ON THE IDENTIFICATION OF VARIOUS EMERALD FILLING SUBSTANCES

By Mary L. Johnson, Shane Elen, and Sam Muhlmeister

Criteria for distinguishing emerald filling substances were investigated. Thirty-nine fillers were divided into six substance categories—three "presumed natural" (essential oils [including cedarwood oil], other oils, waxes) and three "artificial resin" (epoxy prepolymers, other prepolymers [including UV-setting adhesives], polymers). Regardless of their composition, fillers with R.I.'s of 1.54 or above show flash effects in emeralds. On the basis of Raman and infrared spectroscopy, the fillers could be separated into five spectral groups, A through E. Most, but not all, commonly used artificial resins have spectra distinct from that of cedarwood oil. However, the detection of one substance in a fissure does not imply that all others are absent.

ABOUT THE AUTHORS

Dr. Johnson is manager of Research and Development, and Mr. Muhlmeister is a research associate, at the GIA Gem Trade Laboratory in Carlsbad, California. Mr. Elen is a research gemologist at GIA Research in Carlsbad.

Please see acknowledgments at the end of the article.

Gems & Gemology, ***Vol. 35, No. 2, pp. 82ñ107***

© 1999 Gemological Institute of America

The vast majority of emeralds on the market today have undergone clarity enhancement; identification laboratories estimate that about 90% of the emeralds they see (most of which are high quality) have been clarity enhanced in some fashion (Genis, 1997; Hänni et al., 1997). In recent years, however, there has developed a growing need to reach a consensus on acceptable trade practice regarding such clarity enhancements, and to find appropriate ways to disclose this information in the marketplace.

If clarity enhancement is a cause for concern, why is it done? For one thing, as they are recovered, most emeralds have many fissures (see, e.g., Sinkankas, 1981; Ottaway et al., 1994). In addition, there are many more potential emerald buyers with high expectations of color and clarity (see, e.g., figure 1) than there are untreated gems to satisfy this demand. Filling substances that almost match the refractive indices of the host emerald make the fissures less noticeable, especially to the unaided eye (figure 2). Even colorless fillers improve the color appearance: The light that would scatter from an unfilled fissure (and thus lighten the apparent color) is no longer visible (Ringsrud, 1983).

Major colored stone trade organizations—such as the International Colored Gemstone Association (ICA) and the American Gem Trade Association (AGTA)—as well as the international jewelry organization CIBJO, recommend that gemstone treatments be disclosed at every stage of the distribution process. However, the trade continues to debate exactly what should be disclosed and how it should be disclosed. In particular, emeralds are less salable in some markets if they are perceived to contain some filler substances such as "Opticon" (an epoxy resin) rather than others such as cedarwood oil. However, one proposal to distinguish "oiling" from enhancement with epoxy resins was voted down by ICA members as unworkable ("Congress votes. . . ,"

Figure 1. The desire for beautiful emeralds has fueled the practice of filling surface-reaching fissures with oils or resins. This jewelry demonstrates the irreplaceable beauty that emeralds provide. The 5.79 ct oval-cut emerald on the left is surrounded by 2.84 ct of diamonds, while the 5.40 ct emerald on the right is surrounded by 2.59 ct of diamonds. Rings courtesy of Henry Dunay; photo © Harold & Erica Van Pelt.

1995). In 1997, ICA decided to delay an emerald promotion due to lack of a consensus on the enhancement issue ("Review on ruby promotion," 1997).

A number of reasons have been given for the need to determine the nature of a particular filling material. First, there is the growing body of anecdotal evidence that various fillers "age" differently, thus changing the appearance of the enhanced emerald over time. For instance, Ringsrud (1998) reported that the artificial resin "palm oil" (also called "palma") turns white within a few months in about 20% of the emeralds filled with this substance. Federman (1998a) noted that "traditional" natural oils and resins (such as cedarwood oil and Canada balsam) could dehydrate or leak out. Kammerling et al. (1991) experimentally determined that Opticon treatment was somewhat more durable than cedarwood oil and Canada balsam, but that all three treatments were affected by routine cleaning and jewelry-manufacturing processes. In addition, due to the variety of growth conditions, emeralds from different localities may not respond similarly to the same filler. Last, different cultures may find some fillers more acceptable than others.

The purpose of this article is to critically evaluate the effectiveness of various methods for distinguishing among clarity-enhancement substances. The main methods currently in use are the "flash effect" (usually seen with magnification), Raman microspectrometry, and infrared spectroscopy. This investigation is part of an ongoing study of emerald fillers; other aspects of emerald enhancement will be addressed in future articles.

HISTORICAL BACKGROUND

Clarity Enhancement in Emeralds. Emeralds from all sources generally contain fissures, and emerald processing (e.g., mining, fashioning, and jewelry manufacturing) can add fractures as well. The filling of such surface-reaching features (hereafter called fissures) to make them less visible has been practiced for centuries. The first description of "oiling" of green gems (probably turquoise, but possibly emeralds) was made by Pliny the Younger in about 55 AD. At least by the 14th century, reference was being made to the oiling of emeralds in particular (Nassau, 1994).

The first references to emerald treatments and their detection in the gemological literature are much more recent. Nassau (1994) cites the sixth edition of Liddicoat's *Handbook of Gem Identification* (1962) as the first gemology book to mention oiling, although it was occasionally mentioned earlier in *Gems & Gemology* (Crowningshield, 1958, 1960–1961; Benson, 1960). Subsequently, *Gems & Gemology* published two comprehensive articles describing some of the techniques and substances used to "clarity enhance" emeralds (Ringsrud, 1983; Kammerling et al., 1991). Hänni (1988) described the detection of filled fissures.

Disclosure. We examined records from two major auction houses, Christie's and Sotheby's, and found that disclaimers regarding filling substances in emeralds were first published in November 1992 (Sotheby's, 1992a, 1992b) and November 1993 (Christie's, 1993). The clarity enhancement of a particular emerald was first noted in October 1993 (Sotheby's, 1993). Although various classes of possible filling materials—oil, natural resin, and artificial (or synthetic) resin—were noted in these early disclaimers, the specific substance categories were not disclosed for *individual* emeralds (see Box A for a discussion of filler substance classification). The disclosure statements were made more explicit in early 1997 (Federman, 1997). However, specific "types" of enhancements (e.g., "oil type") were first noted in October 1997 (Christie's, 1997a).

Clarity Enhancement Substances. Although there is almost universal agreement that most emeralds need some treatment to be salable, there is still little agreement as to which filling substances are acceptable and why one substance is preferable to another. A good filling substance should have certain properties: It should hide fissures, it should flow into the fractures (i.e., be liquid, at least initially), it should hold up over time or else be easy to restore, and it should be removable or not have any physical properties that might later harm the stone (e.g., during jewelry repair or repolishing). It should also have an R.I. similar to that of the stone being treated.

Several substances have been used by the trade to fill fissures in emeralds. M. Kostetski (pers. comm., 1999) used linseed oil as an emerald filler in the 1930s through 1960s, and C. Altobelli (pers. comm., 1999) used rapeseed oil (now usually called canola oil) from the late 1940s onwards. Crowningshield (1958) mentioned "3-in-1 penetrating" oil, whale oil, and mineral oil. Ringsrud (1983) noted clove oil in addition to Merck cedarwood oil and Merck Canada balsam. Hänni (1988) mentioned also sperm whale oil, paraffin, and an unspecified artificial resin. Kammerling et al. (1991) noted that cedarwood oil and Canada balsam were considered "traditional" filling materials, with Opticon 224 resin (generally only surface hardened) as a newer substitute. Kennedy (1998) described clarity enhancement of emeralds in Brazil: Although baby oil and cedarwood oil ("cedro") were mentioned, Brazilian goods were usually treated with "Opticon." (It is important to remember that, as Federman [1998b] cautioned, not all epoxy resins are Opticon, which is a specific substance with a registered trade name; nevertheless, "Opticon" is often misused as a generic term in the trade.) Ringsrud (1998) wrote that a "synthetic resin" known as "palm oil" was used heavily in Colombia from 1990 to 1996. Three widely discussed enhancement substances at the present time are cedarwood oil, Opticon resin, and "palm oil" (Box B).

In fall 1997, we asked 33 emerald dealers worldwide to tell us which emerald treatments they were aware of. We received 12 responses (one each from Israel, Italy, and Switzerland, and the rest from the U.S.). Each of the following substances was mentioned by at least one dealer: "natural and synthetic oils and resins," Opticon 224 resin (with or without hardener), green-colored oil, wax, paraffin, "cedarwood oil with hardener," "WD 40," Joban oil, "Yehuda treatment," Arthur Groom–Gematrat treatment, linseed oil, epoxy fillers, and plastic sealers.

To many, the most important distinction is that between oils and artificial resins. As summarized by Chalain et al. (1998): "the use of artificial resins to fill emeralds has only been significant in the last fifteen years. . . . Unlike oils, artificial resins act to 'consolidate' emeralds. . . . It is easy to replace oil that oozes out, but hard to get rid of altered resins." *The Guide* reported that 64% of the dealers surveyed at Tucson in February 1997 thought that the clarity enhancement of emeralds with colorless oil was acceptable, while fewer than 48% found "Opticon" treatment acceptable ("Survey: Emerald treatments," 1997). However, no "natural" filler currently in use is found within emeralds *in nature*; all are added during clarity enhancement (Genis, 1997).

From our discussions with members of the trade, we also know that certain fillers are used not only individually, but in mixtures as well. For example, treaters have experimented with mixtures of Canada balsam and cedarwood oil (Ringsrud 1998) to see if an "all-natural" material can replace cedarwood oil as an emerald filler. Such experiments were prompted by reports of a change in the viscosity of Merck cedarwood oil, which had been evident since the late 1980s (as reported by Johnson and Koivula, 1998b). It is also possible that mixtures of oils and artificial resins have been used.

In addition, many stones have undergone several generations of enhancement (i.e., treatment, cleaning, and re-treatment—sometimes with a new substance). Residues of earlier treatments may be left deep within an emerald. This further complicates the identification process (H. Hänni, pers. comm., 1998; C. Smith, pers. comm., 1999).

Previous Work on Characterizing Fillers. Gemological determination of clarity enhancement in emeralds has been described by GIA researchers

Kammerling et al. (1991) and Johnson et al. (1998a), as well as in several *Gems & Gemology* Gem Trade Lab Notes (see, e.g., Fryer et al., 1984; Hurwit, 1989; Kane, 1990; Kammerling, 1993; and Kammerling et al., 1995). One distinguishing feature is the "flash effect" seen with magnification in some filled emeralds, which is similar to that seen in fracture-filled diamonds (Kammerling et al., 1994).

Two relatively recent technological advances have made possible the characterization of specific filling materials within gemstones. The first was the development of a Raman spectrometer designed for gemological use (the Renishaw laser Raman microspectrometer; see, e.g., Hänni et al., 1996a). The second was the adaptation of Fourier-transform infrared (FTIR) reflectance spectroscopy to probe *within* an emerald (see, e.g., Zecchini and Maitrallet, 1998).

In 1994, the Asian Institute of Gemmological Sciences (AIGS; Bangkok, Thailand) was among the first gemological laboratories to use a Raman microspectrometer for gemological characterizations. The Raman spectra of Opticon 224 prepolymer and polymer, and several other fillers, were presented at an ICA-organized meeting in Bangkok in 1994 (K. Scarratt, pers. comm., 1999). Mr. Scarratt currently offers filler identification services at the AGTA Gemological Testing Center, in New York City.

The SSEF Swiss Gemmological Institute has been particularly open in sharing the criteria that they use for filler identification (see, e.g., Hänni et al., 1997; Hänni, 1998; SSEF Swiss Gemmological Institute, 1998; Weldon, 1998b). The techniques employed by SSEF include microscopy, observations of fluorescence, reflectance infrared spectrometry, and (since 1995) Raman microspectrometry. Hänni et al. (1996a) described four substances that are used to fill emeralds: cedarwood oil, an artificial resin, "universal oil," and a wax. Since 1988, SSEF has examined at least 13 different artificial resins (seven epoxy and other hardening resins, and six UV-setting resins; Chalain et al., 1998).

Zecchini and Maitrallet (1998) have used reflectance infrared spectroscopy to characterize eight potential emerald-filling materials and two related substances, both as loose materials and as fillers in emeralds. This research team represents a collaboration between the Université de Franche-Comté and the Service du Contrôl des Diamants, Pierres et Perles of the Paris Chamber of Commerce.

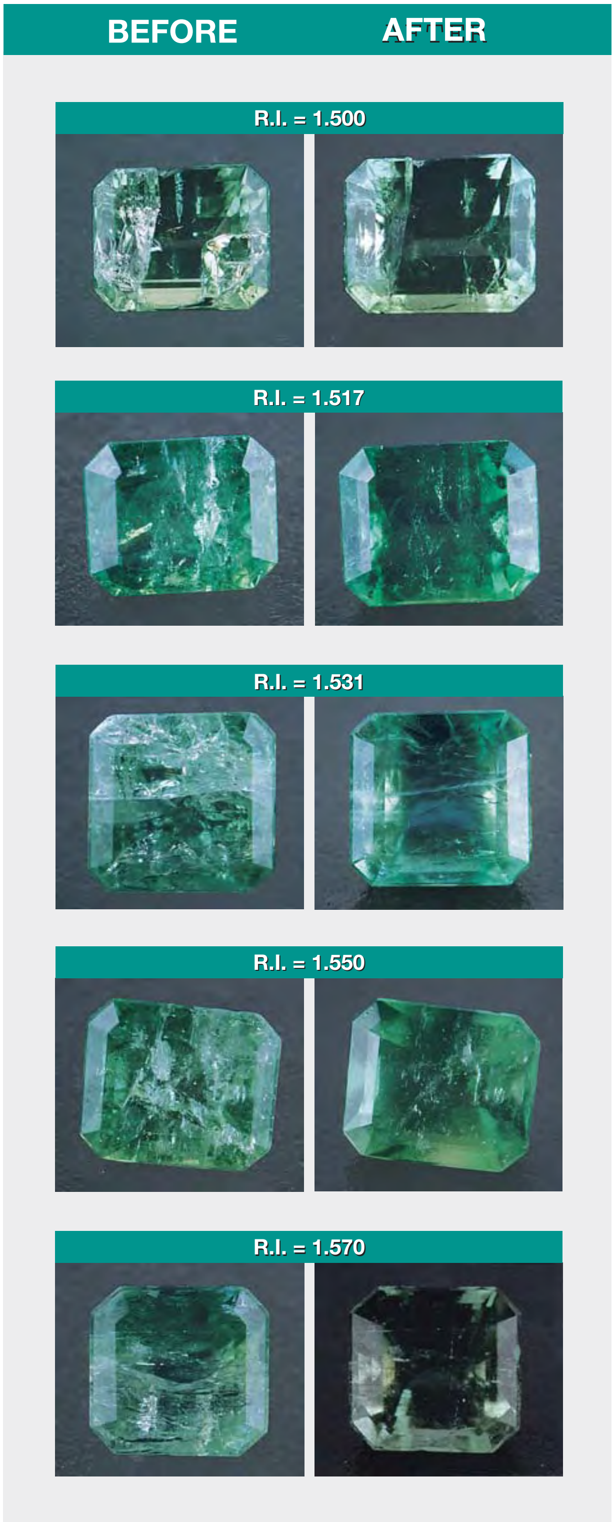


Figure 2. These before-and-after photographs illustrate that the fissures in emeralds become less visible as the R.I. of the filling material increases. Shown are fillers with R.I.'s of 1.500, 1.517, 1.531, 1.550, and 1.570. The refractive indices of the five emeralds ranged from 1.569 to 1.580. Photos by Maha DeMaggio.

BOX A: CLASSIFICATION OF FILLING SUBSTANCES: OILS, ESSENTIAL OILS, RESINS, PREPOLYMERS, AND POLYMERS

Several substances have been used in the clarity enhancement of emeralds. Some are called "oils" (e.g., Cedarwood, paraffin, whale, 3-in-1, "palma"), and some "resins" (e.g., Canada balsam, unhardened Opticon 224). Since the substances used to fill emeralds originally come from various branches of chemistry (from perfumes to polymers), with somewhat different definitions for each field, it is important to create a consistent terminology for use by gemologists.

The following definitions are taken from technical and popular dictionaries, including *Webster's Ninth New Collegiate Dictionary* (Webster's, 1987) for "everyday" English; Stecher et al. (*The Merck Index*, 1968), Alger (1989), and Brady and Clauser (1986) as general chemical and technical dictionaries; Sivry (1985) for European usage; Elias (1993) and Lee and Neville (1967) for plastics; Herout (1982) for perfumes; and Mutton (1982) for the wood products industry. Information on the trees from which certain filling materials are derived is from Lincoln (1986).

OIL

Oil originally meant olive oil, which is not generally used in emeralds today. Its common meaning is one of "numerous unctuous combustible substances that are liquid or at least easily liquefiable on warming, are soluble in ether but not in water, and leave a greasy stain on paper or cloth" (Webster's, 1987). However, *oil* means one thing to petroleum chemists, who use it to refer to long-chain hydrocarbons of a certain weight (e.g., paraffin oil); something else to cooks and nutritionists, who use it to refer to triglycerides (e.g., olive oil, sesame oil); and something else again to perfume chemists, who use it to refer to essential oils (e.g., cedarwood oil, clove oil; see below).

Essential Oils. Some compounds—such as cedarwood oil—are "essential oils." These compounds are extracted from their host plants using solvents. According to the *Polymer Science Dictionary* (Alger, 1989), "an essential oil is the predominantly volatile material isolated by some physical process from an odorous single-species botanical. Over 3000 oils have been identified. . . . Essential oils are generally liquid at room temperature; however, some are semisolid and several are solid. . . . Essential oils are made up of carbon, hydrogen, and oxygen, and occasionally nitrogen and sulfur. . . . It is not uncommon for an essential oil to contain over two hundred components."

The main components of many essential oils have been synthesized (again, including cedarwood oil—see, e.g., Stecher et al., 1968), and commercial essential oils may be partially or wholly synthetic. Because of their volatility, open containers (such as an emerald) of essential oils *cannot* be stable over time, since the fragrant components are continuously lost to the atmosphere (or they would not reach our noses, to be smelled).

Other Oils. Because "essential oils" differ from "other oils" (such as mineral and vegetable oils) in many respects (volatility, viscosity, chemistry, and infrared and Raman spectra), we have treated these as separate categories when reporting the results of our research.

RESIN

Resin originally meant pine sap. Today, *resin* can mean (at least) three different things: natural plant exudates (i.e., saps), either hardened or unhardened; hardened manufactured polymers; or the unhardened prepolymer "building blocks" that can be used to make manufactured polymers (Webster's, 1987; Stecher et al., 1968; Alger, 1989). Natural resins can harden (polymerize) over time (e.g., amber, copal). The emerald filler Canada balsam is generally considered a natural resin, and the essen-

MATERIALS AND METHODS

Almost every chemical product (including natural compounds and extracts) available in the U.S. has a Chemical Abstracts Service (CAS) registry number, and—if there is any possibility of a hazard associated with the material—a Material Safety Data Sheet (MSDS). Details about a chemical compound can be found in many databases if the CAS registry number is known; this is accessible on the World Wide Web at www.cas.org. (Another useful database, *ChemFinder*, is available at www.chemfinder.com.) The MSDS sometimes contains information on the color, odor, specific gravity, and other properties of the material.

Safety is an issue when working with any chemical substance: The MSDS discloses hazardous constituents and their associated risks. Many of the substances in this article pose slight-to-high acute (short-term) health risks. For the most part, they can affect skin, eyes, mucous membranes, tial oil cedarwood oil is considered a resin by the wood pulp industry (Mutton, 1982).

Polymers and Prepolymers. A *polymer* is a large molecule made up of repeating units of smaller molecules. The smallest such unit is a *monomer* (figure A-1). We prefer to use the term *prepolymers* for the small units that are assembled into polymers, since they could be either monomers or a few monomers attached together. They polymerize—or harden—with the use of a chemical catalyst, illumination, heat, or time.

Specific polymers and prepolymers are named after the parts of their chemical structures that attach these units together. Epoxy resins have two carbons bonded to each other and to the same oxygen; bonds in this *epoxide* group break in order for the prepolymers to be linked. Most artificial resins used to fill emeralds (e.g., Opticon 224, Epon 828, Araldite 6010) are based on one type of epoxy molecule, diglycidyl ether of bisphenol A (DGEBA). They are introduced into the emeralds as prepolymers, and then may be polymerized later. However, UV-setting adhesives, which are also used to fill gems, are based on different chemical compounds, usually methacrylates. These also polymerize, but their infrared and Raman spectra are different from those of the epoxies.

"Synthetic" versus "Artificial" Resin. Chemists use the term *synthetic* differently from gemologists: For a chemist, a synthetic chemical is one that was made from other chemicals, regardless of whether or not it has a natural analog; in gemology, only a material with a natural analog can be called a "synthetic." Some of the "natural" filler materials we examined contained synthetic ingredients (e.g., one of the cedarwood oils; see Box B), or were stated to be completely synthetic (Sigma cinnamon oil). We know of no nondestructive technique to determine whether a filler with a "natural" composition within an emerald is "completely" natural. As a consequence, we refer to the possibly natural materials in this article as "presumed natural," since there is no way to independently guarantee that they are completely natural.

The emerald trade frequently uses the terms *resin* or *synthetic resin* to refer to epoxy prepolymers and polymers such as Opticon 224, Epon 828, and Araldite 6010. As we have seen, both *resin* and *synthetic* are ambiguous. However, *artificial resin* is an unambiguous term that can be used for both liquid prepolymers and solid polymers.

WAX

Another material sometimes encountered as a filler (or luster enhancer) in gems is wax. This term originally meant "beeswax," but it now also includes various similar substances (Webster's, 1987) with higher molecular weights, on average, than oils. Common waxes include: beeswax, spermaceti (from the sperm whale), vegetable waxes, and mineral waxes (including paraffin wax; Brady and Clauser, 1986).

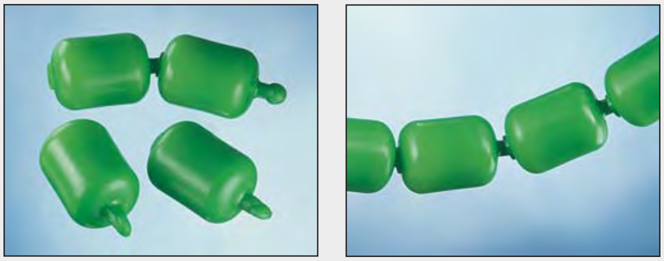


Figure A-1. Snap-Lock™ beads illustrate the concept of polymerization. Polymers are large molecules (right) made from smaller identical pieces—monomers (here, one bead) or other prepolymers (a few linked monomers; here on the left, two beads). Usually, prepolymers are liquid and polymers are solid. Photos by Maha DeMaggio.

and lungs; some can cause mutations in dividing cells; and most are flammable. Persons wishing to experiment with any of these substances should consult the relevant MSDS and follow recommended procedures scrupulously. Although most emerald filling substances present some health hazard to the experimenter, they are probably not dangerous to the ultimate consumer. (However, some people are allergic to cedarwood oil; Bleumink et al., 1973.)

Filling Substances. For this study, we chose fillers that we knew were commonly used in the trade (e.g., Baker and Merck cedarwood oils, Opticon 224 resin), some that have been used previously (e.g., clove oil; Ringsrud, 1983), some that were stated to be in use now (e.g., UV-setting adhesives; C. Osorio, pers. comm., 1998; D. Allen, pers. comm., 1998), and some that were easily available but not known to be in use (e.g., sesame oil, Epo Tek prepolymers). We selected the fillers in this last set because they

Box B: Cedarwood Oil, Opticon, and "Palm Oil" ("Palma")

Three of the most-discussed enhancement substances at this time are cedarwood oil, Opticon 224, and "palma." Cedarwood oil from one source (Merck) and Opticon 224 were profiled by Kammerling et al. (1991).

WHAT IS CEDARWOOD OIL?

Cedarwood oil is one of the most widely accepted filling substances today, both because it is perceived as a natural oil, and because it has a higher R.I. and viscosity than other traditional oils (e.g., linseed, rapeseed oil). Detailed information about this essential oil comes from the perfume industry (see, e.g., Herout, 1982), where it is used in the production of perfumes and soaps; it is also used in medicine and microscopy, and as an insecticide (Stecher et al., 1968).

Natural sources. Cedarwood oil is extracted from several coniferous trees, especially the junipers *Juniperus virginiana* (Virginia cedarwood oil), *J. procera* (Kenya cedarwood oil), and *J. mexicana* (Texas cedarwood oil), among others; however, some cedarwood oil is still produced from the true cedar *Cedrus atlantica* (Atlas cedarwood oil; Herout, 1982). Both Texas and Atlas cedarwood oils have the same CAS registry number, 68990-83-0, while most other cedarwood oils have the CAS registry number 8000-27-9.

Composition. Cedarwood oil is primarily composed of tricyclic compounds (molecules with three carbon rings), including cedrol, cedrene, and cedrenol. All these chemicals are synthesized, and commercial cedarwood oils may contain either the synthetic or natural compounds (or both) plus other (synthetic and/or natural) ingredients (Stecher et al., 1968; Herout, 1982).

We looked at five commercially available cedarwood oils from four different sources, all of which were suggested to us by individuals in the emerald trade. These were: Baker cedarwood oil for immersion, EM (Merck) cedarwood oils for immersion and for clearing, Shemen Tov (Texas) cedarwood oil, and "aceite de cedro" from Antonio Negueruela S.A.

We inquired about the composition of each cedarwood oil from its distributor, and received replies from Russell Lance at Mallinckrodt Baker Inc., Rande Klein at EM Science (Merck), Lee Saal at Shemen Tov, and Antonio Negueruela at Antonio Negueruela S.A. Because some of the information we received was proprietary, we will not describe their responses in detail. None of the distributors manufactured the cedarwood oil themselves, and all regarded their sources as proprietary. Three distributors stated that the material was all natural, but the fourth acknowledged a considerable amount (but less than 50%) of synthetic ingredients. Another distributor mentioned that their cedarwood oil also contained rosin (tree sap from which the turpentine has been distilled, according to Brady and Clauser, 1986) and a castor oil solubilizer. None contained Canada balsam. No distributor specified which species of tree the cedarwood oil came from, or the extraction technique used. Despite the differences in composition, four of the cedarwood oils had the same CAS registry number, 8000-27-9; the Shemen Tov (Texas) cedarwood oil had CAS registry number 68990-83-0.

We also asked the distributors to explain the difference between cedarwood oil for clearing and that for immersion. They replied that these have slightly different formulations because they have different uses in biological microscopy. Cedarwood oil for immersion has a higher refractive index (see table 1 in text), and is the substance typically used to fill emeralds.

Physical and Optical Properties. These are given in table 1 in the text; all were somewhat variable. Infrared spectra (figure B-1) were similar for all but the Merck cedarwood oil for clearing, which had a spectrum closely resembling the spectra of Norland Optical Adhesives 63 and 65. Raman spectra (also in figure B-1) showed small variations in detail, with the Baker cedarwood oil the most distinctive.

In short, there are many slight differences among cedarwood oils, as this substance is not a single chemical compound and it can come from several sources. Although some of these differences

fit into substance categories commonly used as emerald fillers and they have R.I.'s close to those of emerald.

Rather than refer to each substance individually, we sought to establish categories of related materials (e.g., oil, resin). However, when we looked into the definitions of these categories, we found ambiguity, both in the meanings attributed to specific are detectable within emeralds, we do not yet know if any are significant.

WHAT IS OPTICON?

The term *Opticon* should properly refer only to the epoxy resin Opticon 224, manufactured by Hughes Associates, Victoria, Minnesota. This artificial resin may be used in emeralds as a liquid prepolymer or a hardened polymer. The most common procedure (Kammerling et al., 1991) is to fill emeralds with liquid Opticon and brush the catalyst on the surface to provide a hardened surface layer. Because Opticon 224 is a DGEBA (see Box A) epoxy resin, it cannot be separated easily from other DGEBA resins by spectroscopic means, especially when it is within an emerald.

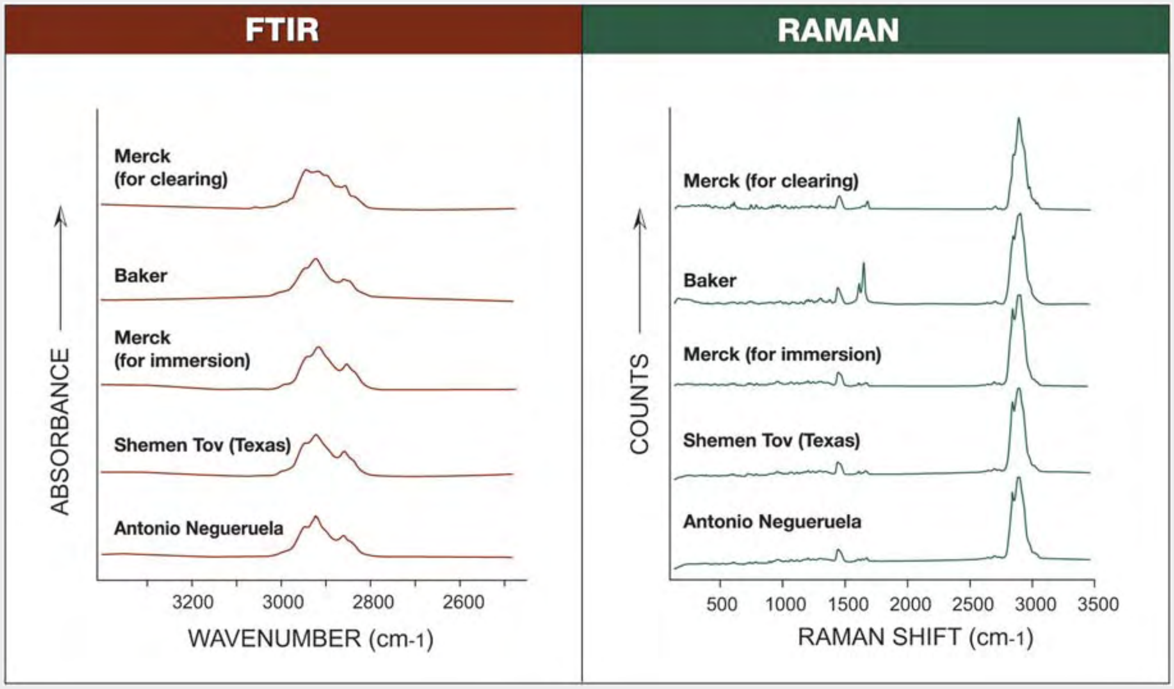
WHAT IS "PALM OIL" OR "PALMA"?

According to anecdotal evidence (J. Rotlewicz and R. Giraldo, pers. comm., 1998), when the viscosity of Merck cedarwood oil changed in the 1980s, Colombian emerald laboratories began using "palma" or "palm oil" instead. This substance more closely matched the R.I.'s of emerald than cedarwood oil did—disguising the fissures well—but it was distinguished from cedarwood oil by its "flash effect" (Ringsrud 1998).

At first, dealers believed from the name that this was another natural oil. "Palm oil" is "aceite" (or "azeite") "de dende" in Spanish, but castor bean oil has been translated as "aceite de palma." However, both of these substances have relatively low refractive indices (about 1.475), so they would not show a "flash effect."

The material represented as "palma" is probably an unhardened epoxy prepolymer resin. Both Araldite 6010 and Epon 828 have been proposed as the identity of "palma" (the former by A. Groom, pers. comm., 1997, and by C. Osorio, J. Rotlewicz, and R. Giraldo, pers. comms., 1998; the latter by C. Beesley, pers. comm., 1998). The R.I.'s and infrared and Raman spectra of these substances are nearly identical.

Figure B-1. The five cedarwood oils we examined had slightly different infrared and Raman spectra.



terms and in the ways these terms are applied by different branches of chemistry (again, see Box A). Nevertheless, on the basis of the MSDS information, we classified the fillers we studied into the following six *substance categories*: essential oils (including natural resins), other oils, waxes, epoxy prepolymers, other prepolymers (i.e., which have different chemistries, including UV-setting adhesives), and (hardened) polymer resins. The first three categories contain both natural and manufactured substances; the last three contain only manufactured substances. The two hard polymers Super Tres and Permasafe are similar in their properties and spectra to hardened Opticon 224 (see below), so we suspect these are epoxy (DGEBA) polymers, at least in part.

The 39 materials studied are listed according to these substance categories in table 1. We examined the liquid filling substances both as droplets and as samples mounted between two glass microscope slides (Corning pre-cleaned micro slides, #2927). The solid substances were examined both as polished blocks and as KBr pellets for infrared spectroscopy. Our investigation of isolated fillers is consistent with the recommendation by Zecchini and Maitrallet (1998) that the spectra of the substances alone should be examined before the fillers are investigated within emeralds. To answer key questions about filler mixtures, however, we did study some materials within emeralds.

We observed the color of each filling substance on a white background, using daylight-equivalent fluorescent light. We determined the refractive index of each liquid by placing a drop on the hemicylinder of a Duplex II refractometer equipped with a sodium-equivalent light source; we polished small flats on blocks of the solid materials to get their R.I. values. We observed fluorescence in a darkened room using a GIA GEM short-wave/long-wave ultraviolet lamp.

We assessed the approximate specific gravity of each filler (relative to de-ionized water at 21.5°C) by inserting a few drops (or, if solid, a small fragment) of the substance below the meniscus of a small vial of water, and observing whether the material sank or floated to the surface. (Although this test is not useful to identify fillers *in* emeralds, many dealers do have access to the material that is being used to fill their stones, and this test may help confirm the identity of that filler.) All observations of viscosity were made at room temperature; the flow characteristics were observed by tilting a transparent container of the material and observing whether the surface shifted back to level on a short (like water) or a long (like honey) time scale.

Experiments with Mixtures. For two specific experiments, we investigated some properties of three groups of our own filler mixtures, both as isolated substances and within emeralds. These experiments were designed to answer two questions: (1) Does a flash effect imply an artificial resin? And (2) how well can "adulterated" cedarwood oil be detected with spectroscopic techniques?

We addressed the first question with the following substances, chosen (or mixed) for their refractive indices (table 2): the epoxy prepolymer Epo Tek 314 (R.I. = 1.500); Baker cedarwood oil (R.I. = 1.517); Sigma clove oil (R.I. = 1.531); mixtures of Epo Tek 314 and Epo Tek 302-3M (R.I.'s = 1.517, 1.531, 1.550, 1.570); and mixtures of Sigma clove oil and Sigma cinnamon oil (R.I.'s = 1.550, 1.570). We also examined the stones filled with these substances to determine the effect of filler R.I. on apparent clarity and to observe the appearance of the fillers within fissures. We addressed the second question using mixtures of two components with very different spectral characteristics: Baker cedarwood oil and Araldite 6010 (table 3).

We made 50 ml batches of each filler mixture. The proper volume of each component was determined by assuming a linear relationship between volume and refractive index. The substances were mixed shortly prior to filling the stones, and the R.I. of each mixture was measured.

From a batch of about 250 natural emeralds approximately 0.5 ct and larger, which we had selected for durability testing, we chose 18 to be cleaned, photographed, and filled. Each was first "emptied" by Arthur Groom–Gematrat in New York, using a proprietary process, and then examined with a Reichert Stereo Star Zoom microscope to check that the previous filler material had been removed. Both macro- and micro-photography were performed before and after filling on the nine stones for the first experiment; only macro-photography was done on the other nine. Refractive indices were measured and fluorescence was observed with the above-listed equipment. Care was taken with the R.I. determinations, to ensure that the R.I. liquid was not drawn (or "wicked") into the fissure. We determined the weight of each stone before and after filling (in carats, to five decimal places) using a Mettler MT5 balance.

For the first experiment (table 2), we filled one each of nine emeralds using a "Mini Oiler" (Zamrot Ashalim Engineering Ltd., Ramat Gan, Israel) for the essential-oil mixtures and a "Color Stone Oiling Unit" (Jairo Vaca Camacho, Bogotá) for the artificial-resin mixtures. In the Mini Oiler, samples were held in an evacuated container (i.e., one from which the air had been pumped out) and suspended in a porous basket over the oil, which was heated to about 50°–60°C. The stones were then plunged into the filler, and 700 mbar overpressure (1.7 bars total pressure) was applied overnight. In the Color Stone Oiling Unit, the emeralds were placed in the bottom of the container and resin was poured over them; the chamber was heated to 50°–60°C and then pressurized to 4000 psi (about 275 bars total pressure) overnight. After the stones were cooled to room temperature, each device was brought to atmospheric pressure and the stones were removed, cleaned with alcohol, and then weighed and rephotographed.

For the second experiment, we examined the mixtures of Baker cedarwood oil and Araldite 6010 both as loose substances and as fillers within emeralds. The measured liquids were poured into brown glass bottles and stirred thoroughly. The three mixtures richest in cedarwood oil and the two richest in Araldite 6010 combined smoothly, but the four mixtures with 30 to 60 volume percent cedarwood oil "unmixed" overnight at room temperature (figure 3). The unmixed fillers were stirred again immediately prior to filling the stones. We filled nine emeralds with these mixtures, using the Zamrot Mini Oiler and the same conditions as above.

Infrared Spectroscopy and Raman Microspectrometry. We analyzed the nine emeralds filled with mixtures in table 3 with a Nicolet Magna 550 Fourier-transform (FTIR) spectrometer, using reflectance infrared spectrometry as described by Zecchini and Maitrallet (1998). For this techique, we adjusted the beam to focus within the emerald, rather than at its surface, to generate a transmission spectrum. We used a known "clean" emerald standard for comparison: a 5.01 ct crystal collected *in situ* from the wall of a mine at Muzo, Colombia, by GIA's Bill Boyajian. We also compared the results for the emeralds filled with these mixtures with those for emeralds we had filled with 100% Baker cedarwood oil or 100% Araldite 6010 as part of the durability study.

Infrared spectra of the loose fillers in tables 1 and 3 were also produced with the Nicolet Magna 550 spectrometer. Spectra were taken of thin films of the liquid fillers made by compressing a drop of the filler between two glass microscope slides, each about 1 mm thick. This collection geometry was chosen so that the strongest infrared-active absorptions would not be too intense to show any features. The IR spectra of solid fillers were obtained using the KBr pressed-powder technique.

Spectra were collected over the range 6000–400 cm^{-1}. We chose a spectral resolution of about 4 cm^{-1}; in general, absorption peaks in polymers are wider than this (5 to 30 cm^{-1}), so peaks can be reported to the nearest cm^{-1} without loss of accuracy (Bower and Maddams, 1989, p. 18). We also examined different resolutions for FTIR spectra of some representative fillers and found no differences in peak position and width for 4 cm^{-1} as compared to 1 cm^{-1} resolution. Because the glass slides had only broad, low background absorption in the region of interest (3200–2400 cm^{-1})—that is, the region in which emeralds are transparent—infrared absorption related to the glass itself did not interfere with the collection of important data, and we observed that the spectra of the loose fillers were practically identical to those taken of the same fillers in emeralds as reported in table 3.

Raman spectra were produced of all the "loose" fillers (both isolated and as mixtures) and of fillers in selected fissures of the filled emeralds in tables 2 and 3. We used a Renishaw 2000 Ramascope laser Raman microspectrometer, with a 514.5 nm argon laser source and five summed 10-second scans on each point. We placed a drop of each liquid filler on a clean piece of aluminum foil, and then analyzed it in the spectral range 100–3500 cm^{-1}. For the loose fillers, we used low (20×) magnification to prevent selective volatilization of the filler substances. In the filled emeralds (tables 2 and 3), we recorded the spectra of fillers in selected fissures at 50× magnification, in the same spectral range. Our Raman spectra had a resolution of about 1 cm^{-1}.

RESULTS

Physical and Optical Characteristics of Loose Filling Materials. All of the substances tested were found to have many properties in common. In some cases, we saw slight differences that might be useful to help determine the substance category or specific filler used in a particular emerald. Properties are listed for the fillers, grouped by substance category, in table 1; significant differences are discussed below.

Color. The Joban oil and green Opticon 224 resin were moderate green, and the Negueruela cedarwood oil was very light green. The rest were colorless or very light, light, or moderate yellow.

TABLE 1. Description and gemological properties of the emerald-filling materials examined for this study.

Substance category	Filler[a]	Source[b]	Used in the trade?[c]	Color	R.I.[d]	Long-wave UV fluorescence	Short-wave UV fluorescence	Relative viscosity[e]	S.G.[f]	IR group, spectrum[g]	Raman group, spectrum[g]
“PRESUMED NATURAL” SUBSTANCES											
ESSENTIAL OILS OR NATURAL RESINS	Cedarwood oil for clearing	Merck	N.R.	Light yellow	1.509	Inert	Inert	Flows sluggishly	Floats	C, 11l	C, 12l
	Cedarwood oil for immersion	Baker	Yes	Yellow	1.517	Strong yellowish white	Weak yellowish green	Flows sluggishly	Floats	C, 11n	C, 12n
	Cedarwood oil	Negueruela	Yes	Very light green	1.518	Moderate white	Inert	Semi-solid	Floats	C, 11n	C, 12o
	Cedarwood oil for immersion	Merck	Yes	Very light yellow	1.520	Weak yellowish green	Inert	Flows sluggishly	Floats	C, 11n	C, 12o
	(Texas) cedarwood oil	Shemen Tov	Yes	Light yellow	1.520	Inert	Inert	Flows sluggishly	Floats	C, 11n	C, 12o
	Canada balsam (natural resin)	Sigma	Yes	Yellow	1.521	Strong yellowish white	Very weak yellowish green	Flows sluggishly	Floats	C, 11n	C, 12n
	Clove bud oil	Spectrum	N.R.	Very light yellow	1.531	Very weak yellowish green	Weak yellowish green	Flows easily	Sinks	D, 11p	D, 12q
	Clove oil	Sigma	Rarely	Light yellow	1.531	Very weak greenish yellow	Weak yellowish green	Flows easily	Sinks	D, 11p	D, 12q
	Clove stem oil	Spectrum	N.R.	Yellow	1.537	Very weak yellowish green	Weak yellowish green	Flows easily	Sinks	D, 11p	D, 12q
	Cinnamon oil (synthetic)	Sigma	N.R.	Yellow	1.589	Inert	Inert	Flows easily	Sinks	D, 11q	E, 12r
	Cinnamon oil (cassia)	Spectrum	N.R.	Yellow	1.589	Very weak green	Inert	Flows easily	Sinks	D, 11p	None
OTHER OILS											
Mineral oil	*Mineral oil*	Spectrum	Yes	Colorless	1.478	Inert	Inert	Flows easily	Floats	B, 11f	B, 12f
	Paraffin oil	Schroeder	Yes	Colorless	1.478	Inert	Inert	Flows easily	Floats	B, 11f	B, 12f
Mineral(?) oil	*“Isocut” fluid*	Buehler	N.R.	Colorless	1.449	Inert	Inert	Flows easily	Floats	B, 11g	None
Vegetable oil	*Sesame oil*	Health Valley	No	Light yellow	1.474	Inert	Inert	Flows easily	Floats	B, 11g	B, 12g
	Azeite de Dende (palm [tree] oil)	Mavalério	No	Yellow	1.473	Moderate greenish yellow	Very weak greenish yellow	Flows easily	Floats	B, 11g	B, 12g
	Castor oil	Spectrum	N.R.	Colorless	1.479	Moderate yellowish green	Very weak yellowish green	Flows easily	Floats	B, 11g	B, 12g
Mineral(?) oil plus vegetable(?) dye	*Joban oil*	Real Gems	Yes	Green	1.478	Moderate yellowish green	Weak yellowish green	Flows easily	Floats	B, 11g	B, 12g
WAX	Paraffin wax	Spectrum	Yes	Colorless	About 1.52	Inert	Inert	Solid	Floats	B, 11h	B, 12h

[a] Fillers in boldface type have R.I.’s greater than 1.54 and should show a flash effect; fillers in italics have R.I.’s less than 1.500 and should not enhance clarity as effectively as others in the table.

[b] Sources: Baker (Mallinckrodt Baker Inc., Phillipsburg, NJ); Buehler (Buehler Ltd., Lake Bluff, IL); Centro Gemológico (Centro Gemológico para la Investigación de la Esmeralda, Bogotá, Colombia); CIBA-GEIGY Corp., Hawthorn, NY; Conservator’s Emporium, Reno, NV; Epo Tek (Epoxy Technology, Billerica, MA); Health Valley Co., New York City; Hughes (Hughes Associates, Victoria, MN); Liquid Resins (Liquid Resins International Ltd., Olney, IL); Malavério (Indústria de Productos Alimentícios Malavério Ltda., Proporinha, Brazil); Merck (EM Science, Gibbstown, NJ); Negueruela (Antonio Negueruela S.A., Madrid, Spain); Norland (Norland Products Inc., New Brunswick, NJ); Real Gems (Real Gems Inc., New York City); Schroeder J. Schroeder Pharm., Geneva, Switzerland); Shell (Shell Oil Co., Houston, TX); Shemen Tov (Shemen Tov Corp., West Orange, NJ); Sigma (Sigma Chemical Corp., St. Louis, MO); Spectrum Chemical Manufacturing Corp., Gardena, CA; Treatment World (Treatment World Emerald Gemológico Universal, Bogotá, Colombia).

[c] N.R. = not reported.

[d] The R.I. of the filler increased (by about 0.03) on curing for the three cases we examined (Opticon 224, Epo Tek UVO114, Norland type 65).

[e] Flows easily = flows like water; flows sluggishly = flows like honey. These were evaluated at room temperature (21.5ÞC).

TABLE 1 (cont'd). Description and gemological properties of the emerald-filling materials examined for this study.

Substance category	Filler[a]	Source[b]	Used in the trade?[c]	Color	R.I.[d]	Long-wave UV fluorescence	Short-wave UV fluorescence	Relative viscosity[e]	S.G.[f]	IR group, spectrum[g]	Raman group, spectrum[g]
ARTIFICIAL RESINS											
EPOXY PREPOLYMERS											
	Epo Tek 314	Epo Tek	N.R.	Colorless	1.500	Weak yellowish green	Very weak yellowish green	Flows sluggishly	Sinks	C, 11m	C, 12m
	HXTAL	Conservator's Emporium	N.R.	Colorless	1.501	Inert	Inert	Flows sluggishly	Sinks	B, lli	B/C, 12i
	Epo Tek 301	Epo Tek	N.R.	Colorless	1.538	Weak to moderate greenish white	Very weak yellowish green	Flows sluggishly	Sinks	A, 11c	A, 12a
	Opticon Resin 224	Hughes	Yes	Colorless	1.550	Inert	Inert	Flows sluggishly	Sinks	A, 11c	A, 12c
	Opticon Resin (green)	Hughes	N.R.	Green	1.550	Weak greenish yellow	Inert	Flows easily	Sinks	A, 11c	A, 12c
	Araldite 506	Sigma	N.R.	Colorless	1.551	Weak yellowish green	Very weak yellowish green	Flows sluggishly	Sinks	A, 11c	A, 12c
	Araldite 502	Sigma	N.R.	Very light yellow	1.559	Weak yellowish green	Strong yellow	Flows sluggishly	Sinks	A, 11c	A, 12c[h]
	Araldite 6005	Sigma	N.R.	Colorless	1.570	Weak yellowish green	Inert	Flows sluggishly	Sinks	A, 11c	A, 12c
	Araldite 6010	CIBA-GEIGY	Yes	Very light yellow	1.572	Weak yellowish green	Inert	Flows sluggishly	Sinks	A, 11c	A, 12c
	Epon 828	Shell	Yes	Light yellow	1.575	Weak yellowish green	Weak greenish yellow	Flows sluggishly	Sinks	A, 11c	A, 12c
	Epo Tek 302-3M	Epo Tek	N.R.	Colorless	1.577	Very weak yellowish green	Inert	Flows sluggishly	Sinks	A, 11b	A, 12b
OTHER PREPOLYMERS											
	Liquid Resin (green cap formula)	Liquid Resins	N.R.	Colorless	1.481	Inert	Inert	Flows easily	Sinks	C, 11o	C, 12p
UV-setting	Epo Tek UVO114	Epo Tek	N.R.	Colorless	1.527	Moderate green	Green	Flows sluggishly	Sinks	A, 11c	A, 12a
	Norland Optical Adhesive type 65	Norland	Yes	Colorless	1.501	Weak greenish yellow	Inert	Flows easily	Sinks	C, 11j	C, 12j
	Norland Optical Adhesive type 63	Norland	N.R.	Colorless	1.519	Strong blue	Inert	Flows easily	Sinks	C, 11j	C, 12j
POLYMERS											
	Permasafe	Centro Gemológico	Yes	Very light yellow	1.565	Strong blue-white	Weak blue	Solid	1.11	A, 11e	A, 12e
	Super Tres	Treatment World	Yes	Light yellow	1.570	Strong bluish white	Moderate grayish blue	Solid	1.11	A, 11e	A, 12e
	Opticon Resin 224 (cured)	Hughes	Yes	Very light yellow	1.580	Strong light blue	Moderate light blue	Solid	Sinks	A, 11d	A, 12d
UV-setting	Norland Optical Adhesive type 65 (cured)	Norland	Yes	Colorless	1.529	Moderate blue	Weak green	Solid	Sinks	C, 11k	C, 12k
	Epo Tek UVO114 (cured)	Epo Tek	N.R.	Light yellow	1.553	Strong blue	Moderate blue	Solid	Sinks	A, 11a	A, 12d

---

[f] *S.G. is reported relative to water: floats—S.G. less than 1.0; sinks—S.G. greater than 1.0. Both Permasafe and Super Tres had hydrostatically measured S.G.'s of 1.11.*

[g] *Spectral groups as discussed in text; individual spectra shown in figures 11 and 12. "None" means that the sample was too fluorescent to get a Raman spectrum with the 514.5 nm argon laser source.*

[h] *Plus two additional Raman peaks.*

TABLE 2. Emeralds clarity enhanced for R.I. tests of "presumed natural" and artificial fillers.

Filler	R.I. of filler[a]	Microscopic features of filled fissures in emerald	Fluorescence to longwave UV in emerald	Raman spectrum of filler in emerald
Epo Tek 314 (artificial resin)	1.500	Not notable	Not seen	Weak aliphatic feature, possibly group C
Baker cedarwood oil ("natural" oil)	1.517	Not notable	Very weak yellow-green in fissures	Positive match to Canada balsam or Baker cedarwood oil; group C
Mixture of Epo Tek 314 and Epo Tek 302-3M (artificial resins)	1.517	Not notable	Very weak yellow-green in fissures	Group C
Sigma clove oil ("natural" oil)	1.531	Incomplete filling; white residue	Not seen	Not identifiable as to group
Mixture of Epo Tek 314 and Epo Tek 302-3M (artificial resins)	1.531	Incomplete filling; flow structure	Very weak yellow-green in fissures	Good match to spectra for both components groups A and C
Mixture of Epo Tek 314 and Epo Tek 302-3M (artificial resins)	1.550	Orange and blue flash effects; incomplete filling; iridescence in fissure; light brownish yellow substance in fissure	Very weak yellow-green in fissures	Shows features of both groups A and C, less distinct overall
Mixture of Sigma clove oil and Sigma cinnamon oil ("natural" oils)	1.550	Yellow-orange and blue flash effects (evaporating rapidly); incomplete filling; iridescence in fissure	Very weak yellow-green in fissures	Weak unidentifiable spectrum
Mixture of Epo Tek 314 and Epo Tek 302-3M (artificial resins)	1.570	Yellow-orange and blue flash effects; incomplete filling; iridescence in fissure; white residue	Very weak yellow-green in fissures	Good match to group A reference spectrum
Mixture of Sigma clove oil and Sigma cinnamon oil ("natural" oils)	1.570	Flash effects (disappearing rapidly as filler evaporates); incomplete filling; iridescence in fissure; brownish yellow substance in fissure; white residue	Not seen	Not identifiable as to group

[a] *All the emeralds for this experiment had R.I. values of 1.571 (± 0.002) to 1.577 (± 0.003).*

Refractive Index. The fillers had R.I.'s of 1.449 to 1.589; by comparison, the R.I. values of emerald range from 1.564 to 1.593 (extraordinary ray), and 1.570 to 1.602 (ordinary ray), depending on their source (Webster and Read, 1994). The UV-setting adhesives we studied had low R.I. values relative to emerald, 1.501–1.527; however, the R.I. values increased to 1.529–1.553 as they cured. The R.I. value of Opticon 224 also increased with curing.

For the mixtures of essential oils and those of artificial resins, the R.I. of the mixture could be predicted from the measured volumes and R.I.'s of its components. However, the mixtures of Baker cedarwood oil with Araldite 6010 behaved nonlinearly, so the R.I.'s did not agree with their predicted values (see table 3).

Fluorescence. As indicated in table 1, not all cedarwood oils fluoresce and those that do fluoresce do not all fluoresce alike. Similarly, although most epoxy prepolymers fluoresced very weak yellowish green to short-wave UV, or were inert, Araldite 502 fluoresced strong yellow and Epon 828 fluoresced weak greenish yellow.

All but one of the polymers displayed strong bluish white to blue fluorescence to long-wave UV, and the same fillers fluoresced weak to moderate blue to short-wave UV. The exception, Norland Optical Adhesive type 65, fluoresced moderate blue to long-wave UV and weak green to short-wave UV.

Viscosity. Some essential oils flowed readily (like water); however, the cedarwood oils and Canada balsam were sluggish (like honey). The cedarwood oil from Antonio Negueruela was nearly solid at room temperature (similar to "petroleum jelly"). The "other oils" all flowed easily. The paraffin wax was a soft solid. The epoxy prepolymers flowed sluggishly, and the UV-setting adhesives flowed easily (Norland Optical Adhesives) or sluggishly. All of the hardened polymers were solids.

Specific Gravity. Some essential oils floated in water (cedarwood oils, Canada balsam), whereas others sank (clove oils, cinnamon oils). The other oils we studied floated, as did paraffin wax. All of the epoxy prepolymers and other prepolymers sank, and all of the hardened resins we studied also sank.

Gemological Characterization of Filling Materials in Emeralds. *Effect of Refractive Index on Apparent*

Clarity. Examination of the emeralds filled with the nine substances in table 2 revealed that as the R.I. of the filling material increases toward the R.I.'s of emerald, the fissures become less prominent (see, e.g., figure 2).

Internal Appearance and Flash Effect. Although most of the substances we used for these R.I. tests are not common filling materials, we were able to reproduce features seen in filled emeralds, including brownish yellow filled voids (figure 4), flow structure (figure 5), incomplete filling (figure 6), and natural iridescence in fractures as well as white residues (figure 7). The white residues were seen in three of the stones (one filled with pure clove oil, one with an Epo Tek mixture, and one with a clove oil–cinnamon oil mixture), deep within the fissures at the time of first examination.

None of the five stones filled with a substance that had an R.I. of 1.53 or lower showed a flash effect, whereas all four stones filled with substances that had R.I.'s of 1.55 or higher *did* show a flash effect (table 2 and figure 8). However, the "natural" fillers were quite volatile, so often this effect was gone within hours. We refilled one emerald with the 1.550 R.I. natural oil mixture, and photographed it within minutes of completing the filling process.

Figure 3. These four bottles of Baker cedarwood oil–Araldite 6010 mixtures show the unmixing of intermediate mixtures with 40% to 70% Araldite (left to right). Photo by Maha DeMaggio.

TABLE 3. Properties of emeralds filled with cedarwood oil–Araldite 6010 mixtures for spectroscopy.

Composition of the filler		Properties						
Baker cedarwood oil (%)	Araldite (%)	Color of the loose filler	R.I. of the filler	Predicted R.I. of the filler[a]	Flash effect in stone?[b]	Unmixing of fillers in bottle?	IR result (in emerald)	Raman result (in emerald)
100	0	Yellow	1.517	—	No	No	Cedarwood oil (reference spectrum)	Cedarwood oil (reference spectrum)
90	10	Yellow	1.522	1.522	Weak blue brightfield	No	Cedarwood oil	Cedarwood oil
80	20	Yellow	1.528	1.528	No	No	Cedarwood oil	Features of both
70	30	Yellow	1.533	1.534	No	No	Cedarwood oil	Features of both
60	40	Yellow	1.539	1.539	Weak blue brightfield	Yes	Cedarwood oil	Features of both
50	50	Yellow	1.544	1.544	Very weak orangy brown darkfield	Yes	Features of both	Features of both
40	60	Light yellow	1.545	1.550	Weak brown darkfield	Yes	Features of both	Features of both
30	70	Light yellow	1.547	1.556	Yellow-orange darkfield	Yes	Features of both	Features of both
20	80	Very light yellow	1.559	1.561	Yellow-orange darkfield, blue brightfield	No	Features of both	Features of both
10	90	Very light yellow	1.564	1.566	Yellow-orange darkfield	No	Araldite 6010	Araldite 6010
0	100	Near-colorless	1.572	—	Yes	No	Araldite 6010 (reference spectrum)	Araldite 6010 (reference spectrum)

[a] *R.I. predicted by: R.I. = [(% cedarwood oil) × 1.517 + (% Araldite) × 1.572] / 100. Where the measured R.I. and predicted R.I. differ by more than 0.002, this indicates that the two components are not mixing ideally.*

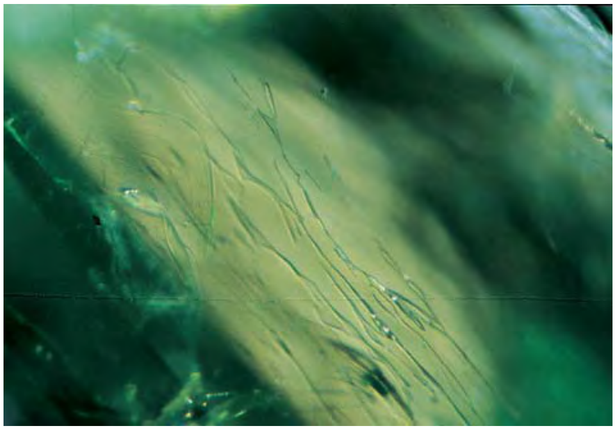
[b] *The emeralds in this test had the same refractive indices, 1.571–1.578.*

Figure 4. The filler (mixture of Epo Tek resins, R.I. = 1.550) in this 0.70 ct emerald appears brownish yellow. Photomicrograph by John I. Koivula; magnified 25×.

The flash effects disappeared while we watched as the stone was being photographed (figure 9).

Fluorescence of Filled Fissures. If enough of a fluorescent filling material is present, the fluorescence may be visible within the stone (for example, in six of the nine stones in table 2, we saw very weak yellow-green fluorescence to long-wave UV in the fissures; strictly speaking, we might have expected to see this in all nine stones). In those cases where fluorescence can be observed, this property can be especially useful to target specific fissures for Raman analysis (see Chalain et al., 1998).

Figure 5. Flow structure is evident in the filling material (mixture of Epo Tek resins, R.I. = 1.531) in this 0.82 ct emerald. Photomicrograph by John I. Koivula; magnified 20×.



Weight Added. The Epo Tek mixtures added about 0.03%–0.10% to the weight of the stones (i.e., 0.0002–0.0008 ct for a 0.5–1 ct stone). The cinnamon oil mixtures were so volatile that they evaporated before the stones could be reweighed.

FTIR and Raman Spectra. In the infrared region, emerald has a transmission window between about 3200 and 2400 cm^{-1}; therefore, this is the region that we studied for the loose filling substances. The absorption spectra of the glass slides that we used, and of a never-filled Colombian emerald crystal, are shown in figure 10.

The infrared and Raman spectra enabled us to place the loose filler materials into five spectral groups—designated here A, B, C, D, and E—with 17 infrared (figure 11) and 18 Raman (figure 12) subgroups (i.e., each spectrum may represent more than one filler). The five spectral groups are based on assignments of peaks to functional groups (see "Discussion," below), but they can be summarized in terms of the appearance of certain key peaks:

- *Group A* spectra have many peaks, especially at about 2926, 3006 (stronger in the Raman spectrum, and weak in some examples), 3058 (IR) or 3068 (Raman), and—only seen with Raman in emeralds—1609 cm^{-1}. (Recall that peak assignments can vary ± 4 cm^{-1}.) The 2962 cm^{-1} peak is usually, but not always, present. Typical group A IR spectra (see, e.g., figure 11c) show a pattern of three strong peaks decreasing in height from 2962 to 2926 to 2872 cm^{-1}. Typical group A Raman spectra (figure 12c) have a distinctive pattern of five strong peaks in the region between 2870 and 3070 cm^{-1}.
- *Group B* spectra also have many peaks, including those at 2853 (2848 cm^{-1} for paraffin wax), 2882 (Raman only), 2926 (±5), and 2954 cm^{-1} (IR only); there may be Raman peaks at 3010 and 1655 cm^{-1}. The IR spectra of the liquids show a pattern of two peaks, each with shoulders at a higher wavenumber (figures 11f, g); and the Raman spectra show plateaus centered at about 2890 cm^{-1} (figures 12f, g). In contrast, the IR spectrum of the paraffin wax has a broad central feature (figure 11h), while the Raman spectrum is sharp (figure 12h).
- *Group C* spectra exhibit peaks at 2870 (±5), 2929 (ranging to 2942 cm^{-1} in figure 12i), usually 2958, and 1442 (Raman only) cm^{-1}. Sometimes Raman peaks are seen at 1725 (figures 12j, m, and p) or

1643 cm^{-1} (figures 12j, n, and p). Typical IR (figure 11n) and Raman (figure 12l) spectra have an overall "triangular" appearance in the 2800–3050 cm^{-1} region.

- *Group D* spectra exhibit features resembling those of group A *and* group B or C, with six or more peaks in the 2800–3100 cm^{-1} region (see, e.g., figures 11p and 12q).
- The *Group E* Raman spectrum is notable for the low intensity of the 2800–3100 cm^{-1} region (only one peak at 3064 cm^{-1}: figure 12r), compared to three strong peaks at 1598, 1626, and 1674 cm^{-1}.

Additional details were used to place these spectra into subgroups. Although many of these details are unlikely to be discernible in a filled emerald, they may be important in some cases. For example, Raman microspectrometry can distinguish Baker cedarwood oil and Canada balsam from other cedarwood oils, but not from each other (compare figures 12n and o); these IR spectra are identical (figure 11n). In addition, the IR and Raman spectra of "Permasafe" and "Super Tres" (figures 11e and 12e) are slightly different from those of cured Opticon (figures 11d and 12d), although these distinctions (e.g., a peak at 1000 cm^{-1} in the Raman spectrum) might not be obvious in a filled emerald. Last, the Norland Optical Adhesives show a distinctive Raman peak at 2575 cm^{-1} (figure 12j); this peak diminishes significantly on curing (figure 12k).

The IR and Raman spectra of the cedarwood oil–Araldite 6010 mixtures as loose fillers are shown in figure 13. These spectra contain no new features; detection limits based on these results are discussed below.

As noted earlier, the spectra of the fillers in emeralds taken with reflectance IR spectroscopy were almost identical to the IR spectra of the corresponding loose fillers (compare, e.g., figure 10 inset with figure 11n). Consequently, we will refer to the IR spectra of the loose fillers and mixtures throughout the discussion.

DISCUSSION

Separating Filler Materials on the Basis of Their Optical and Physical Characteristics. The following optical and physical characteristics of loose filler materials may be useful in distinguishing among filling substances within emeralds: color, refractive index (and flash effect), fluorescence, viscosity, and distinctive microscopic features.

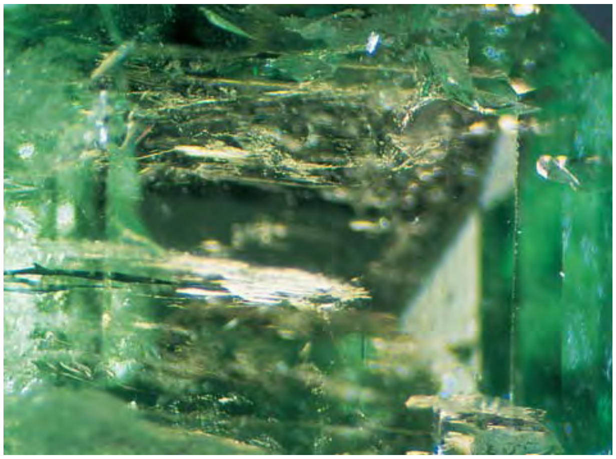


Figure 6. Note the incomplete filling by clove oil (R.I. = 1.531) in the fissures of this 0.94 ct emerald. Photomicrograph by John I. Koivula; magnified 15×.

Color. Dyed filler materials are distinctly colored (e.g., green Opticon and Joban oil; see table 1). However, other features can be mistaken for dye, including the green polishing compound chromic oxide (Ringsrud, 1983; Hänni, 1988) and green internal reflections. If dye is suspected, the observer should examine the distribution of color within the stone using diffuse transmitted light; another technique is to check whether the fissures are green from all angles and to look for color concentrations along fractures. The yellow color of other materials listed in table 1 is unlikely to be seen in an emerald unless the filler is present in broad fissures or cavities (Koivula, 1999).

Refractive Index (and Flash Effect). As the refractive index of the filling material increases toward the R.I.'s of emerald, the filled fissures become less prominent (again, see figure 2). For the emeralds we studied, which had R.I. values between 1.569 and 1.580, we saw flash effects for all fillers with R.I. values of 1.54 or above. Of the fillers in this study, only those in spectral groups A, D, and E (epoxy prepolymers and polymers, and some essential oils) have R.I.'s above 1.54. Only fillers in spectral group B (other oils) and C (the prepolymer Liquid Resin) have R.I.'s below 1.50, and these are much less effective at disguising fissures in emerald. Mixtures gave intermediate R.I.'s.

An indication of a filler's R.I. value can be provided by the prominence of the filled fissures and

Figure 7. A white residue was seen deep within a fissure in this 0.47 ct emerald, which had been filled with a mixture of clove and cinnamon oils (R.I.= 1.570). Natural iridescence is also visible in this fissure (top of the image). Photomicrograph by John I. Koivula; magnified 20×.

the presence of a flash effect. Because most materials that show flash effects in emeralds are artificial resins, and the high-refractive-index essential oils we examined are extremely volatile, it is likely that an emerald showing this effect contains an artificial resin. However, there are many artificial resins with lower R.I. values, so the *absence* of a flash effect does not mean that the substance should be considered natural. For instance, the early formulation of Arthur Groom–Gematrat had a lower R.I. value than other commonly used artificial resins, as evidenced by the greater prominence of the filled fissures and the lack of a flash effect (see, e.g., Johnson et al., 1997).

Fluorescence. Most of the fillers we studied were inert, or fluoresced very weak or weak yellow-to-green to long-wave UV. However, two of the five cedarwood oils fluoresced moderate white or strong yellowish white, and most of the cured (hardened) polymers fluoresced strong white to blue, so *strong* fluorescence in fissures may be useful for distinguishing cured and surface-hardened fillers from liquid fillers. (Of course, one risks hardening the UV-setting adhesives by exposing them to UV radiation.) Recent formulations of Arthur Groom–Gematrat are said to contain a fluorescent tracer (Weldon, 1998a). We were not able to study the Arthur Groom–Gematrat filler as an isolated material; however, all five polymer samples we examined fluoresced blue to bluish white to long-wave UV, and all but the cured Norland Optical Adhesive 65 fluoresced blue to short-wave UV (again, see table 1).

Viscosity. All filling materials are liquid when they are emplaced in emeralds, but some are hardened once in the fissures (e.g., UV-setting adhesives), others are frequently surface hardened (Opticon: Kammerling et al., 1991), and others slowly solidify over time (e.g., Canada balsam: Kammerling et al., 1991). It is also possible that certain internal characteristics—such as gas bubbles, flow structures, and incomplete filling of fractures—are related to the viscosity of a filling material, but we have not tested this hypothesis.

Before the viscosity of a filler in an emerald can be inferred, its presence must be established. Johnson et al. (1998a), among others, have described procedures for finding evidence of clarity enhancement in emeralds. Using a microscope at low magnification with reflected light will reveal the trace of the fissure on the surface; switching to darkfield illumination will show the extent of the fissure inside the stone. Higher magnification is then used

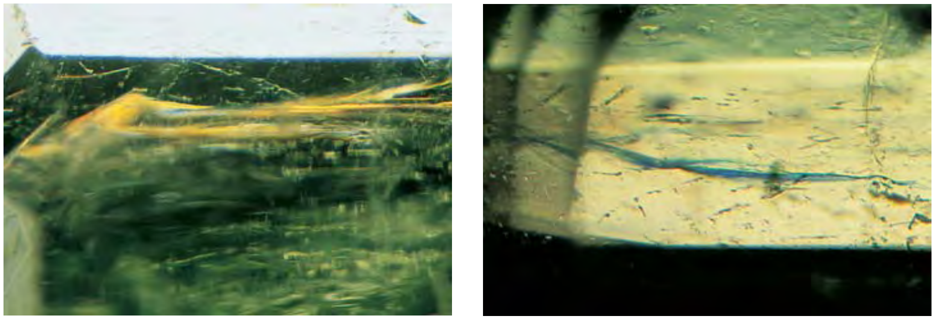


Figure 8. This 0.59 ct emerald filled with a mixture of epoxies (R.I. = 1.570) shows orangy yellow (darkfield, left) and blue (brightfield, right) flash effects. Photomicrographs by John I. Koivula; magnified 15×.

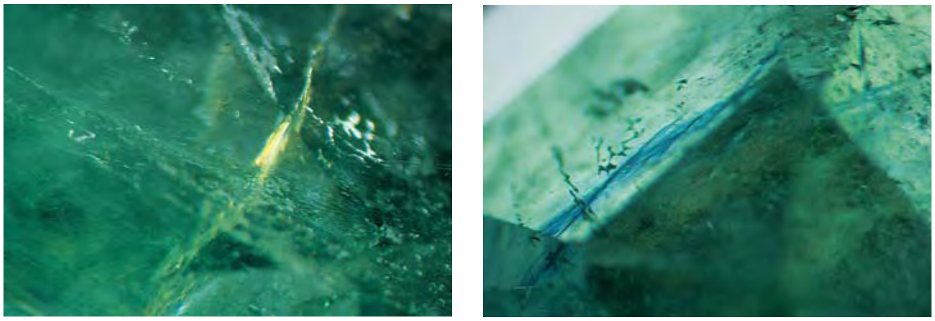


Figure 9. This emerald, filled with a mixture of the natural essential oils clove oil and cinnamon oil (R.I. =1.550), also shows yellow-orange (darkfield) and blue (brightfield) flash effects. Photomicrographs by John I. Koivula; magnified 15×.

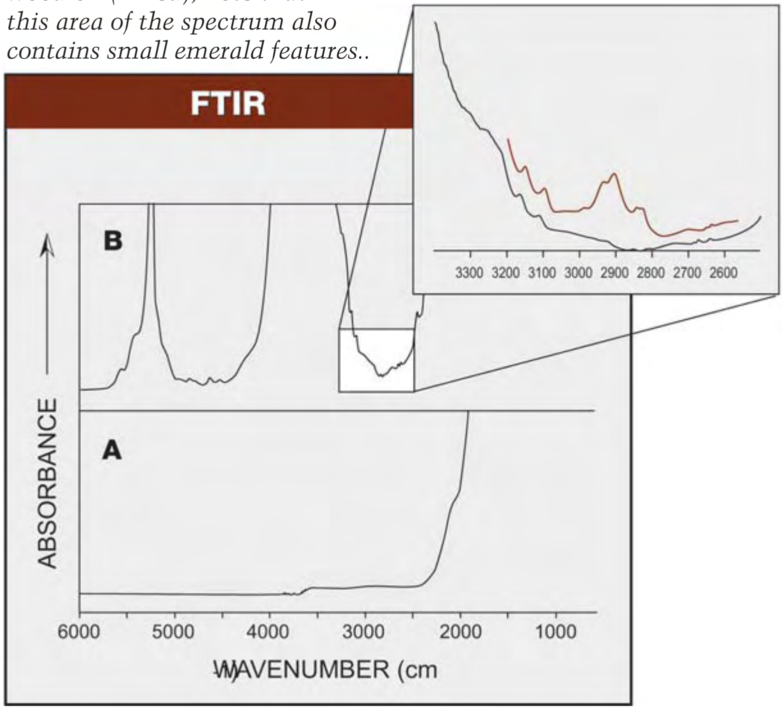
to reveal features indicative of a filled fissure: flow structure, gas bubbles (which may be flattened or round), incomplete filling, or yellowish voids (sometimes shaped like crystal inclusions).

Once the presence of a filler has been established, there are at least two ways to see whether the filler is fluid: (1) Watch the emerald as it warms with exposure to the microscope lamp, and see if there is any movement of the filler within the stone; and (2) while observing carefully with the microscope, bring a heated sharp point near—but not touching—the surface of the emerald, and watch for movement of the filler (it may even form droplets on the surface of the stone). In either case, use extreme care to avoid damaging the emerald by extending fissures. A liquid filler may show motion with these techniques, but the absence of a reaction does not guarantee that the filler is solid, because surface-hardened fillers might act the same (Johnson et al., 1998a).

Distinctive White Cloudy Inclusions. Although this internal feature is commonly attributed to "palma" (see, e.g., Ringsrud, 1998), we did see such inclusions in emeralds filled with "natural" essential oils (clove and cinnamon), and with a mixture of epoxy prepolymers (Epo Tek 314 and Epo Tek 302-3M). We suspect that they result from some sort of emulsification, which can be demonstrated—but not proved—by the following test: Place nearly equal amounts of filling material (here, Araldite 6010) and water in a bottle, then close and shake the bottle (figure 14). The white cloudy mixture that forms is an emulsion of small droplets of one substance in the other substance; the droplets are prevented from coalescing by the coating of the other substance. Perhaps in the case of our experimentally filled emeralds, this emulsion formed deep within the filled fissures, where not all the water had been removed from the emeralds before filling. (This could also happen with other substances.)

Another possible source of fine, white surface contamination seen in the trade is quartz dust, which contaminates some polishing compounds used in Bogotá (R. Giraldo, pers. comm., 1999). As volatile filling material evaporates from the surface of an emerald, the 1.54-R.I. quartz dust left behind would gradually become visible.

Figure 10. For reference purposes, we recorded the FTIR spectra of (a) the glass slides we used as "windows" for obtaining the spectra of filling materials, and (b) a 5.01 ct natural (unfilled) emerald crystal. The inset shows a detail of the emerald spectrum in the region where filler peaks are seen, together with the spectrum of an emerald that had been filled with Baker cedarwood oil (in red); note that this area of the spectrum also contains small emerald features..



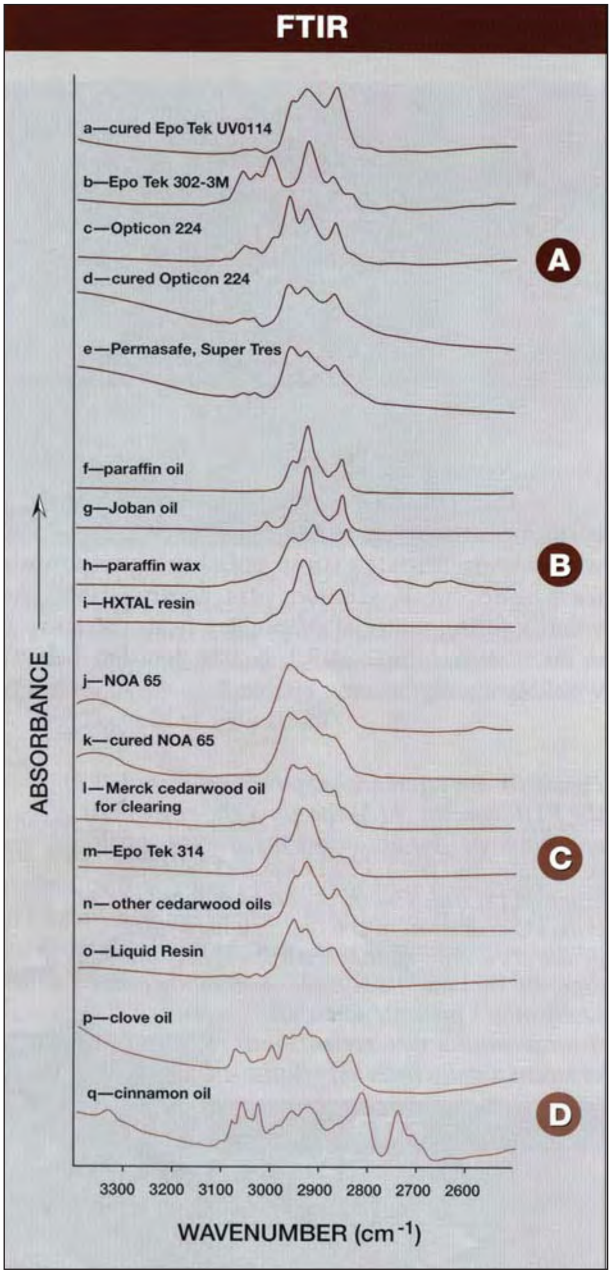


Figure 11. On the basis of their spectra, the filling substances examined were placed in four infrared groups (A–D) and 17 subgroups (a–q). Representative spectra for each subgroup are illustrated here. The appropriate group and spectrum for each of the fillers studied are listed in table 1. NOA = Norland Optical Adhesive.

FTIR and Raman Spectrometry: Complementary Techniques, Similar Information. Peaks in infrared and Raman spectra have the same cause: The radiation excites vibrations between atoms. In crystalline substances, IR and Raman spectra of the same material may look quite different, because the two techniques often excite different vibrations, depending on the symmetry of the material and on quantum mechanical "selection rules" (Harris and Bertolucci, 1978). However, liquids and polymers are less "ordered" than crystalline solids (i.e., they have less overall structural order and greater variability in bond lengths and angles, etc.), so the IR and Raman spectra of a particular liquid or polymer look quite similar in general, with a few differences in peak position and (especially) in relative intensity.

When it comes to examining spectral information of fillers within emeralds, FTIR and Raman often provide similar information from distinct regions within the emerald. With the reflected-beam geometry, FTIR spectroscopy gathers spectral information from much of the interior of the emerald, and it is not necessary to find the filled fissures prior to analysis. In contrast, the Renishaw Raman microspectrometer must be focused at or near the surface of the stone, and the fissures to be examined must first be located with the microscope. Because the spectral information only comes from the near-surface area, other filler substances deeper in the stone would not be detected.

In addition, the emerald host has a different effect on the results obtained with each technique. With FTIR, only the limited spectral region between 3200 and 2400 cm^{-1} is visible in the emerald (again, see figure 10). Fortunately, this region includes one of the two diagnostic spectral regions for polymers. With Raman, the emerald (and some fillers) may luminesce to the 514 nm laser beam that induces the Raman effect; this luminescence causes a large interfering background signal in the spectrum that generally begins at wavenumbers above 3000 cm^{-1} or so (but can be a problem in some emeralds even at 2000 cm^{-1}). With both techniques, the distinctive filler peaks are very small compared to the features of the emerald host.

Reference infrared spectra for many of the materials we tested are available in atlases such as Pouchert (1985) and Julian et al. (1991), software such as the *Omnic Interpretation Guide* (Nicolet, 1992), and references such as those cited by the *ChemFinder* Web site. The Raman peaks (especially for liquids) can be interpreted as if they were infrared peaks. However, the interpretation of both types of spectra requires the terminology of organic chemistry. *Functional groups* are the pieces of a molecule's structure that produce distinctive spectral features. Certain peak

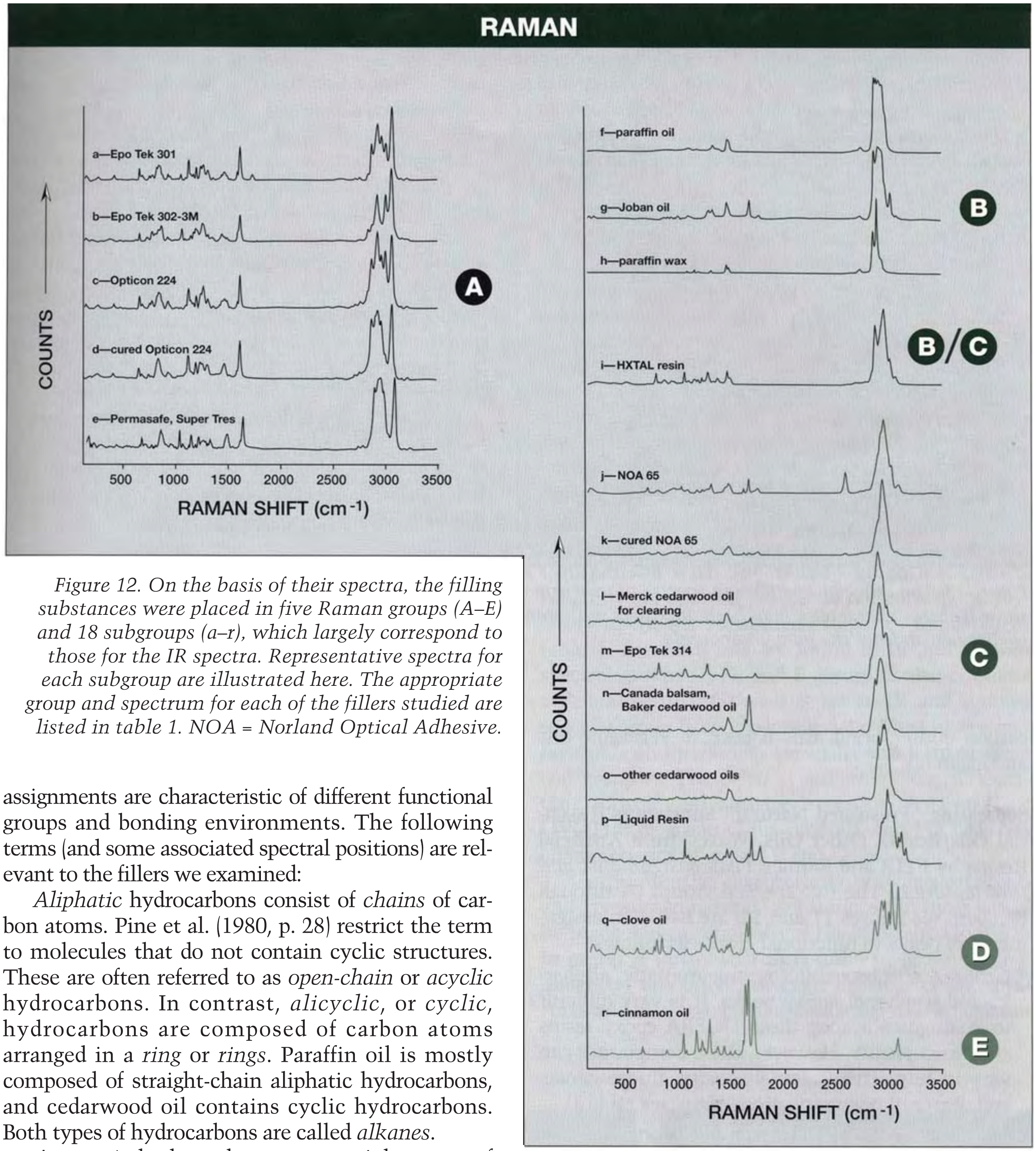


Figure 12. On the basis of their spectra, the filling substances were placed in five Raman groups (A–E) and 18 subgroups (a–r), which largely correspond to those for the IR spectra. Representative spectra for each subgroup are illustrated here. The appropriate group and spectrum for each of the fillers studied are listed in table 1. NOA = Norland Optical Adhesive.

assignments are characteristic of different functional groups and bonding environments. The following terms (and some associated spectral positions) are relevant to the fillers we examined:

Aliphatic hydrocarbons consist of *chains* of carbon atoms. Pine et al. (1980, p. 28) restrict the term to molecules that do not contain cyclic structures. These are often referred to as *open-chain* or *acyclic* hydrocarbons. In contrast, *alicyclic*, or *cyclic*, hydrocarbons are composed of carbon atoms arranged in a *ring* or *rings*. Paraffin oil is mostly composed of straight-chain aliphatic hydrocarbons, and cedarwood oil contains cyclic hydrocarbons. Both types of hydrocarbons are called *alkanes*.

Aromatic hydrocarbons are special groups of cyclic compounds that usually have six-member rings that may be visualized as having alternate single and double bonds (i.e., benzene rings). Cinnamon oil contains benzene rings. When an OH (hydroxyl) group is connected to a carbon atom of a benzene ring, the compound is known as a *phenol* (Pine at al., 1980, pp. 28, 47). DGEBA resins (see Box A) contain phenol groups that are connected together in pairs (*bisphenol* groups). These artificial resins are rich in aromatic bonds (e.g., a large peak at 3066 cm^{-1} is seen in the Raman spectrum of Opticon 224).

Hydrocarbons that have one or more carbon-carbon double bonds are called *alkenes* or *olefins* (Pine at al., 1980, p. 37). For instance, a peak in the 3000–3020 cm^{-1} region is associated with a hydrogen atom attached to one of the carbons in a carbon-

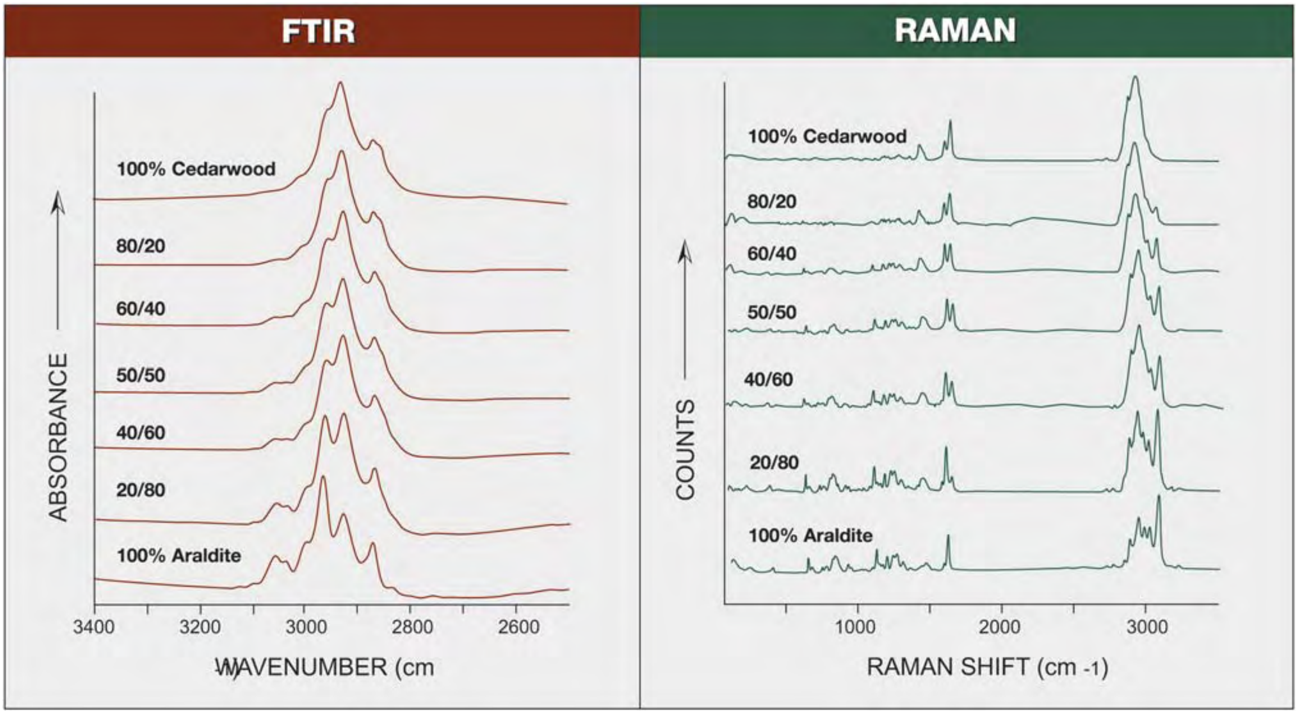


Figure 13. The infrared and Raman spectra of mixtures of (Baker) cedarwood oil and Araldite 6010 show features characteristic of both; mixtures with much more of one filler than the other are hard to distinguish from the pure compounds.

carbon double bond; this is seen in vegetable oils and Joban oil.

Separating "Presumed Natural" Substances (Essential Oils/Resins, Other Oils, Waxes) from Artificial Resins by FTIR and Raman. *Peak assignments and Interpretation.* The five spectral groups (A through E; again, see figures 11 and 12) are based on assignments of peaks to functional groups as follows:

- *Group A* spectra exhibit strong aromatic, aliphatic, and bisphenol epoxy peaks. It is very difficult to distinguish among these DGEBA epoxy resins spectroscopically. However, these compounds can vary in refractive index, viscosity, fluorescence, and degree of polymerization (again, see table 1).
- *Group B* spectra exhibit multiple strong aliphatic peaks, generally producing several distinct peaks in the 2925–2850 cm^{-1} region of the IR spectrum (or a broad overall peak in the Raman spectrum); some spectra also exhibit traces of alkene (olefin). The artificial resin HXTAL has a group B infrared spectrum (figure 11i), and affinities to both groups B and C in its Raman spectrum (figure 12i).
- *Group C* spectra exhibit less-distinct multiple IR peaks, but a single dominant aliphatic Raman peak, with small aromatic features seen in some compounds.
- *Group D* spectra exhibit both aromatic and aliphatic features.
- The *Group E* spectrum is a Raman spectrum only. The substance (cinnamon oil) that has this spectrum is unusual in that it exhibits both aliphatic and aromatic IR features (so its IR spectrum is in group D), but mostly aromatic Raman features. We observed no Raman spectrum for the other (cassia) cinnamon oil due to its strong fluorescence.

Spectra versus "Flash Effect" as a Detection Technique for Mixtures. Looking again at our experimental mixtures of Baker cedarwood oil and Araldite 6010, we found that mixtures with up to 20% Araldite (for Raman) or 40% Araldite (for IR) could not be distinguished from pure cedarwood oil on the basis of their spectra. Similarly, the spectra of the mixture with 90% Araldite–10% cedarwood oil could not be distinguished from those of pure Araldite 6010 with either technique (again, see figure 13 and table 3).

The fractures in stones filled with these mixtures became less apparent as the filler increased in refractive index. Although a weak flash was noted in the stone filled with the 1.522 R.I. mixture (90% cedarwood oil–10% Araldite), in general the flash effect became noticeable (as a weak blue flash) in the 1.539 R.I. mixture (60% cedarwood–40% Araldite), growing stronger as the R.I. increased. We concluded that, in this case, the variation in relative peak heights in the IR and Raman spectra was about as sensitive as flash effect for determining the presence of the high-R.I. artificial resin in the cedarwood oil mixtures.

Comparison with Previous Published Work. In general, there is good agreement between the Raman spectra published by Hänni et al. (1996a) and this study. Our results are similar to Hänni's for Permasafe ("New type of epoxy resin," 1998), but we saw an additional peak at 2928 cm^{-1}. According to Hänni et al. (1996b), artificial resins can be distinguished from "presumed natural" substances by the 1250, 1606, 3008, and 3069 cm^{-1} peaks in the Raman spectra of the former. In our filling substances, however, we could see (generally small) examples of each of these peaks in the spectra of certain cedarwood oils, other essential oils, or other vegetable oils. Hänni et al. (1996b) also saw features for cedarwood oil at 1440–1457 cm^{-1}, which we observed in some prepolymers as well.

Chalain et al. (1998) examined several UV-setting materials with lower R.I. values than the ones we studied; they also mentioned natural hydrocarbons in emerald, which we have not seen. They did not report the spectra for any of these, however.

Zecchini and Maitrallet (1998) looked at the IR spectra of several emerald fillers and related substances, including cedarwood oil, methyl methacrylate polymer, olive oil, "Israeli" (paraffin?) oil, Opticon 224, "palm oil," Indian Joban oil, red-colored Indian oil, and the Arthur Groom–Gematrat treatment, as well as the oil from human fingerprints. Our results agree with most, but not all, of theirs, in the cases where we studied the same materials. However, they interpreted the 3009 cm^{-1} peak in Joban and red oil as a dye band, whereas we saw this olefin band in all the vegetable oils we examined.

Sometimes, complete characterization cannot be done using FTIR or Raman, and only the type of chemical class can be identified (Julian et al., 1991). This is especially true for DGEBA epoxies, and neither FTIR nor Raman is likely to be useful in distinguishing prepolymers from hardened polymers in emeralds (but see the discussion of fluorescence, above, for another test).

Comparison with Substance Categories. Unfortunately, our spectral groups do not correspond precisely to the six substance categories indicated in table 1. *Essential oils* are found in IR and Raman spectral groups C, D, and E (group C also contains artificial resins). *Other oils* are in IR and Raman spectral group B; so is paraffin *wax*. Most *epoxy prepolymers* and *polymers* are in IR and Raman spectral group A. The *other prepolymers* (e.g., UV-setting adhesives) can be in group A (Epo Tek UVO114) or group C (in general), and HXTAL has characteristics of groups B and C.

Consequently, distinctions between artificial and "presumed natural" substances can most easily be made spectroscopically if the substance found is in group A (artificial resins only) or group D or E (essential oils only; but even in these cases, mixtures and multiple compounds must also be consid-

Figure 14. When water-insoluble filling substances (here, Araldite 6010) are mixed with water, they form a white cloudy emulsion. Left: Araldite 6010 and water before mixing; right: the substances shaken together. Photos by Maha DeMaggio.

ered). Distinctions between artificial and "presumed natural" substances are more problematic if the substance shows a group B or C spectrum. The distinctions within a spectral group may not be evident in filled emeralds, although this remains to be tested. The distinctions among groups C, D, and E can also be difficult to discern in a filled stone.

As another complication, the presence of spectral features indicating one particular compound does not preclude the existence of some other substance. As mentioned above, there can be almost 40% Araldite 6010 ("palma") in cedarwood oil—and the IR spectrum will still look like cedarwood oil, and not a mixture (although the Raman spectrum of the 20% Araldite mixture shows a DGEBA peak at 3068 cm^{-1}). Similarly, there can be about 10% cedarwood oil in Araldite before its presence is detected.

Combining the Approaches. That different gemological laboratories already determine the nature of filling materials is evident from auction records and other publications. Auction records (cited below) indicate that the identification of clarity enhancement substances by category or type has been performed by at least two laboratories: the SSEF in Basel, Switzerland, and the American Gemological Laboratory (AGL) in New York City.

SSEF provides identification reports, or "treatment slips," which state the category of filling material present (or the categories of fillers that are *not* present). This information is based on gemological examination as well as on Raman microspectrometry and FTIR spectroscopy (see, e.g., SSEF Swiss Gemmological Institute, 1998). The categories of fillers mentioned in SSEF treatment slips, as quoted in auction catalogs, include: oil, "natural oil," "natural resin," "artificial resin," and wax (Christie's, 1997b, 1997c, 1998a). According to Dr. Hänni (pers. comm., 1999), the categories currently in use are "oil," "Canada balsam," and "artificial resin."

As reported in auction catalogs, the AGL categories for "types" of filling materials include: "oil type," "Opticon/oil type," and "unidentified type" (Sotheby's 1997; Christie's 1998b). As of July 1997, AGL did not have Raman microspectrometry, and relied on the "flash effect" to identify the "vast majority" of fillers in emeralds examined there (Edry, 1997).

Our research has shown that the best results come from a combination of all the testing methods we have described. For instance, the conclusion that a material showing a flash effect is probably an artificial resin (DGEBA-based epoxy) is reasonable but not perfect; and the Raman and IR spectra of the common epoxy fillers are easily distinguished from those of available cedarwood oils. Raman and IR are more effective than gemological observation for distinguishing low-R.I. artificial resins from commonly used essential oils (all of which have no flash effect), and high-R.I. essential oils from DGEBA epoxies (all of which show a flash effect). However, the artificial resins in spectral group C all have low R.I.'s (and no flash effect) and may not be distinguishable from cedarwood oils.

CONCLUSIONS

Filler Terminology. On the basis of the findings presented here, and the discussion in Box A, we recommend the following terminology:

- The term *natural* should be avoided in discussions of emerald fillers, as "natural" substances are not currently distinguishable from their chemical equivalents synthesized in the laboratory (with the nondestructive tests we have available). Instead, substances such as essential oils, other oils, natural resins, and waxes should be referred to as "presumed natural."
- A distinction should be made between essential oils and other oils, as essential oils have different properties (e.g., they must be volatile) and a broader range of chemical structures (e.g., they can contain aromatic compounds). This difference may also be relevant to durability concerns.
- The term *synthetic* should be avoided, as it does not have the same meaning in chemistry that it has in gemology. Instead, manufactured prepolymers and polymers should be referred to as "artificial resins," as they have no natural equivalent.
- Prepolymers and polymers should be distinguished wherever possible, as their different mechanical properties are probably significant (e.g., liquid versus solid states), and may affect their durability in an emerald.
- Artificial resins should not be called "epoxies" unless they contain epoxide groups—if still liquid—or were joined into polymers with these groups (if solid; again, see Box A).
- Artificial resins should not be called "Opticon" or "Opticon type" unless they are known to be the

specific resin Opticon 224 (manufactured by Hughes Associates).

- Because a large quantity of one filler may make small amounts of another undetectable, we recommend restricting comments to the filler identified, and making no assurances that any others are absent.

Separating Fillers by Categories: Possible? Of the thousands of possible filling materials—about 3,500 essential oils and natural resins, many other oils, and several thousand commercially available polymers and prepolymers—we studied fewer than 40. None of the microscopic features (e.g., flash effect, fluorescence of the filled fractures) fully differentiates between the various categories of substances (again, see table 1), although such features may provide important clues.

Using Raman and FTIR spectroscopy, we found that the 39 isolated materials could be categorized into five spectral groups. The two groups that contain the most important "natural" fillers—cedarwood oil, Canada balsam, and vegetable oils—also contain materials that are not natural (Epo Tek 314 resin, UV-setting adhesives, Isocut fluid). Hence, identification of the spectral group alone is not sufficient to prove that a filling material is "natural." (However, the most commonly used artificial resins—Opticon 224, Araldite 6010, Epon 828—do occur in a spectral group that is easily distinguished from those in which the "presumed natural" fillers occur.)

Most of the isolated fillers we tested were "loose," that is, not in an emerald. A number of factors may limit the effectiveness of spectroscopic testing of substances after their emplacement in an emerald. In particular, transmission IR techniques are complicated by the fact that emerald is opaque in one diagnostic region (below 2000 cm^{-1}). Raman microspectrometry only samples near-surface areas of fissures, and fluorescence in the 3000 cm^{-1} region may interfere with the strongest Raman peaks. For both techniques, the filler peaks are generally much less prominent than the emerald spectral features.

On the basis of our results, we believe that the artificial resins most commonly used as emerald fillers can, *as pure substances*, be distinguished from cedarwood oils by a combination of gemological and spectroscopic properties, but other artificial resins also used in the trade cannot be so separated. The UV-setting adhesives are particularly problematic. At this time, we recommend the following procedure to identify individual fillers (or at least a substance category or spectral group): first, estimate the filler's refractive index (based on the presence or absence of a "flash effect"), and then obtain IR and/or Raman data. Other properties, such as fluorescence, also may be useful.

New filling materials and mixtures will continue to be discovered or adapted from other branches of science and technology. Competing factors make it unlikely that one best filler exists, and filler development continues. Kammerling et al. concluded their 1991 article with the comment: "It would, therefore, seem both inappropriate and misleading, in describing a filled fracture, to use wording that implies that the filling substance has been conclusively identified if in fact it has not." We must keep these uncertainties in mind as we try to identify specific substances.

However, the issue of filler identification is not the only one that must be addressed to understand fully the use of fillers in general, or of a specific filler in a particular emerald. Key questions remain: What is the effect of the degree of enhancement on an emerald's appearance? How does the enhancement change with time, normal wear, and other typical events in the life of a piece of jewelry? Given these questions, we are focusing on two main topics as we continue our research: (1) determination of the extent to which any particular emerald has been clarity enhanced; and (2) durability testing of several common emerald treatments.

Acknowledgments: The authors thank the following individuals for sharing their knowledge of emerald enhancements: Ricardo Alvarez Pinzon, Luis Ernesto Vermudez, and others at Treatment World Emerald, Gemológico Universal, Bogotá, Colombia; Dr. Rodrigo Giraldo, Centro Gemológico para la Investigación de la Esmeralda, Bogotá; Carlos Osorio, Mineralco, Bogotá; Jaime Rotlewicz, C. I. Gemtec, Bogotá; the staff of Alagecol (Asociación de Laboratorios Gemológicos), Bogotá; Ray Zajicek, Equatorian Imports, Dallas, Texas; Darrold Allen, Gemological Laboratory of Los Angeles, California; Kenneth Scarratt, AGTA Gemological Testing Center, New York City; Amnan Gad, Amgad Inc., New York City; Michael and Ari Gad, Gad International Ltd., New York City; Arthur Groom and associates, Arthur Groom–Gematrat, New York City; Morty Kostetsky, Arigad Gems, New York City; Dr. Kumar Shah, Real Gems Inc., New York City;

I. Z. Eliezri, Colgem Ltd., Ramat Gan, Israel; Ron Ringsrud, Constellation Colombian Emeralds, Saratoga, California; and Jess Williams and Andy Rendle, EmeraldStone Inc., Vancouver, BC.

Dr. Henry Hänni, Dr. Lore Kiefert, and J.-P. Chalain, SSEF Swiss Gemmological Institute, Basel, provided hospitality and information about the identification techniques used in their laboratory. MLJ also thanks the organizers of the First World Emerald Congress in Bogotá for their warm hospitality, and Mark Parisi for his support. Dr. George Rossman, of the California Institute of Technology in Pasadena, California, supplied much useful chemical information and advice.

Many GIA colleagues provided support for this project, including: Shane McClure, Maha DeMaggio, John Koivula, and Dino DeGhionno, GIA Gem Trade Laboratory (GTL), Carlsbad, California, and curator Jo Ellen Cole, GIA Carlsbad, who determined gemological properties; Margot McLaren of GIA's Richard T. Liddicoat Gemological Library and Information Center, Carlsbad, who located auction records; and GIA and GIA GTL colleagues Dr. James Shigley, Tom Moses, Dr. Ilene Reinitz, and Phil York, who gave suggestions that improved this manuscript.

GIA thanks Jewelers' Circular-Keystone, Radnor, Pennsylvania, and Kyocera Corp., Kyoto, Japan, for financial support of this research project. Michael Scott generously donated a Renishaw Raman microspectrometer to GIA, which was used in this research.

REFERENCES

Alger M.S.M. (1989) *Polymer Science Dictionary*. Elsevier Applied Science, London.

Benson L. (1960) Highlights at the Gem Trade Lab in Los Angeles. *Gems & Gemology*, Vol. 10, No. 1, pp. 3–6, 30–31.

Bleumink E., Mitchell J.C., Nater J.P. (1973). Allergic contact dermatitis from cedar wood (Thuja plicata). *British Journal of Dermatology*, Vol. 88, No. 5, pp. 499–504.

Bower D.I., Maddams W.F. (1989) *The Vibrational Spectroscopy of Polymers*. Cambridge University Press, Cambridge, England, 326 pp.

Brady G.S., Clauser H.R. (1986) *Materials Handbook: An Encyclopedia for Managers, Technical Professionals, Purchasing and Production Managers, Technicians, Supervisors, and Foremen*, 12th ed. McGraw-Hill Book Co., New York, 1038 pp.

Chalain J.-P., Hänni H.A., Kiefert L. (1998) Détermination des substances de remplissage dans les émeraudes. In D. Giard, Ed., *L'émeraude: Connaisances Actuelles et Prospectives*. Association Française de Gemmologie, Paris, pp. 107–115. (Translations where cited are by Mary Johnson.)

Christie's (1993) *Magnificent Jewels*. Auction catalog for Christie's Geneva, November 16 and 18, 1993.

Christie's (1997a) *Magnificent Jewels*. Auction catalog (in two parts) for Christie's New York, October 27–28, 1997.

Christie's (1997b) *Magnificent Jewels*. Auction catalog for Christie's Geneva, November 20, 1997.

Christie's (1997c) *Important Jewellery*. Auction catalog for Christie's London, December 16, 1997.

Christie's (1998a) *Important Jewels*. Auction catalog for Christie's St. Moritz, February 20–21, 1998.

Christie's (1998b) *Magnificent Jewels*. Auction catalog (in two parts) for Christie's New York, April 6–7, 1998.

Congress votes yes to promotion, no to codes (1995). *ICA Gazette*, August 1995, p. 9.

Crowningshield, G.R. (1958) Ascertaining the nature and extent of damage or inherent flaws in gemstones. *Gems & Gemology*, Vol. 9, No. 5, pp. 131–133, 159.

Crowningshield, G.R. (1960–1961) Developments and highlights at the Gem Trade Lab in New York. *Gems & Gemology*, Vol. 10, No. 4, pp. 114–123.

Edry S.G. (1997) Emerald filling: More research sought. *National Jeweler*, Vol. 41, No. 13, pp. 1, 64, 65.

Elias H.-G. (1993) *An Introduction to Plastics*. Weinheim, New York.

Federman D. (1997) Beyond buyer beware. *Modern Jeweler*, Vol. 96, No. 3, pp. 50, 51, 53–55.

Federman D. (1998a) *Modern Jeweler's Consumer Guide to Emeralds*. Supplement to *Modern Jeweler*, Vol. 97, No. 1, 7 pp.

Federman D. (1998b) Fair play. *Modern Jeweler*, Vol. 97, No. 2, p. 108.

Fryer C., Crowningshield R.C., Hurwit K., Kane R.E. (1984) Gem trade lab notes: Emerald, oiled. *Gems & Gemology*, Vol. 20, No. 1, pp. 46–47.

Genis R. (1997) The emerald controversy. *Rapaport Diamond Report*, Vol. 20, No. 38, pp. 69, 72–73.

Hänni H.A. (1988) An oil well in your garden. *Swiss Jewellery Journal*, No. 3, pp. 461–464.

Hänni H.A. (1998) Fracture filling in emeralds and its detection with laboratory methods. *ICA Gazette*, July/August 1998, pp. 5–7.

Hänni H.A., Kiefert L., Chalain J.-P., Wilcock I.C. (1996a) Ein Renishaw Raman Mikroskop im gemmologischen Labor: Erste Erhfarhrungen bei der Anwendung. *Zeitschrift der Deutschen Gemmologischen Gesellschaft*, Vol. 45, No. 2, pp. 55–70.

Hänni H.A., Kiefert L., Chalain J.P. (1996b) How to identify fillings in emeralds using Raman spectroscopy. *Jewellery News Asia*, No. 145, pp. 154, 156.

Hänni H.A., Kiefert L., Chalain J.P. (1997) Renishaw Raman nothing new. *Rapaport Diamond Report*, Vol. 20, No. 40, p. 11.

Harris D.C., Bertolucci M.D. (1978) *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*. Oxford University Press, Oxford, England, 550 pp.

Herout V. (1982) Sesquiterpene alcohols. In E.T. Theimer, Ed., *Fragrance Chemistry: The Science of Smell*. Academic Press, New York, pp. 222–263.

Hurwit K. (1989) Gem trade lab notes: Emerald, with plastic-like filling. *Gems & Gemology*, Vol. 25, No. 2, p. 104.

Johnson M.L., Koivula J.I. (1997) Gem news: A new emerald filler. *Gems & Gemology*, Vol. 33, No. 2, pp. 148–149.

Johnson M., McClure S., Koivula J., Moses T. (1998a) How to detect clarity enhancement in emeralds. *Modern Jeweler*, Vol. 97, No. 1, pp. 58–61.

Johnson M.L., Koivula J.I. (1998b) Gem news: A preliminary report from the First World Emerald Congress. *Gems & Gemology*, Vol. 34, No. 1, pp. 56–57.

Julian J.M., Anderson D.G., Brandau A.H., McGinn J.R., Million A.M., Brezinski D.R. (1991). *An Infrared Spectroscopy Atlas* *for the Coatings Industry*, 4th ed., Vol. 1. Federation of Societies for Coatings Technology, Blue Bell, PA.

Kammerling R.C., Koivula J.I., Kane R.E., Maddison P., Shigley J.E., Fritsch E. (1991) Fracture filling of emeralds: Opticon and traditional "oils." *Gems & Gemology*, Vol. 27, No. 2, pp. 70–85.

Kammerling R.C. (1993) Gem trade lab notes: Emerald, with large filled etch channels. *Gems & Gemology*, Vol. 29, No. 4, p. 280.

Kammerling R.C., McClure S.F., Johnson M.L., Koivula J.I., Moses T.M., Fritsch E., Shigley J.E. (1994) An update on filled diamonds: Identification and durability. *Gems & Gemology*, Vol. 30, No. 3, pp. 142–177.

Kammerling R.C., Maddison P., Johnson M.L. (1995) Gem trade lab notes: Emerald, with unusual flash-effect colors. *Gems & Gemology*, Vol. 31, No. 1, p. 54.

Kane R.E. (1990) Gem trade lab notes: Emerald, with filled fractures. *Gems & Gemology*, Vol. 26, No. 1, pp. 95–96

Kennedy H.F. (1998) Brazilian emeralds: Oiling at the source. *National Jeweler*, Vol. 42, No. 10, pp. 36–52 passim.

Koivula J.I. (1999) Gem trade lab notes: Emerald, the case of the invisible filler. *Gems & Gemology*, Vol. 35, No. 1, pp. 43–44.

Lee H., Neville K. (1967) *Handbook of Epoxy Resins*. McGraw-Hill Book Co., New York.

Liddicoat R.T. Jr.(1962) *Handbook of Gem Identification*, 6th ed. Gemological Institute of America, Los Angeles, 396 pp.

Lincoln W.A. (1986) *World Woods in Color*. Linden Publishing, Fresno, CA, 320 pp.

Mutton, D.B. (1982) Wood resins. In W.E. Hillis, Ed., *Wood Extractives and Their Significance to the Pulp and Paper Industries*. Academic Press, New York, pp. 331–365.

Nassau K. (1994) *Gemstone Enhancement: History, Science, and State of the Art*, 2nd ed. Butterworth-Heinemann, Oxford, England, 252 pp.

New type of epoxy resin. (1998) *Jewellery News Asia*, No. 172, p. 60.

Nicolet (1992) *Omnic Interpretation Guide: Infrared Spectroscopy*, Version 1.0, Nicolet Instrument Corp., Madison, Wisconsin.

Ottaway T.L., Wicks F.J., Bryndzia L.T., Kyser T.K., Spooner E.T.C. (1994) Formation of the Muzo hydrothermal emerald deposit in Colombia. *Nature*, Vol. 369, pp. 552–554.

Pine S.H., Hendrickson J.B., Cram D.J., Hammond G.S. (1980) *Organic Chemistry*, 4th International Student Edition. McGraw-Hill International, Tokyo, 1039 pp.

Pouchert, C.J. (1985). *The Aldrich Library of FT-IR Spectra*, Vol. 1. The Aldrich Chemical Co., Milwaukee, WI.

Review on ruby promotion. (1997) *Jewellery News Asia*, No. 158, p. 58.

Ringsrud R. (1983) The oil treatment of emeralds in Bogotá, Colombia. *Gems & Gemology*, Vol. 19, No. 3, pp. 149–156.

Ringsrud (1998) Stick with cedarwood. *Modern Jeweler*, Vol. 97, No. 3, p. 10.

Sinkankas J. (1981) *Emeralds and Other Beryls*. Chilton Book Co., Radnor, PA, 665 pp.

Sivry B. (1985) Colles et adhédifs. *Encyclopaedia Universalis*, Corpus 5, pp. 74–78. (Translations where cited are by Mary Johnson.)

Sotheby's (1992a) *Magnificent Jewels*. Auction catalog for Sotheby's Geneva, November 18, 1992.

Sotheby's (1992b) *Jewels*. Auction catalog for Sotheby's London (Colonnade), November 26, 1992.

Sotheby's (1993) *Magnificent Jewelry*. Auction catalog for Sotheby's New York, October 20–21, 1993.

Sotheby's (1997) *Magnificent Jewels*. Auction catalog for Sotheby's New York, October 29–30, 1997

SSEF Swiss Gemmological Institute (1998) *Standards and Applications for Diamond Report, Gemstone Report, Test Report*. SSEF, Basel, Switzerland, 118 pp.

Stecher P.G., Windholz M., Leahy D.S., Bolton D.M., Eaton L.G. (1968) *The Merck Index*, 8th ed. Merck & Co., Rahway, NJ.

Survey: Emerald treatments (1997). *The Guide Quarterly Report*, Vol. 16, No. 2, p. 15.

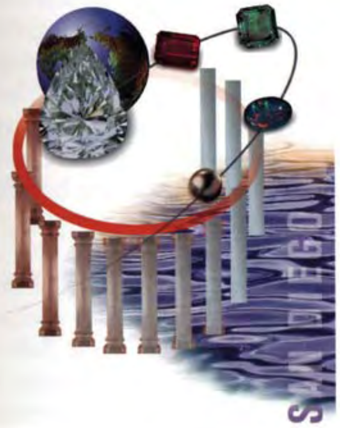
Webster R., Read P.G. (1994) *Gems: Their Sources, Descriptions, and Identifications*, 5th ed. Butterworth-Heinemann, Oxford, 1026 pp.

Webster's Ninth New Collegiate Dictionary (1987) Merriam-Webster Inc., Springfield, MA, 1,563 pp.

Weldon R. (1998a) Treatment tracer. *Professional Jeweler*, Vol. 1, No. 3, p. 50.

Weldon R. (1998b) Filling a need. *Professional Jeweler*, Vol. 1, No. 5, pp. 80, 82, 84.

Zecchini P., Maitrallet P. (1998) Que peut apporter la spectrographie infrarouge dans l'étude des émeraudes? In D. Giard, Ed., *L'émeraude: Connaisances Actuelles et Prospectives*. Association Française de Gemmologie, Paris, pp. 81–96.



Coming . . .

in the Fall Issue of *Gems & Gemology*:

PROCEEDINGS OF THE THIRD INTERNATIONAL GEMOLOGICAL SYMPOSIUM