u> 6010 or Epon 808. Unfortunately, Araldite is in some countries a brand name for a strong glue. This falsely creates the impression to the public that emeralds treated with Araldite are "glued", a different subject treated later on.

Another synthetic (epoxy) resin has the trade name **Opticon**. It is transparent in colour, slightly fluorescent and comparable in viscosity to that of Canada balsam. It has refractive index of about 1.545. Despite its being relatively durable, Opticon is still a non-permanent filler.

As mentioned above, oil and resin fillers can prove to be unstable over time, or partially seep out from the emeralds. A clarity enhancement with synthetic resins can be made more durable if a hardener is added to stabilise the filler, or by exposing it to UV light. Sometimes, only the surface of the filled fractures is sealed with a hardener or using long-wave UV light. Hardening or surface-hardening are, however, not that common, because they complicate the cleaning of the emeralds and the removal of the filler. While hardeners extend the life of the clarity enhancement, this is not a permanent modification as - over time - the stabilisers themselves will decompose or dry out.

Manufactured Polymers

A polymer is a large molecule made up of repeating units of smaller molecules. The term "prepolymers" is used to describe the small units that are assembled into polymers. They polymerise, or harden, with the use of a chemical catalyst, illumination, heat, or time. Polymers are very durable and therefore mainly used on emeralds that require a significant amount of clarity enhancement and that may have larger fissures. They are in theory great fillers, but it is the association with bad quality gemstones and some fraudulent practices (more on that later) that imply that most dealers try to steer clear of these types of fillers. In addition, when subjected to temperature changes, these polymers may end up damaging the emerald itself. Despite their permanent nature, - and contrary to popular belief among the public, and even those gemstone dealers who lack experience in dealing with emeralds, these fillers can still be removed, returning the emerald to its natural state. It is, however, a tedious and acrimonious process involving acid, which is another reason, why most dealers do not like to get involved with these types of fillers.

EXCel (formerly known as Gematrat) is a proprietary epoxy resin and hardener process created by Arthur Groom & Co. The result is a colourless polymer with the refractive index similar to an emerald. A newer version, called "EXCel 1.52" has a lower refractive index, closer to that of cedar oil.

Permasafe is another colourless polymer with a refractive index similar to that of emeralds. As the name implies, it is very durable and from that point of view it is a great filler. The following table summarises the properties of the most common clarity enhancements:

Clarity Enhancer	Refractive Index	Chemical Classification	Natural	Synthetic	Durability	Consistency / Viscosity	Cleaning
Canada Balsam	1.52-1.55	Resin	(⁄)	1	medium	liquid / medium	Ethanol / Acetone
Cedarwood Oil	1.49-1.502, 1.51	Oil	(√)	\checkmark	low	liquid /low	Ethanol / Acetone
EXCel (old: Gematrat)	1.52-1.60	Polymer	×	1	high	solid /high	Acid
Opticon	1.545	Resin	×	\checkmark	medium	liquid / medium	Ethanol / Acetone
"Palma" (Araldite 6010 or Epon 808)	1.573	Resin	×	1	medium	liquid / medium	Ethanol / Acetone
Paraffin Oil	1.45-1.49	Oil	×	\checkmark	low	liquid /low	Ethanol / Acetone
"Perma" / Permasafe	1.56-1.60	Polymer	×	1	high	solid / high	Acid
Silicone	varies	Polymer	×	1	high	solid / high	Acid
	(Emerald: 1.578-1.59)						

Note:

Unlike heat or radiation treatments on other gemstones, ALL emerald treatments are reversible!

"Natural" substances are not currently distinguishable from their chemical equivalents that are artificially produced in a laboratory!

Laboratories will not normally indicate whether resins or oils have been used, but only the degree to which the gemstone has been treated. This is firstly because emerald treatments are reversible and the filler could be altered after certification and secondly because the presence of one filler does not necessarily mean that all others are absent!

Prepolymers and polymers should be distinguished wherever possible, as their different mechanical properties are probably significant (e.g., liquid versus solid states) and affect their durability in an emerald!

Oils vs Resins

In the 1990s, controversies erupted over the increasing use of modern epoxy resins and similar substances to fill emeralds, as little was known about them and they were considered "unnatural" by some in the trade. This coincided with a period of some fraudulent activities such as dyeing of emeralds with green colour to improve their appearance. Consumers, most of whom were not even aware that emeralds are commonly treated, stopped buying emeralds as a result and the emerald market took a dive. Ever since, there is some apprehension about emerald treatments in general and the issue of emerald clarity enhancements is deemed a very complicated topic - mostly due to misinformation or lack of information.

The public discourse often centres around whether emeralds should be enhanced with resins or oil (in particular cedarwood oil), or which of the two is better. The current trend in the high-end trade is to prefer emeralds containing only oil (e.g. cedarwood oil) and no artificial resin (e.g. opticon) in fissures. As a consequence, many emeralds originally fissure-filled with artificial resin are cleaned chemically and eventually refilled later with oil, so that the visibility of the fissures remains reduced. Proponents of cedarwood oil argue that it is the most traditional way of enhancing the clarity of an emerald, and that it is a "natural" substance. Supporters of resins argue that they are more durable and have a refreactive index closer to that of the emerald.

This is actually not so much a topic in the scientific community: The consensus at the First World Emerald Congress (held in Bogotá in 1998) was that, since none of the fillers are permanent and emeralds can be cleaned and re-oiled, the actual type of filler does not matter. A more important indicator of quality is the degree of clarity enhancement as it determines how much an emerald's appearance could potentially deteriorate were the filler to disintegrate. As can be seen in the table on the previous page, there are natural resins and manmade resins, as well as natural and manmade oils, so the traditional distinctions are not very useful.

Mary L. Johnson in her work Durability Testing of Filled Emeralds chooses a better categorisation into soft (liquid) fillers, semi-hard fillers, surfacehardened fillers and hard fillers. It makes sense to group clarity enhancements into groups according to their viscosity, as the fillers within each group perform in a similar way, making it possible to generalise the findings.

In her work, the author describes research undertaken by the GIA laboratory, where researchers tested the performance of emeralds treated with different fillers by exposing them (along with unfilled emeralds) to common conditions of wear and cleaning: "All emeralds were held for about six years, and most were then subjected to one of the following durability tests: exposure to long-wave UV radiation (a component of sunlight), to mild heat and incandescent light in a display case, to five chill-thaw cycles, and to a desiccation environment; ultrasonic cleaning with either warm water or BCR; and *cleaning with steam or mild chemical solvents.* Changes were evident in about 35% of the filled emeralds after the mild exposure tests (i.e., time, UV radiation, display case); those with *liquid fillers were especially susceptible. The* desiccation environment made fissures visible in a majority of emeralds. Hard fillers damaged their host emeralds by expanding cracks during durability testing, while chill-thaw cycling extended cracks in both filled and unfilled emeralds. Emeralds with liquid fillers were most susceptible to appearance changes due to ultrasonic cleaning and exposure to ethanol or acetone."

The fillers chosen to represent the four different groups of clarity enhancements were as follows:

1. *Soft (liquid) fillers*: Araldite 6010 ("Palma"), cedarwood oil, unhardened Opticon 224, and paraffin oil

Semi-hard (slow-flowing and possibly solidifying) fillers: the 50:50 mixture of cedarwood oil and Canada balsam
 Surface-hardened fillers: Norland Optical Adhesive 65 (NOA 65, a long-wave UV-setting adhesive, typically used fully hardened, but surface-hardened in the study) and Opticon 224
 Hard fillers: Gematrat and Permasafe

All clarity enhancements were affected by desiccation tests, which suggests that treated emeralds, like opals, should not be kept in very dry conditions.

Soft (liquid) fillers are most susceptible to the passage of time and to changes in environmental conditions. Intuitively this makes sense. They are also easily cleaned just using ethanol. For other groups of fillers acetone is required and in the case of hard fillers even acetone is not strong enough.

Hard fillers are quite durable, but, most notably, the samples suggest that hard fillers may cause appearance changes —or even damage emeralds—without being subjected to particularly harsh circumstances.

With respect to the issue described at the outset, whether oils or resins are superior, it can be said that resins and oils behave very similarly. Moreover, both resins and oils used for oiling emeralds are usually synthetic, even in the case of cedar oil, thereby neutralising the argument that one filler is more natural than another.

The quality of the original gemstone that requires clarity enhancement will often determine the choice of appropriate filler:

- a gem quality stone that hardly requires any enhancement, could be oiled with cedar oil, because even a deterioration in the oil will hardly affect the stone's appearance

- a bracelet of emerald beads or cabochons of minor quality, which will be subjected to heavy wear and tear might require a more durable filler, hence a hardened resin or polymer might be an appropriate choice.

Gemological laboratories report that nowadays often more than one filler, or a mixture of fillers is detected in emeralds, and rarely ever only one single substance. This could be intentional (in order to improve stability of the filler), or it could be the result of re-oiling with a different substance, when the stone has not been cleaned between treatments.

Disclosure of treatments is key in establishing trust and only with a thorough understanding of the subject can jewellers educate the consumer and dispel any concerns or myths. Emerald dealers should be able to confirm, if possible even in writing, the type of filler that has been used. If they are unsure, this could indicate that they are further down the value chain buying from other importers and that they may have had little control over the journey the emerald has taken. Possibly, they are not the owners of the emerald, but merely an intermediary, or they simply do not have their own oiling facilities and have this task performed by a third party. If the dealer you are buying from is unwilling to tell, it could also mean that the seller is trying to hide the nature of treatment, in which case caution is advised.

Clarity enhanced emeralds require some maintenance, in the same way that jewellery is occasionally cleaned of watch batteries replaced. Jewellers can explain the benefits of "oiling," and offering a service to re-condition emeralds, they can take a positive approach to a subject that is often avoided. With proper care, treated emeralds can last a lifetime.

At Monteverde Emeralds we only ever sell natural emeralds that are untreated or that have been treated with a generally accepted, liquid filler that is easy to remove.

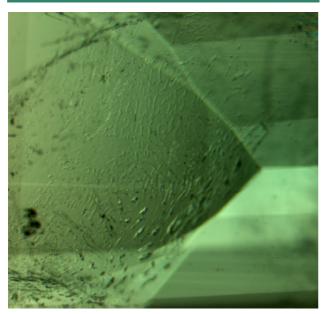
Note: Never clean emeralds with acetone, vapour, soap, or ultrasound! The former may remove or at least impact the clarity enhancement while the latter may break the gemstone. Emeralds are best cleaned with a water-dampened, soft cloth. Common sense indicates it is not a good idea to wear an emerald ring during gardening, dish-washing or any intense physical activity.



Identification of Emerald Clarity Enhancements

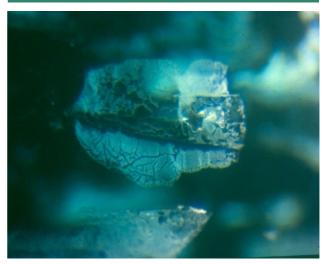
If the emerald displays cracks and fissures but does not look visibly impaired, then it is very likely that some sort of oiling has taken place. The filled cavities can be identified under magnification and darkfield or surface-reflected illumination. The recognition of clarity enhanced emeralds and the identification of these treatments can be performed by a variety of means.

Using conventional optical methods, such as a microscopic examination, it is often possible to recognise whether an emerald has been oiled, though not which type of filler is present. If air bubbles have formed within the oil or resin, their existence will give away the position of the fissures that have been filled.



Typical "fingerprint-like" structures of artificial resin, photo courtesy of DSEF, Dr C.C. Milisenda

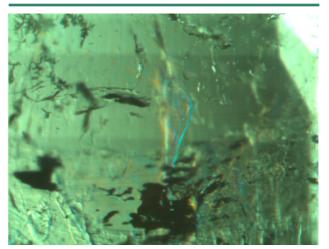
Whether the emerald has been treated with oil or resins, it can be assumed that the filler will change over time. Organic substances can change colour or clot, which means their structure changes and they become less transparent. If this has been the case, these typical alterations in filled fractures and channels can be observed under a microscope. In particular oils tend to dry out over time, leaving residues that are easily spotted. When the emerald has been subjected to heat - for example during the jewellery making process - sometimes part of the filler burns away, leaving dark little burn marks that can be spotted.



Reflecting residues of artificial resin in reflective light , photo courtesy of DGemG, Dr. Ulrich Henn

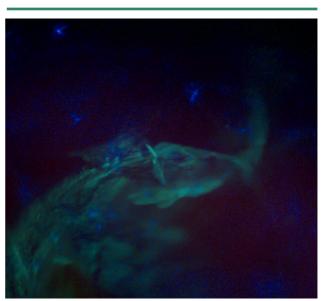
Sometimes, green coloured oils are used on very pale stones (note that this is not at all an accepted practice and it requires special disclosure!). Under a microscope, concentrations of colour on fracture surfaces are easily recognised. It is possible, but uncommon, to use immersion microscopes in the examination of emeralds and their clarity enhancements. The immersion into an oily liquid itself will result in the emerald being oiled during the examination process. Other liquids may act as solvents and attack the filler, which is also undesirable. When an immersion liquid with a refractive index close to that of the emerald (n=1.57) is used, then anything within the immersed stone should be visible to the degree to which its refractive index varies from that of the emerald¹. It is then possible to spot whether green dyes with lower refractive indices have been used together with the fillers. These will show up as patches of colour inside the emerald.

The "flash effect" is an important characteristic that can help identify whether an emerald has been oiled. When rotating the emerald in the light source, or changing direction of the light source, an orange, blue or multi-coloured flash can sometimes be observed. This is caused by interference or diffraction when the light passes through the layer of oil or resin. The flash effect will be more pronounced and colourful when there is a big difference between the refractive indices of the emerald and the filler medium. It will be weaker if the layer of filler is quite thick.



Orange-blue flash-effect, photo courtesy of DGemG, Dr. Ulrich Henn

Fluorescence is another give-away: Some, but not all, fillers can be spotted when pointing a long-wave UV-lamp (365nm) or laser beam (405nm) at the emerald. Canada Balsam, and less so mineral oil and Johnson's baby oil, will fluoresce yellow. "Palma" and Opticon will fluoresce white.



Fluorescence of a filler substance in laser light (405 nm – laser pointer), photo courtesy of DGemG, Tom Stephan

¹ Fracture-Filling of Emeralds: Opticon and Traditional "Oils", By Robert C, Kammerling, John I. Koivula, Robert E. Kane, Patricia Maddison, James E. Shigley, and Emmanuel Fritsch

Today, the most advanced and precise forms of examination performed in gemological laboratories are infrared spectroscopy and Raman-spectroscopy.

In infrared spectroscopy, the infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond or collection of bonds, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). Each compound has a typical fingerprint region where a pattern of many troughs can be observed. This pattern is unique to the compound encountered, thereby enabling identification of the compound that is present.

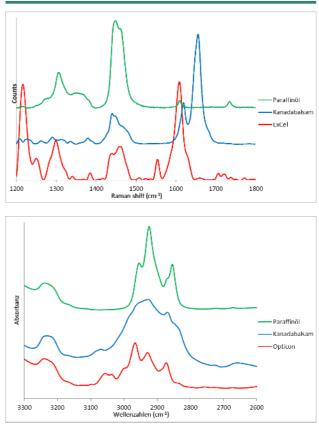
Raman spectroscopy is used in chemistry and physics to identify molecules, study chemical bonding and intramolecular bonds and characterise materials. In a nutshell: A low-energy laser beam is directed at the emerald. The vast majority of light radiation passes through the sample or is reflected/scattered without interacting with the molecules, thereby not yielding any additional information (elastic scattering). However, a very small portion of the light interacts with the molecules of the sample and is scattered in a way that is typical for the material in question (inelastic scattering). What happens precisely is that a photon hits a molecule and this molecule briefly passes from its normal state of vibration into a higher state of vibration. When the molecule falls back to its normal state of vibration, it emits a photon that may have a lower or higher energy level than the photon that entered, depending on whether energy is absorbed or freed in this process. This shift in energy between incoming and outgoing photon is unique for each material in question and serves like a fingerprint. The spectral properties of the inelastically scattered light can be measured and each material has known characteristic peaks in certain areas of wavelengths. When the light beam passes through several substances, the resulting spectrum will show peaks characteristic of all of these substances.

In gemology, both of these techniques are non-destructive ways to determine types of gemstones, their inclusions, and the fillers in cracks and fissures. When emeralds are examined, the spectrum will show peaks that are typical of the emerald and peaks that can be attributed to the filler that is used for clarity enhancement. Each filler has certain characteristic peaks that act as a fingerprint.

Using these methods, it is possible to determine the exact type of clarity enhancement used by observing the spectral properties. In Raman-spectroscopy, the Raman-shift in the spectral areas between 1200 - 1800 cm⁻¹ and 2700 - 3200 cm⁻¹ is particularly suitable for examination as this is where the fillers exhibit their characteristic peaks and there is no "interference noise" from the beryl peaks.

In infrared-spectroscopy, particular attention is given to wavelengths in the spectral area between 3300 – 2600 cm⁻¹, because emeralds are highly transparent in that area and this is where the fillers display their specific characteristic peaks. In addition, the fillers tend to be quite infrared-active, which - in most cases makes the determination between oil or resin relatively straightforward.

The essay "On the Identification of Various Emerald Filling Substances" by Mary L. Johnson, Shane Elen, and Sam Muhlmeister in Gems & Gemology (Summer 1999) is a very complete scientific work on the subject.



Top: Raman-spectra of different filler substances in emerald in the spectral area from 1200 – 1800 cm-1 (green = paraffin oil, blue = Canada balm, red = ExCel);

Bottom: Raman-spectra of different filler substances in emerald in the spectral area from 2700 – 3200 cm-1 (green = paraffin oil, blue = Canada balm, red = ExCel); Photos courtesy of DSEF, Stefan Müller



Having covered in depth the topic of emerald clarity enhancements, it must also be mentioned that some at best dubious practices have also been employed at times and mostly not with the best intentions. They have had a profound effect on the industry and brought it into disrepute as they were not disclosed at the time.

<u>Dyes</u>

Adding green-coloured dyes to the liquid that is used for clarity enhancement, it is possible to visually "improve" the colour of low grade emeralds or even colourless beryl so that they would pass as emeralds of better quality. Between reputable dealers, this is a strictly forbidden and unethical practice. It would ruin your reputation in the market permanently if you were found to engage in such fraudulent activity and not disclose it. Clarity enhancements should always be close to colourless. Using coloured substances is absolutely not acceptable and must be declared! Nevertheless, sometimes, it is still possible to come across dyed emeralds - not so much in Colombia, but sometimes in Brazil and more often in the Indian subcontinent. While both oiling and dyeing serve the same purpose of improving the looks of emeralds, the practice of dyeing alters the inherent colour of the emerald and thus dramatically alters

the perceived value of the stone in question. Anything other than colourless liquids used in the oiling of emeralds has to be disclosed, or it is considered fraud. Luckily, it is not too difficult to spot this alteration with experience and with the help of gemological instruments, such as a loupe with 10x magnification: Concentrations of colour can be noticed in the filled fissures.

Perma-treated Rough Emeralds

Permanente ("Perma"), or Permasafe has been mentioned above as one of the common fillers used in the clarity enhancement of emeralds. In theory, Perma is actually a very good filler, as it is extremely durable, and it has a refractive index close to that of the emerald. But it is the misuse of Perma that has brought it into disrepute. Much of the rough emerald material that leaves the mines is of low quality. Some of it of such low quality that it could not even be facetted because of a multitude of cracks and inclusions. Some miners soak these rough emeralds in Perma, which is such a strong filler that it is then possible to cut and polish the rough material into facetted emeralds. The bond created by Perma will hold it together and the filler itself is not impacted by the procedure. The emerald resulting from such a process looks like any normal

emerald to the bare eye. The problem arises when Perma, like any other filler, deteriorates after a long period of time. When it is then attempted to clean and reoil the emerald, the gemstone will fall into its composite pieces once the Perma is removed, thereby destroying the emerald irrevocably. Often, this will only be discovered many years after the stone has been set and the jewellery sold. The unsuspecting consumer or goldsmith then have very little possibility to prove that they have been the victim of a fraud. To the trained eye it is again easily possible to spot if an emerald might have been treated with Perma in its rough state: with a loupe (10x) it is possible to see fine cracks and hairlines on the surface of the emerald that can be followed all the way around the gemstone. The technical term for such an emerald is "composite emerald". When a gemological laboratory recognises such a stabilising effect of the filler on the emerald, this will be mentioned in the gemological report and it will have a significantly value-reducing effect on the price of the gemstone.

Even before the arrival of the more recent Perma, some fraudulent characters in the gemstone business have tried this with epoxy resins. As a result, the term "epoxy resin" sends alarm bells ringing in the consumers' minds who are unaware that an epoxy resin without hardener is merely the liquid pre-polymer. This has probably been one of the most damaging practices to the emerald trade, as misconceptions about "emeralds that are glued together" still prevail today and have brought all resins across the board into disrepute.

DOUBLETS AND SYNTHETIC EMERALDS will not be covered in this report on emerald oiling.

Emerald Certification Standards

Gemstone certificates offer peace of mind and play an important part in establishing trust. It is therefore important to rely on a reputable institution to offer such certificates and to have harmonised standards to achieve comparability.

Laboratory reports only evaluate and indicate the degree of apparent enhancement that the filled features represent; they do not take into account inherent inclusions, such as mineral crystals, or primary and secondary fluid inclusions and they do not give an overall "clarity grade" of the emerald.

Most laboratories will not specify in writing on a report or certificate, which type of filler has been used as a clarity enhancement. Firstly, it is pointless to specify which treatment has been used, because the emerald could be cleaned and re-treated with a different filler after certification. Secondly, it is nowadays often observed that — unintentionally or intentionally — a mix of fillers is present in fissures and it is rare to encounter emeralds that have only been treated with a pure filler. Thirdly, distinctions can be made in some cases for "pure" fillers, but the detection of one substance in a fissure does not prove that all others are absent. Laboratories only state what can be said with 100% accuracy. Missing one fissure

that has been filled with a different type of clarity enhancement could lead to doubts over the laboratory's competence and taint its reputation.

In Europe, DSEF (Germany), Gübelin and SSEF (both Switzerland) have for many decades achieved high standards and have a high reputation in certification and teaching. DSEF, being based in the European gemstone capital of Idar-Oberstein has access to many dealers and has certified a large number of emeralds from various sources. They dispose of a large gemstone collection and state-of-theart teaching facilities. Gübelin and SSEF, being based in the jewellery hub of Switzerland analyse and certify many fine Colombian emeralds that are later used by the top jewellery houses in the world.

In the US, the GIA has done an enormous amount of scientific work on the study of emeralds and on educating gemstone professionals. They inspect and certify many of the emeralds coming out of Colombia and from other sources. One of their former gemologists, Ronald Ringsrud, pioneered research into emerald treatments and has subsequently successfully entered the dealing market, where he gained a high reputation. The GIA Gem Trade Laboratory has developed its own system of colour and quality grading emeralds, using the

diamond clarity grading system as a framework. However, the emerald clarityenhancement classification system is distinctive from the system for diamond clarity grading. While the latter incorporates all inclusions, the categories in the emerald clarity-enhancement classification system consider only *filled fissures* and other *surface-reaching features* in a stone — it is a visual assessment of their number, size, and extent relative to the size of the stone, and where they are located. For example, a small filled fissure directly beneath the table of an emerald would have a greater impact on the appearance of the stone than a larger filled fissure along the girdle, and thus the smaller fissure could result in the stone receiving a more severe enhancement classification.

The World Jewellery Confederation, CIBJO, aims to harmonise industry standards and protect the confidence of consumers in jewellery products. The CIBJO Blue Books are definitive sets of grading standards and nomenclature for among others — coloured gemstones and gemological laboratories. According to the current CIBJO-standards, emeralds which have been clarity enhanced with a nearly colourless organic substance, which does not improve the colour, are classified as gemstones requiring general information about their treatment. If the fissure or cavity fillings are detectable by a trained observer with a 10x magnifying loupe

because of a different surface luster in comparison to the emerald itself, then the treatment has to be classified as a specific information. The same is valid for dyeing.

DEUTSCHE STIFTUNG EDE	LSTEINFORSCHUNG (DSEF)		
GERMAN FOUNDATION FO	BERSTEIN		
Edelsteinbefundberic	ht – Gemstone Report		
Origina	025814		
Datum - Date	15.04.2016		
Untersuchungsobjekt - Item	One transpurent, cut, green stone		
Beschreibung - Description			
Sohliffart - Cut	Seep cui		
Schlifform - Shape	Octagon		
Abmessungen - Measurements	8.46 x 8.29 x 6.76 mm 2.78 ct.		
Gewicht - Weight	2.76 ().		
Ergebnis - Result	Natural Beryl		
	Variety: Emerald		
Bemerkungen - Comments	Indications of minor clarity enhancement		
	Emeralds are commonly clarity enhanced		
	Origin: Colombia		
	Deutsche Stiftung Edelsteinforschung (DSEF)		
	German Foundation for Gemstone Research		
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Gemstone Report by DSEF

Previously, laboratories located in different continents and markets were using their own report wording and language to describe the results of their testing and analysis. Owing to the global nature of the trade, there was a need for greater harmony in the wording used in gemological laboratory reports. This issue is addressed by the Laboratory Manual Harmonisation Committee (LMHC), which is comprised of representatives from laboratories located in Europe, USA and Asia, among them:



- the DSEF German Gem Lab in Idar
 Oberstein, Germany²
- the GIA Laboratory (USA)
- the G
 übelin Gem Lab Ltd. in Lucerne, Switzerland
- the Swiss Gemmological Institute -SSEF, located in Basel, Switzerland

The LMHC Information Sheet #5: "Emerald – fissure filling/clarity enhancement"³ standardises the nomenclature that these institutes use to describe an emerald. The gemological laboratories, which are member of the Laboratory Manual Harmonisation Committee, divide the following categories on their certificates:

"Emerald - indications of fissure filling/ clarity enhancement"

For these gemstones, the mineral species "(Natural) beryl" with the variety "emerald" is stated on the certificate, together with the remark: "fissure filling" or "indications of clarity enhancement/modifications" as well as a quantification of the clarity enhancement, according to the following categories: "indications of minor (F1) / moderate (F2) / significant (F3) clarity enhancement/modification".

- "Emerald indications of cavity filling" If additionally cavities or hollow spaces are filled with filler substances, then another information appears in the certificate: "minor" / "moderate" / "significant" amount of resin/wax in cavities" and/or the alphanumeric description C1/C2/C3.
- "Emerald indications of coloured fissure filling/clarity and colour enhancement"

In this case, the comment "Coloured filler in fissures/fractures" or "Indications of clarity and colour enhancement/modification by a coloured substance" as well as the grade of enhancement appears in the certificate. Additionally the variety is described as treated.

"Emerald with/and resin"

Where the original emerald rough have been stabilised with artificial resin before the cutting process, these stones are described as "Manufactured product" or "(Natural) beryl with/and resin". Additionally the variety could be declared as "Emerald with/and resin". As a comment, it is written "This stone is a combination of resin and emerald".

² At Monteverde Emeralds, we primarily work with DSEF, GIA or Gübelin for certification, depending on clients' preferences.

^{3 (}http://www.lmhc-gemology.org/pdfs/IS5_20121209.pdf)

EMERALD TREATMENTS - SUMMARY

- Nearly all emeralds are 'oiled' to improve their appearance. Clarity enhancement is the technical term. This practice is commonly accepted.
- * Surface-reaching fractures are filled in a process involving heat and pressure.
- * A clarity enhancement liquid should have a refractive index close to that of the emerald, be relatively durable, but easy to remove and be colourless.
- The quality of an emerald will depend primarily on colour, then clarity, cut and carat weight - the oiling affects mainly clarity, but also the way colour is perceived.
- A "normal" oiled emerald will display evidence of "moderate" clarity enhancement. Between two otherwise identical emeralds, the one with less treatment is more valuable, but the absence of treatment does not per se make a low quality emerald valuable.
- The most commonly used substances for oiling emeralds are today all synthetically produced. Each treatment has its use. Disclosure is key!
- Liquids used for clarity enhancements are usually oils (natural or synthetic), liquid resins (pre-polymers, natural or synthetic) and manufactured polymers. They can be further categorised into soft (liquid) fillers, semi-hard (slow-flowing and possibly solidifying) fillers, surface-hardened fillers and hard fillers.
- All emerald treatments can be reversed and the stone be put back into its original state. All fillers deteriorate over time and emeralds require re-oiling.
- Each filler can be identified in a gemological laboratory. Gemstone certificates will state the degree of enhancement and provide comfort that no fraudulent practices have been used.

Physical Properties of Filler	Chemical Classification of Filler	Examples	Natural / Synthetic	Durability	Refractive Index	Cleaning
Liquid	Oil	Cedarwood Oil Paraffin Oil	N/S S	low	1.49 - 1.51 1.45 - 1.49	Ethanol / Acetone
	Resin	Canada Balsam Palma Unhardened Opticon	N / S S S	medium	1.52 - 1.55 1.573 1.545	Ethanol / Acetone
Semi-Hard	Oil / Resin - Mix	50/50 Cedar Oil & Canada Balsam	N/S	medium	~1.51 - 1.53	Ethanol / Acetone
Surface- Hardened	Resin	NOA 65 Opticon	S S	high	1.525 1.545	Acetone / Acid
Hard	Polymer	Permasafe ExCel	S S	very high	1.56 - 1.60 1.52 - 1.60	Acid



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