

THE CHARACTERIZATION OF TORTOISE SHELL AND ITS IMITATIONS

Thomas Hainschwang and Laurence Leggio

Tortoise shell has long been used as an ornamental gem material for art objects, jewelry, and personal items such as combs and eyeglass frames. Though humans have used tortoise shell for thousands of years, the material reached the height of its popularity during the 18th, 19th, and early 20th centuries. The advent of plastic imitations, as well as the passage of laws protecting sea turtles beginning in the 1970s, have led to a drastic reduction in the amount of tortoise shell in the market. Nevertheless, because older material can still be traded, especially in antique pieces, and because numerous imitations exist, proper identification is still important. This study summarizes the gemological properties of tortoise shell and its imitations. In addition to standard gemological data, the results of several spectroscopic techniques are presented; transmission and specular reflectance infrared spectroscopy were found to be of particular value.

The term “tortoise shell” generally refers to the carapacial (dorsal shell) and plastron (belly) plates of the hawksbill sea turtle (*Eretmochelys imbricata*). The use of tortoise shell dates at least to pre-dynastic Egypt (3500–3100 BC), from which period dishes, combs, bracelets, and the like are known (“Animal products...,” 2005). Tortoise shell objects were popular with both the ancient Greeks and wealthy citizens of ancient Rome (Bariand and Poirot, 1998). The commercial exploitation of this material in Europe began as early as the 15th century in Spain (“Natural plastics,” 2005), and many types of tortoise shell objects have been produced since then. These include furniture inlays, eyeglass frames, decorative boxes, rings, bracelets, and earrings (see, e.g., figure 1). In Japan, tortoise shell crafting, or *bekko*, has been an important industry since at least the 17th century, most of it centered in Nagasaki (Pedersen, 2004). *Bekko* objects such as hair ornaments are still being created today from stockpiled material.

The vast majority of worked tortoise shell material comes from the shells of two species of sea turtles: the hawksbill and, more rarely, the green turtle (see box A). The shells of these turtles exhibit attractive patterns that normally consist of light to dark brown

patches, though a homogeneous “cream”-colored variety called *blond tortoise shell* also exists. The popularity of tortoise shell during the 18th through early 20th centuries caused these animals to be hunted almost to extinction, leading to a near-worldwide ban on collection in the 1970s, as well as a ban on international trade in tortoise shell products (Spotila, 2004; box B). For the modern gemologist, tortoise shell has become a rather exotic material, for which a thorough gemological study is lacking.

BACKGROUND ON TORTOISE SHELL AND PLASTICS

Tortoise shell is composed of β -keratin, an insoluble protein (Voet et al., 2005), and is almost identical in composition to hair and nail. The structure of tortoise shell defines this material as a natural polymer: It consists of long chains of organic molecules and thus has a high molecular weight. Each of these organic molecules is called a *monomer* (from the Greek meaning

See end of article for About the Authors and Acknowledgments.
GEMS & GEMOLOGY, Vol. 42, No. 1, pp. 36–52.
© 2006 Gemological Institute of America



Figure 1. A popular and often-seen gem material during the 18th and 19th centuries, tortoise shell has since become a rare oddity for most gemologists. Shown here are a pair of Egyptian revival earrings, approximately 6.5 cm long. From Mona Lee Nesseth, *Custom and Estate Jewels*, Los Angeles; courtesy of Tricia and Michael Berns. Photo © Harold & Erica Van Pelt.

“single part”); they combine to form a *polymer* (from the Greek meaning “many parts”). *Polymer* is a generic term for a long molecule with repeating parts; a molecule is considered a polymer when it exceeds about 1,000 atoms in length (Bloomfeld, 2000). There are many types of polymers, both organic and inorganic, with a wide variety of properties. All the materials described in this study are organic polymers; other natural organic polymers include horn, tree resins and fossilized tree resins (amber), natural rubber, bitumen, and waxes (Langenheim, 2003).

The term *plastic* refers to a broad class of materials of various chemical combinations, mainly of the organic elements carbon, oxygen, nitrogen, and hydrogen (and sometimes including inorganic elements such as chlorine). Plastics are covalently bonded polymers with various added components

(Bloomfeld, 2000; Van der Vegt, 2002) and can be classified as *natural*, *semisynthetic*, and *synthetic*. Natural plastics include shellac, rubber, asphalt, cellulose, and tortoise shell. Semisynthetics (so-called because they are natural materials that have been chemically modified) include cellulose nitrate (e.g., Celluloid, Xylonite, Parkesine), cellulose acetate (e.g., Safety Celluloid, Bexoid, Clarifoil, Tenite), and casein formaldehyde (e.g., Lactoid, Erinoid, Galalith; Van der Vegt, 2002). Most plastics used today are fully synthetic; these include phenol formaldehyde resin (Bakelite) and polyester resins (e.g., PET and polyurethane), among many others.

Plastics can also be divided into *thermosetting* and *thermoplastic* materials. Thermosetting plastics can be liquefied and hardened only once, similar to concrete. Once such a material has been hardened (poly-

BOX A: SEA TURTLE CLASSIFICATION AND BIOLOGY

As explained in Perrine (2003) and Spotila (2004), turtles are reptiles belonging to the order of the Chelonians, a very ancient group that originated in the late Triassic, about 230 million years ago. Marine turtles appeared about 80 million years ago and represent reptiles that had adapted to life in the sea. There are only two families of contemporary marine turtles: the Cheloniidae and the Dermochelyidae. The first corresponds to the sea turtles that have a shell, and today this family consists of six species:

- Hawksbill turtle, *Eretmochelys imbricata* (Linnaeus, 1766)
- Green turtle, *Chelonia mydas* (Linnaeus, 1758)
- Loggerhead turtle, *Caretta caretta* (Linnaeus, 1758)
- Kemp's Ridley turtle, *Lepidochelys kempii* (Garman, 1880)
- Olive Ridley turtle, *Lepidochelys olivacea* (Eschscholtz, 1829)
- Flatback turtle, *Natator depressa* (Garman, 1880)

The black turtle (*Chelonia agassizii*; Bocourt, 1868) was at one time regarded as a separate species,

Figure A-1. The shell of a hawksbill turtle is the traditional source for the tortoise shell used as a gem and ornamental material. Commercial harvesting of hawksbill turtles is now prohibited by international treaties. Photo by Johan Chevalier.



but recent research using mitochondrial DNA testing has shown that it is in fact a variety of green turtle (Karl and Bowen, 1999).

Of these six species, only the shell of the hawksbill turtle (figure A-1) and, more rarely, the green turtle (figure A-2) is typically used for ornamental objects and jewelry. The shells of these two species often cannot be easily distinguished, especially after being worked into objects, except by analysis of the ratio of the two amino acids lysine and histidine (Hendrickson et al., 1976).

The second family corresponds to turtles that have a body covered only by a leathery skin. Today, this family consists of only one species: the Leatherback turtle, *Dermochelys coriacea* (Vandelli, 1761). Marine turtles are migrating species with worldwide distribution.

The Hawksbill Turtle. The name originates from the turtle's bill, which has a shape reminiscent of a hawk's. The 13 plates of its carapace overlap one another like the tiles of a roof, which is the source of the scientific name *Eretmochelys imbricata* (*imbricatus* being Latin for "covered with tiles"). The plates have a maximum thickness of 9–12 mm (Bariand and Poirot, 1998). The relief of the carapace diminishes with age, as the plates become thicker and lose the typical imbrications. The carapace can be brown-red to brownish orangy yellow, with dark brown to black marbling or yellow to brownish yellow striations; the plastron scutes (horny plates; figure A-3) that cover the "belly" of the animal are white to yellow, sometimes with a little dark pigmentation. This turtle, which represents the only species that has been commercially exploited for ornamental tortoise shell, has a maximum length of about 95 cm (a little over 3 ft.) and an average weight of 62 kg (137 lbs.).

The Green Turtle. The name *green turtle* originates from the color of its flesh; the carapace of adult animals is olive or brown, patchy or marbled. The coloration varies considerably from one individual to another. In young adults, the carapace typically is mahogany brown with light striations; later, the green-yellow color becomes predominant. *Chelonia mydas* is a large species (80–130 cm long) with an average weight of 160 kg (a maximum of 400 kg has been reported).

Only rarely has the carapace of the green turtle



Figure A-2. Though it superficially resembles that of a hawksbill turtle, the shell of the green turtle (shown here) has only rarely seen use as a gem material because its thinner shell plates are much more difficult to work. Photo by Erich Frederico Betz.

been used as an ornamental material, since it is usually not as attractive as the shell of the hawksbill turtle, and since the scutes are much thinner and thus more difficult to work. Nevertheless, it can occasionally be seen, especially as inlay in "Boulle" furniture from the 17th and 18th centuries. The species is considered to be in danger of extinction because of over-harvesting and unsustainable exploitation.

Figure A-3. The plastron (belly) plates of the hawksbill turtle have also been worked into objects; the resulting material is often referred to as blond tortoise shell. Photo © Smaro Touliatou/ARCHELON.



merized), generally it cannot easily be melted. Thermoplastic materials have properties similar to those of wax, as they can be melted and shaped multiple times. The reason for these differences is that the polymer chains in thermoplastic materials remain linear (i.e., they do not undergo a chemical change during molding) and thus can be separated easily by heat. In contrast, the polymer chains in a thermosetting plastic are chemically altered during molding and form a three-dimensional network by "cross-linking." Cross-linked plastics tend to have superior properties compared to linear plastics, such as greater resistance to heat and chemicals (Bloomfeld, 2000).

Tortoise shell is a natural thermoplastic material, and behaves very much like certain synthetic or semisynthetic plastics. Using heat and pressure (molding), the artisan can fuse several thin pieces into one thick piece and then, to a certain degree, form it into desired shapes (Bariand and Poirot, 1998).

Imitations of tortoise shell (see, e.g., figure 2) first appeared after the development of artificial plastics in the 19th century. Possibilities for using natural plastics were identified in the 17th century by the Englishman John Osbourne ("Natural plastics," 2005), who produced moldings from horn. The first semisynthetic plastic, and the first material used to imitate tortoise shell, was cellulose nitrate, also known as *Celluloid*, which was invented in 1862 by Alexander Parkes (Sears, 1977; Buist, 1986). The problem with this material, however, was its high flammability. In 1892, cellulose acetate was developed by Cross, Bevan, and Beadle (Sears, 1977); this material, which is much less flammable than celluloid, was marketed as *Safety Celluloid*. Around the same time, in 1897, casein formaldehyde was invented by Adolf Spitteler (Gibbs, 1977); it is produced by the interaction of the milk protein casein with formaldehyde. Bakelite, invented and patented around 1907 by Leo Baekeland (Farrar, 1968; Buist, 1986), was the first fully synthetic plastic, produced by the condensation of phenol and formaldehyde. Many of the other plastics commonly used for imitating tortoise shell, such as polyester, were developed between 1930 and 1950 (Buist, 1986).

Typically, tortoise shell can be readily identified by microscopy and luminescence techniques. In some cases, however, it may be difficult to separate tortoise shell from other organic materials in polished objects unless spectroscopic methods are used.

Although tortoise shell is a natural plastic, the term *plastic* alone in this article refers to semisynthetic or synthetic imitations.

BOX B: LEGAL ASPECTS OF TRADE IN TORTOISE SHELL

A number of international treaties and conventions govern trade in tortoise shell. The most comprehensive and important is the Convention on International Trade in Endangered Species (CITES), which was first agreed upon in 1973. The primary aims of CITES are surveillance of the international trade in wild animals and plants, and assurance that this commercial exploitation does not endanger the survival of protected species. There are currently more than 160 CITES member countries, including the United States, Canada, Japan, Australia, and all members of the European Union. Since this convention became effective, no protected species has become extinct.

CITES governs all trade (export, re-export, and import from international waters) of the species listed in its three Annexes, depending on the degree of protection necessary. Annex I, which includes sea turtles, covers species in danger of extinction. Trade in these species or in products derived from them is authorized only in exceptional conditions, such as for purely scientific research. (Annexes II and III provide lesser degrees of protection for species not in danger of extinction.) Only older tortoise shell material, dating prior to 1975, can be traded under CITES; all other trade is prohibited. For more information on the legal aspects of tortoise shell, see "Special issue..." (2002), Perrine (2003), and Spotila (2004).

MATERIALS AND METHODS

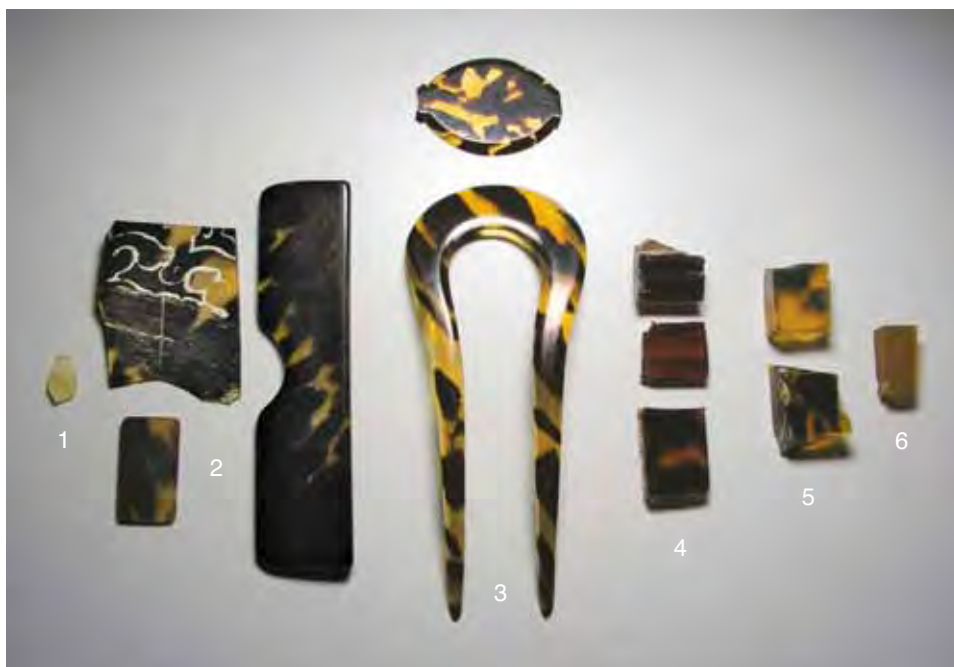
Several samples of tortoise shell and its imitations were analyzed for this study (see, e.g., figure 3). The tortoise shell materials included five unworked pieces (one from a green turtle from French Guyana and four samples from hawksbill turtles, two from Cameroon and two of unknown origin), 10 polished samples of unknown origin, and one object (a small box) made of blond tortoise shell; one polished sample stabilized with artificial resin was analyzed prior to this study,

and its properties will be mentioned only briefly in the Discussion section. During the examination of a large collection of jewelry by one of the authors (TH), 15 objects made of tortoise shell were analyzed, all of which had been worked in part by heat and pressure. The observations made on these objects are also included in this study. The synthetic and semisynthetic plastic imitations included the following (number of samples in parentheses): cellulose nitrate (3), cellulose acetate in various colors (10), polyester (3),

Figure 2. Because of the expense of the genuine material and legal restrictions on its collection, tortoise shell has frequently been imitated by various plastics. Inexpensive imitations such as these are very common in the consumer market. Photo by D. Mengason.



Figure 3. A wide variety of materials have been used to imitate tortoise shell, and their appearances are often superficially similar. Shown here are some of the materials examined in this study. From left: horn (1), tortoise shell (2), cellulose nitrate (3), cellulose acetate (4), polyester (5), and casein formaldehyde (6). Photo by T. Hainschwang.



casein formaldehyde (1), and phenol formaldehyde (1). The plastics were obtained from two manufacturers of polymer materials in the Rhône-Alpes region (France) and from various collections. A piece of horn (similar in appearance to blond tortoise shell) and a sample of human nail also were included to investigate their similarities to tortoise shell.

The samples were analyzed by standard gemological methods including microscopy, fluorescence to long- and short-wave UV radiation (all samples), specific gravity (hydrostatic method; one sample of each type of material, except nail), and refractive index testing (on all polished samples, representing all substances, except nail) using a GIA Instruments refractometer.

Characteristic odors were noted by hot point and hot water testing on one randomly selected sample of each material. For the hot point testing, the material was touched with a needle that had been heated by a simple flame; the hot water testing was performed by immersing the sample for 30 seconds in water with a temperature of approximately 60°C (140°F).

Infrared (IR), visible-near infrared (Vis-NIR), and photoluminescence (PL) spectral analyses were performed for selected samples of all materials included in this study. Samples were chosen based on their color, transparency, and thickness. IR transmission spectra were recorded at room temperature with a PerkinElmer Spectrum BXII Fourier-transfer infrared (FTIR) spectrometer (4 cm⁻¹ resolution) using a deuterium triglycine sulfate (DTGS) detector. The spec-

tra were recorded from samples of ~5 mm thickness and thin films. The “thick” spectra (recorded for five samples of tortoise shell and one or two samples each of the other materials) were taken because most samples of tortoise shell and imitation tortoise shell may not be damaged or destroyed for analysis, and these will commonly have a thickness of ~5 mm. These spectra, taken in the range of 7800–3700 cm⁻¹, are representative of what can generally be obtained from finished objects by nondestructive transmission FTIR spectroscopy. Since pieces of this thickness show too much absorption below ~5000 cm⁻¹, thin films were prepared from randomly selected samples of all materials included in this study, to obtain spectra of the entire range between 7800 and 400 cm⁻¹. A total of 11 thin films were tested: one for each of the plastics and one for each of the natural materials, except for the tortoise shell, for which four samples were polished into a thin film. To collect such complete spectra without the use of the KBr powder method, we had the thin samples polished down to a thickness of <0.01 mm.

Specular reflectance IR spectra were recorded for four samples of tortoise shell and one or two samples each of the other materials (except nail) with the same FTIR system using a PerkinElmer specular reflectance accessory, with 4 cm⁻¹ resolution. This method is commonly employed to observe the mid-infrared spectra of polished minerals without using the destructive KBr pellet technique; the infrared beam is not transmitted through a sample, but rather is reflected off the polished surface. This

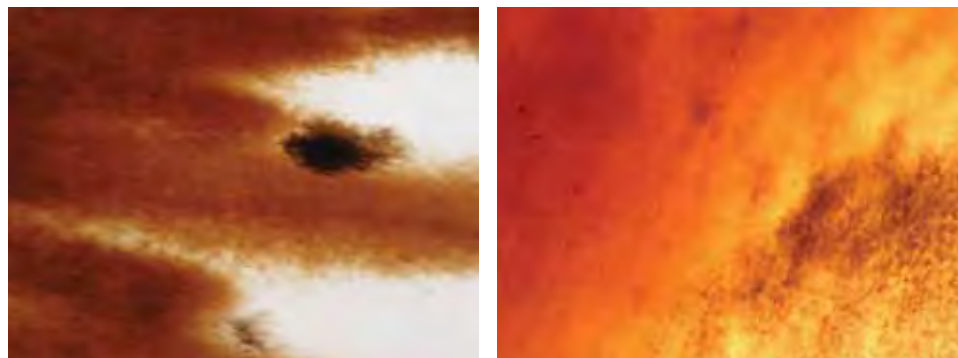


Figure 4. When examined with magnification, tortoise shell typically has a distinctive appearance consisting of tiny spots that make up the large brown patches. Photomicrographs by T. Hainschwang; magnified 25× (left), 60× (right).

produces data similar to KBr powder absorption spectra but with some differences, such as shifted and asymmetric peaks, depending on the materials analyzed. In the authors' experience, organic materials such as tortoise shell show significantly different spectra in reflectance versus transmission modes, whereas other gem materials such as garnet produce very similar spectra in both modes. Specular reflectance spectra can be transformed into true absorption spectra by the Kramers-Kronig transform (White, 1974).

Vis-NIR transmission spectra in the range of 400–1000 nm were recorded for two samples of tortoise shell, three samples of cellulose acetate, and one sample of each of the other materials with a custom SAS 2000 system equipped with an Ocean Optics SD2000 dual-channel spectrometer (optical

resolution 1.5 nm) using a 2048-element linear silicon charged-coupling device (CCD)-array detector; samples were analyzed in an integration sphere. The spectra are shown in transmission mode to enhance the visibility of the broad bands useful for distinguishing these materials.

PL spectra were recorded for one sample of each material using a 532 nm semiconductor laser, with the same spectrometer and CCD detector that were used for the Vis-NIR spectra, at a resolution of 1.5 nm. All spectra were recorded at room temperature.

RESULTS

Visual Appearance and Gemological Properties. The tortoise shell samples varied in color, the most common being a light brownish yellow with darker

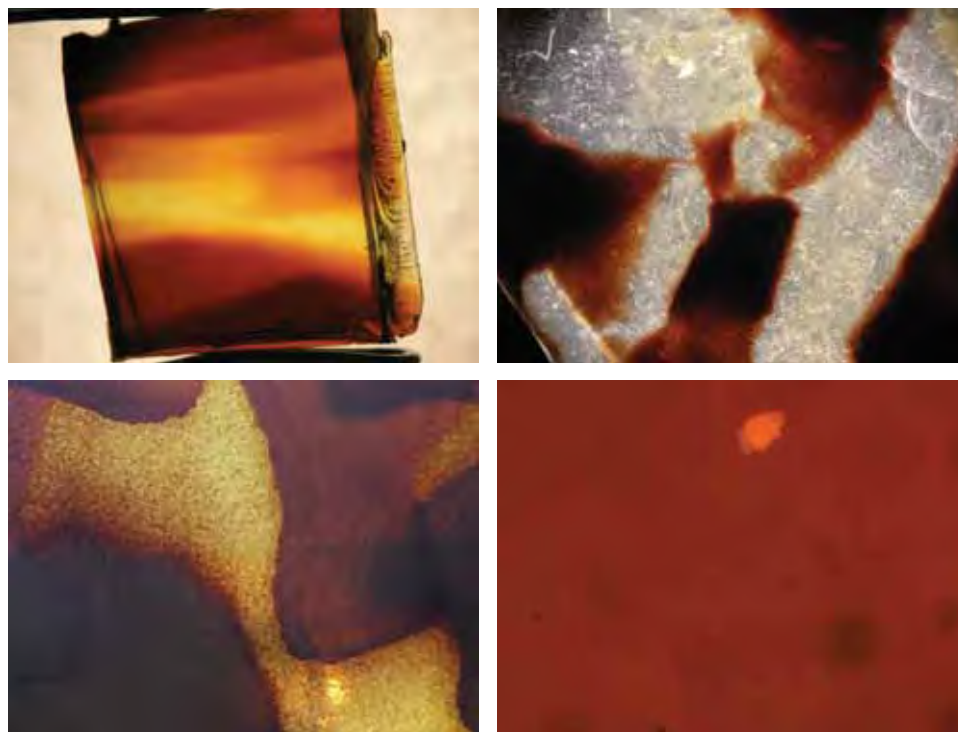


Figure 5. In contrast to tortoise shell, imitations such as cellulose acetate (top left) and cellulose nitrate (top right) show a homogenous appearance lacking the tiny spots of pigment typical of tortoise shell. In some polyester imitations (bottom), the color is distributed as small spots, though these do not resemble the pigment spots in natural tortoise shell. These inclusions are typically small white to black flakes, likely unmelted source material. Photomicrographs by T. Hainschwang; magnified 15× (top left), 10× (top right), 13× (bottom left), 80× (bottom right).

brown patches. The small box made of blond tortoise shell was a largely homogenous “cream” color. One unworked sample was almost entirely dark brown to nearly black. Microscopic observation revealed that the dark patches were made up of tiny spots (figure 4).

The plastic imitations covered a range of colors from “blond” to patchy to nearly black. Their color appearance was commonly very different from that of tortoise shell. Even if they were macroscopically similar, magnification revealed an absence of the “spotty” micropattern; instead, the brown patches were quite homogenous and unlikely to be confused with true tortoise shell. In some polyester imitations, the color was distributed in small spots (figure 5), but these were still very different from the pigment spots seen in tortoise shell.

Three samples of tortoise shell that had been worked by the use of heat and pressure into desired shapes and thickness lacked the typical spotty appearance. Thus, these somewhat resembled the plastic samples under the microscope. Interestingly, none of the plastic samples contained the trapped gas bubbles that are frequently seen in plastics and could help

identify such materials. However, all the plastic samples contained small flaky particles of unknown nature (again, see figure 5), which were most likely unmelted remnants of the source materials.

Standard gemological properties for tortoise shell and its plastic imitations are given in table 1. Often these properties will be sufficient to identify the material; however, there is overlap in some properties, especially specific gravity and refractive index. Unfortunately, the most useful gemological test for the identification of these substances, the hot point, is a destructive one: Tortoise shell smells like burned hair (as does horn), while plastics have very different odors. An alternative to the hot point is the hot water test, which involves rinsing the materials under hot tap water. It was noted in this study that this test will provoke the characteristic odor of most plastics without damaging them. Cellulose nitrate, cellulose acetate, casein formaldehyde, and phenol formaldehyde may be identified in this fashion. Tortoise shell does not have a discernable odor when tested by this method, and as long as the water temperature does not exceed ~80°C, the material will not be damaged.

TABLE 1. The standard gemological properties of tortoise shell and its imitations.

Material	R.I. ^a	S.G. ^a	Long-wave UV ^b	Hot point odor ^c	Crossed polarizers
Tortoise shell	1.54	1.26–1.35	Chalky blue-white (light areas), dark patches appear brown with super-imposed chalkiness. Intensity: medium	Burnt hair	Light appearance (aggregate-like); cross-hatched interference colors in worked/bent samples
Horn (pale yellow, to imitate blond tortoise shell)	1.54	1.26–1.35	Chalky blue-white. Intensity: medium-strong	Burnt hair	Light appearance (aggregate-like)
Cellulose nitrate (<i>Celluloid</i>)	1.50–1.51	1.36–1.42 (rarely up to 1.80)	Chalky bluish yellow (light areas). Intensity: medium. Dark patches fluoresce orange brown. Intensity: weak	Camphor	Dark appearance
Cellulose acetate (<i>Safety Celluloid</i>)	1.49–1.51	1.29–1.40 (rarely up to 1.80)	Variable: chalky bluish green to chalky bluish white. Intensity: very weak to weak. Sometimes brown patches fluoresce orange. Intensity: medium	Vinegar	ADR (4 times dark in 360° rotation), in some samples very weak ADR only
Polyester	1.56	1.23	Chalky yellowish green. Intensity: weak	Acrylic	ADR (4 times dark in 360° rotation)
Casein formaldehyde (<i>Galalith</i>)	1.55–1.56	1.32–1.34	Chalky yellow. Intensity: medium	Burned milk	ADR (cross-hatched extinction)
Phenol formaldehyde (<i>Bakelite</i>)	1.61–1.66	1.25–1.30	Inert to chalky yellowish blue. Intensity: very weak	Formaldehyde, acrylic	ADR (cross-hatched appearance)

^aR.I. and S.G. ranges are from Webster, 1994 (except for polyester, the values of which were determined by the authors); values of samples included in this study were determined to be within the given ranges.

^b Short-wave UV radiation excited the same luminescence, but the intensity was considerably weaker in all materials

^cThe odor, even if weaker, can be readily provoked in most plastics by immersion in hot water (~60°C).



Figure 6. When exposed to long-wave UV radiation, the fluorescence reactions of the materials in figure 3 are quite distinct despite their similarities in normal light. As seen here, tortoise shell's chalky blue-white reaction usually can allow easy separation from imitations. From left: horn (1), tortoise shell (2), cellulose nitrate (3), cellulose acetate (4), polyester (5), and casein formaldehyde (6). Photo by T. Hainschwang.

Fluorescence to both long- and short-wave UV radiation was chalky blue-white for the light areas of tortoise shell, while the dark patches appeared brown with a superimposed chalkiness (figure 6). The plastics showed variable luminescence, which depended on the dyes used to color the materials. The plastics themselves generally luminesced chalky blue with a yellow modifier (and thus sometimes appeared green) to chalky yellow (again, see figure 6). Dyes may induce a different luminescence: The cellulose nitrate samples showed a very slight

orange-brown luminescence in the brown areas, while the brown patches in certain samples of cellulose acetate exhibited an orange luminescence of medium intensity. For all samples, the only noticeable difference between long- and short-wave UV was the strength of the emission excited by the two sources; the luminescence color was the same.

When rotated between crossed polarizers, the tortoise shell samples appeared light in all positions (i.e., an aggregate reaction similar to, for example, chalcedony and jadeite). The same was true for the

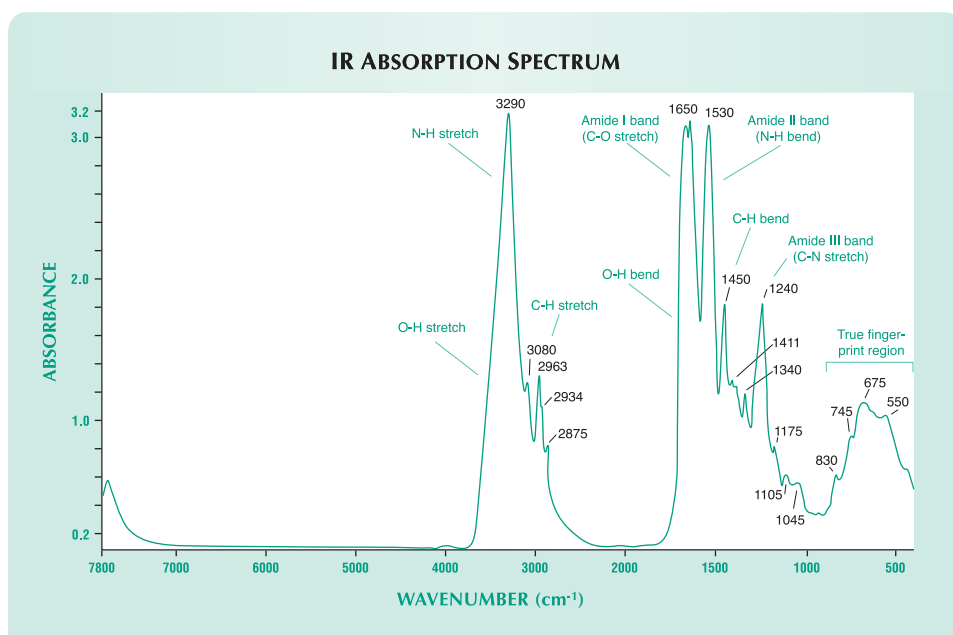


Figure 7. The IR spectrum of a thin film (<0.01 mm thick) of tortoise shell shows several distinctive absorption peaks. It is almost identical to that of the protein keratin, and thus shows characteristic absorptions due to organic functional groups such as CH, NH, and OH. The region below 2000 cm^{-1} is expanded for clarity.

samples of horn and nail. This appearance in tortoise shell was seen as long as the material had not been forced into a curved shape; in curved objects such as bangles, a weak cross-hatched pattern of interference colors could be observed, but no extinction. The reactions of all the plastic imitations were distinctly different from that of tortoise shell, with none of those samples exhibiting tortoise shell's aggregate-like reaction. The cellulose nitrate samples stayed dark when rotated between crossed polarizers; this was the only truly isotropic material seen in this study. All the other plastics showed anomalous double refraction (ADR) either as cross-hatched extinction patterns or as four sequential extinctions per full rotation. Such ADR reactions indicate the presence of strain.

Transmission IR Spectroscopy. The thin-film IR spectrum of the tortoise shell was mainly characterized by strong absorptions around 3290, 1500, and 600 cm^{-1} (figure 7). The strong band at 3290 cm^{-1} corresponds to the N-H stretch (Coates, 2000; Naumann, 2000). OH-related absorption found in the same region was superimposed by the strong NH absorption and therefore was not visible. The absorptions around 2900 cm^{-1} correspond to the C-H stretch. The CH bend was visible as a distinct band at 1450 cm^{-1} . (*Stretch* and *bend* are terms used in IR spectroscopy to

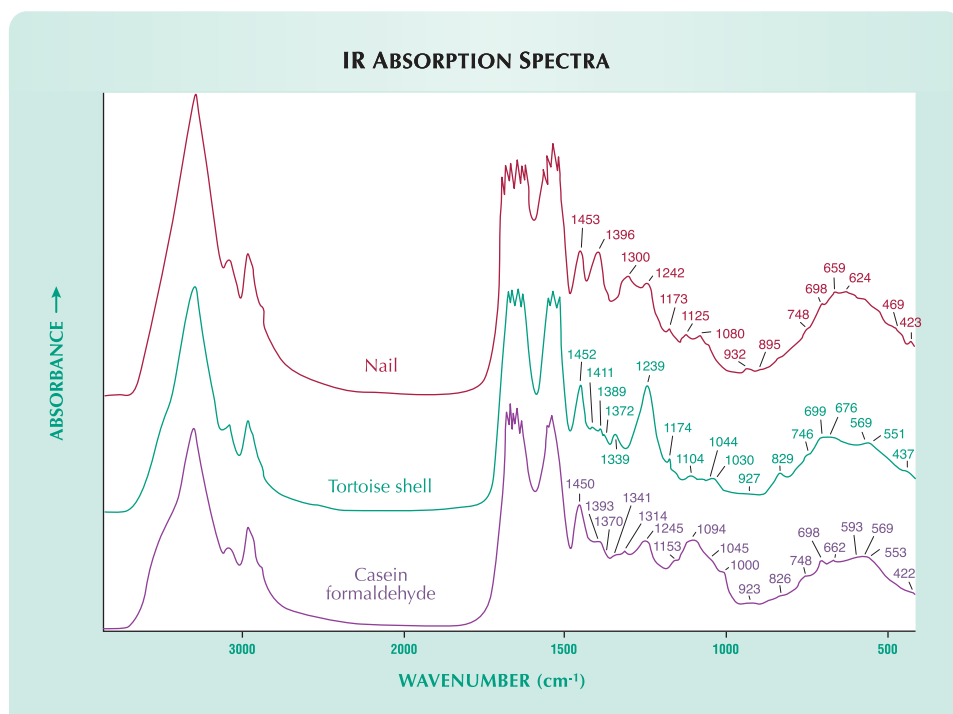
describe absorptions due to the stretching and bending motions of molecules; *overtone* and *combination* describe additional smaller absorptions produced by transitions to higher energy levels. These are found at multiple and combined [sum and difference] frequencies of the stretching and the bending vibration [Coates, 2000]).

The strong bands at 1650, 1530, and 1240 cm^{-1} are called *amide bands* (amide I, II, and III; Naumann, 2000) and correlate to the C-O stretch, N-H bend, and C-N stretch, respectively. The broad, complex band between 900 and 400 cm^{-1} has been called the “true fingerprint region” of proteins by Naumann (2000), because it is more characteristic of protein-based substances than the region ~2000 to 400 cm^{-1} , which is commonly used as the “fingerprint region” to identify substances such as gem materials.

The IR spectra of tortoise shell, horn (not shown), and human nail were nearly identical (figure 8); this confirms that horn-like materials and tortoise shell are chemically very similar and mainly composed of proteins, in these specific cases keratin.

The thin-film IR spectra of the plastic imitations were distinctly different from the spectrum of tortoise shell. Most of the plastics were characterized by distinct CH- and often OH-related bands at 3200–2900 and at 3600–3400 cm^{-1} , respectively (figure 9), and by complex bands that are due to other structural groups

Figure 8. The thin-film IR spectra of human nail, tortoise shell, and casein formaldehyde plastic are very similar due to their similar chemical compositions. The inset shows the distinctive features that are found in the region between 1500 and 400 cm^{-1} . The region below 2000 cm^{-1} is expanded for clarity.



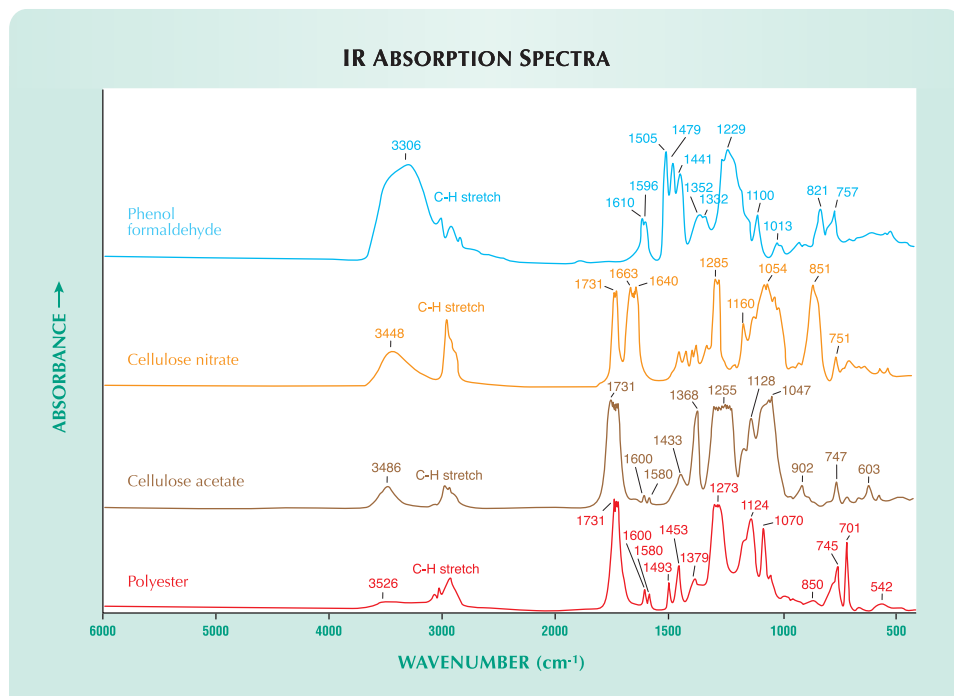
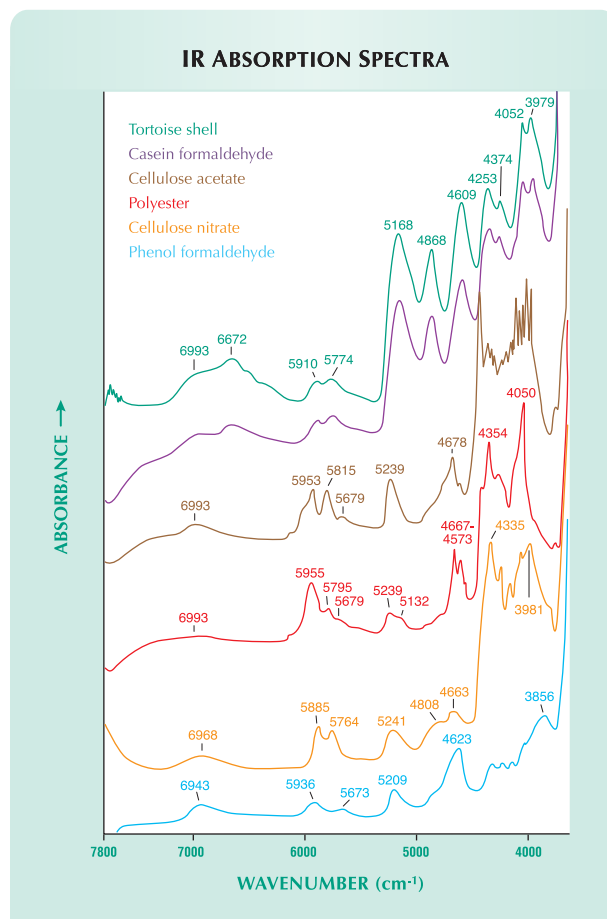


Figure 9. The IR spectra of thin films of the other plastic imitations are distinctly different from the spectrum of tortoise shell seen in figures 7 and 8. The CO-, NH-, and CN-related bands are missing in these materials. The region below 2000 cm^{-1} is expanded for clarity.

and the “backbone” (C-C) structure. It would be far too complex for the purposes of this article to discuss all structural groups present in each of the plastic imitations and even more so to assign specific bands visible in the FTIR spectrum to a particular group. The combination of functional group absorptions and backbone-related absorptions is characteristic of all polymers and allows their identification as such (Coates, 2000). Most of the plastics analyzed lacked the CO-, NH-, and CN-related absorption features that are typical of tortoise shell and other protein-based substances. The only exception, casein formaldehyde, had an IR spectrum very similar to that of tortoise shell (figures 8 and 10). Differences that distinguish these materials in the infrared can be found in the limited region of 1500 to 400 cm^{-1} (again, see

Figure 10. The IR spectra of thicker (~5 mm) samples of tortoise shell and its imitations also show distinct differences. These spectra are closer to what can be obtained nondestructively from large objects fashioned from tortoise shell or one of its imitations. The bands in the NIR will be distinct, while the absorptions below 4000 cm^{-1} will not be visible because of their intensity and the limitations of the detector. Most of the materials tested could be distinguished based on this limited region, except the samples of tortoise shell and casein formaldehyde, which were identical.



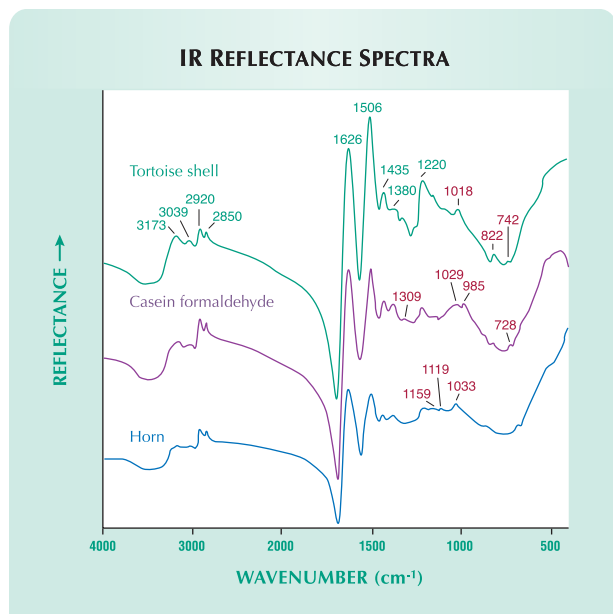


Figure 11. Although the specular reflectance IR spectra of tortoise shell, horn, and casein formaldehyde are similar, they can be distinguished by the minor features indicated in red. The spectrum of the nail is not included, because the sample was too small and irregular for acceptable specular reflectance FTIR analysis. The region below 2000 cm^{-1} is expanded for clarity.

figure 8): The spectrum of casein formaldehyde exhibited a rather strong, complex, broad band centered at 1094 cm^{-1} , which was absent from the spectrum of tortoise shell. In addition, many of the bands were shifted and their general shape varied, especially the very broad, complex band extending from 900 to 400 cm^{-1} . Additionally, the absorption at $\sim 1240 \text{ cm}^{-1}$ was much more intense in the spectrum of tortoise shell than in that of casein formaldehyde.

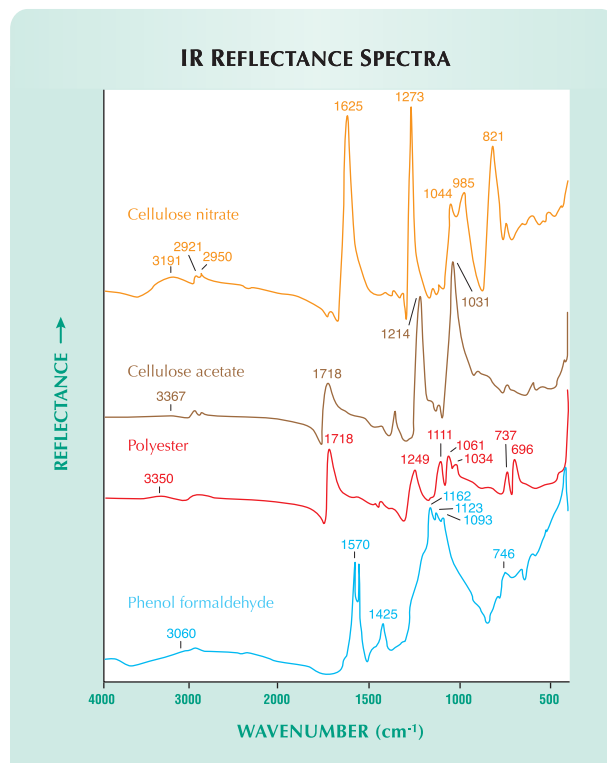
The IR spectra of the same materials in 5-mm-thick samples showed strong absorptions in the near-IR region between 7800 and 3700 cm^{-1} . All absorptions from 3700 to 400 cm^{-1} were too intense and thus not resolvable. In all but one case, the NIR region of the spectra of the plastics was distinctly different from that of tortoise shell; the exception was casein formaldehyde, which could not be distinguished from tortoise shell based on the limited NIR region of its spectrum (again, see figure 10).

Specular Reflectance IR Spectroscopy. All the samples tested, natural and artificial, exhibited relatively weak reflectance. In the experience of the authors, this is typical for such organic materials (including plastics). The reflectance spectra again showed a close similarity between tortoise shell and

casein formaldehyde (figure 11), and distinct differences between these two substances and all the other imitation materials (figure 12). However, we did note minor differences between casein formaldehyde and tortoise shell: Weak bands at 1018, 822, and 742 cm^{-1} were characteristic for tortoise shell, while features at 1309, 1029, 985, and 728 cm^{-1} were only seen in casein formaldehyde (again, see figure 11). The spectrum of horn, shown here for comparison, again illustrates the similarity between the two organic materials.

Vis-NIR Spectroscopy. The Vis-NIR transmission spectra of the tortoise shell samples and all of the plastic imitations revealed differences, even though these were sometimes subtle. The spectra of the light and dark parts of the tortoise shell samples (figure 13A) were characterized by a smooth rise in transmittance toward the NIR region without distinct absorption bands. The darker spots showed total absorption below 530 nm. The spectra of the imita-

Figure 12. Again, the specular reflectance IR spectra of the non-protein-based plastic imitations are very different from the tortoise shell spectrum seen in figure 11. The region below 2000 cm^{-1} is expanded for clarity.



VIS-NIR TRANSMISSION SPECTRA

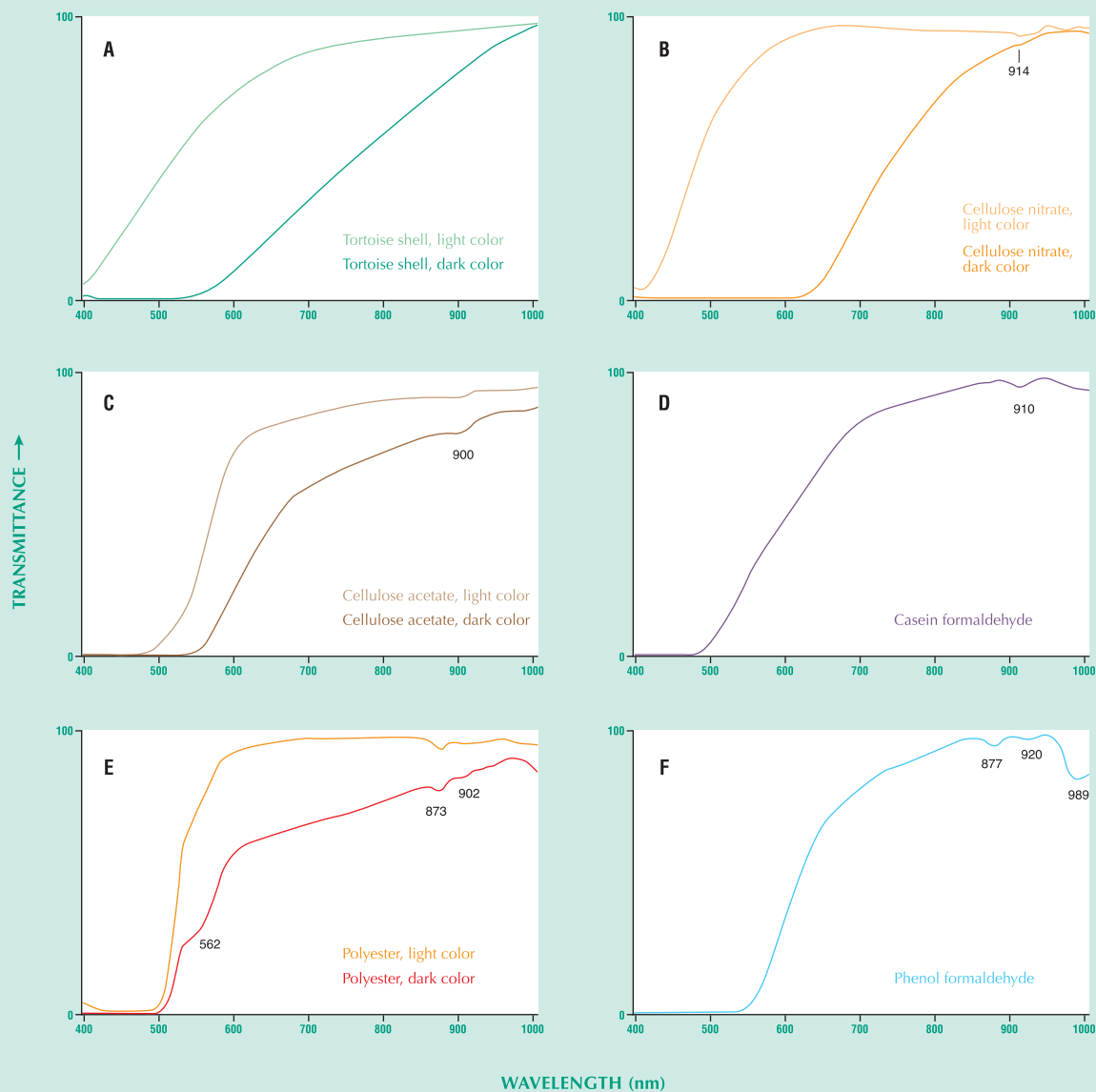


Figure 13. The Vis-NIR transmission spectra of tortoise shell show few if any notable features compared to the plastic imitations, exhibiting a lack of distinct absorption bands and a smooth rise in transmittance. More-irregular transmission curves, including absorption bands mainly in the NIR, are typical for the plastic imitations. Horn and nail show spectra (not shown) that are similar to those of tortoise shell.

tions were not as smooth and exhibited a different curvature. Broad bands, mainly in the NIR, could be seen in the spectra of all the imitations: at 914 nm for cellulose nitrate (figure 13B); at 900 nm for cellulose acetate (figure 13C); at 910 nm for casein formaldehyde (figure 13D); at 562, 873, and 902 nm for polyester (figure 13E); and at 877, 920, and 989 nm for phenol formaldehyde (figure 13F). Most of the imitations showed total absorption below around 500 nm.

Photoluminescence Spectroscopy. The PL spectra of the materials analyzed (figure 14) showed differences in their general shape. Tortoise shell, horn, and casein formaldehyde exhibited nearly identical emissions that consisted of one broad band that was most intense at 578 nm. Cellulose nitrate and cellulose acetate showed a broad band at 603 nm, while polyester showed two broad bands, one at 578 nm and one at 628 nm. Despite these general

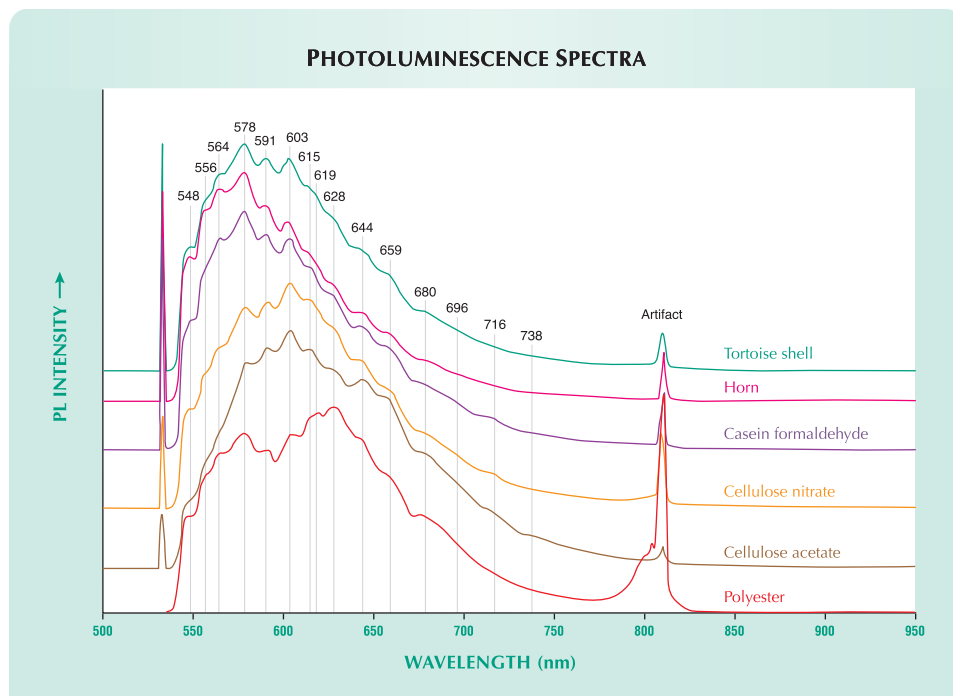


Figure 14. The photoluminescence spectra of tortoise shell and its plastic imitations show differences in curve shape, but, surprisingly, the same individual peaks are present in all spectra.

differences, the same individual PL peaks were present in the spectra of all samples.

DISCUSSION

The separation of tortoise shell and its imitations is not difficult with standard gemological testing, provided all the necessary tests can be performed. The combination of microscopy, R.I., S.G., UV fluorescence, and appearance between crossed polarizers is sufficient to determine whether a sample is tortoise shell or an imitation. Even though horn can be very similar in overall appearance to blond tortoise shell, its structure is distinctly different, since it is rather fibrous. As seen in figure 6, UV fluorescence alone may be sufficient to separate tortoise shell from visually similar material. Any orange and green luminescent plastic is quickly identified, as are samples with the characteristic “brown and cream” tortoise pattern that have homogeneous luminescence, since the patches in tortoise shell show a very different reaction from that seen in the cream-colored parts.

That said, the identification is not always straightforward, for several reasons:

1. Plastics and horn can imitate blond tortoise shell effectively, and the differences in luminescence are far less obvious.
2. Tortoise shell and its imitations are normally

worked into objects, and thus standard gemological tests beyond UV luminescence and a “hot point” may not be feasible (e.g., the S.G. of a tortoise shell box inlaid over gold will not be useful for identification). In addition, the relatively poor polish of tortoise shell and plastics, especially antiques, often does not allow the precise determination of a refractive index.

3. Mixtures of resins and tortoise shell and resin-stabilized tortoise shell exist. This material, at least one sample of which has been analyzed by the authors, shows properties intermediate between tortoise shell and plastic.
4. Plastics are materials with properties that can be drastically altered by slight compositional variations, changes in polymerization or cross-linking, or the use of dyes. Thus, there is always the possibility that new materials that imitate tortoise shell much more effectively will enter the marketplace.
5. In some cases, the exact identity of the plastic is important to the owner of an imitation, since some collectors are looking for specific plastics such as Bakelite.

These factors indicate that in some cases there may be a need for testing beyond that done with standard gemological tools.



Figure 15. Though new production of tortoise shell objects has nearly ceased as a result of legal restrictions, gemologists must still be prepared to identify older material that is still on the market. Shown here is an archeological revival necklace; the carved urn pendant is approximately 4 × 8 cm. From Mona Lee Nesseth, *Custom and Estate Jewels*, Los Angeles; courtesy of Tricia and Michael Berns. Photo © Harold & Erica Van Pelt.

Transmission IR spectroscopy can reliably identify all materials based on their intrinsic and material-specific absorptions between 2000 and 400 cm^{-1} ; however, complete spectra can be obtained only if a small amount of the substance is polished into a thin section or powdered and prepared into KBr pellets. Because these preparation techniques are destructive, they are of only limited usefulness for the gemologist. Nevertheless, transmission IR spectra of thicker samples commonly supply enough information to distinguish tortoise shell

from its imitations and to identify the plastics. The absorptions in the near-infrared region are generally quite specific for the analyzed material, but the fact that not all features are observable may prevent a conclusive identification, as can be seen in the case of casein formaldehyde plastic. The complex IR spectra are not easily interpreted; simplified, it can be stated that the spectra of organic substances are a combination of absorptions due to functional groups such as C-H or N-H and those due to the skeletal vibrations associated with the “backbone,” commonly the C-C linkages of a substance. The slightest differences in structure, molecule length, and composition will change the IR spectra. Such differences are present in all organic materials even if very similar, as with horn and tortoise shell; thus, they can all be distinguished by transmission IR spectroscopy, given proper sample preparation (Coates, 2000).

Vis-NIR spectra can supply useful information, but the presence of different dyes may change the spectra considerably. Some of the bands seen in the region around 900 nm may be interpreted as combination bands and/or overtones of OH-related vibrations (Adamo et al., 2005). This proposal is supported by the fact that the intensity of the OH-related band at $\sim 3500 \text{ cm}^{-1}$ correlates well with the intensity of the bands in the 900 nm region. It is apparent that tortoise shell contains very little OH compared to artificial plastics. Such near-infrared OH-related bands are known from water-containing minerals such as beryl, topaz, and euclase (see, e.g., Adamo et al., 2006), although in the experience of the authors the bands in these materials are much sharper. This is probably due to the crystallinity of such minerals as compared to the amorphous structure of the plastics. While some plastics can be mostly crystalline (with minor amorphous domains), such materials are translucent or opaque (Bloomfeld, 2000). The main drawback of transmission IR spectroscopy and Vis-NIR spectroscopy is their very limited use for large or irregular objects. In many cases, an analysis by these methods is impossible without breaking off a piece of the material in question.

Kiefert et al. (1999) showed that resins can be easily identified by Raman spectroscopy. This result is applicable to tortoise shell and its plastic imitations, but it needs further research to be confirmed. The method found most suitable during the course of this study was specular reflectance IR

spectroscopy, which allows the analysis of large objects with a simple accessory. In the experience of the authors, this method is highly effective in the identification of mineral species, and this study has shown that it is also useful for the separation of these various natural and synthetic organic materials.

Photoluminescence spectroscopy may also be used, but the substances in this study showed very similar emissions and in at least one case, that of casein formaldehyde, the spectrum was identical to that of tortoise shell. The reason for the presence of the same 15 emissions in all these materials is not known to the authors.

CONCLUSIONS

Although trade in contemporary tortoise shell has been largely banned internationally since the early 1970s, jewelry (figure 15) and other objects (figure 16) fashioned during the more than two centuries when it was a popular ornamental material can still be seen in the marketplace. This study has shown that, typically, tortoise shell can be easily distinguished from all materials used to imitate it, and that only protein-based plastics such as casein formaldehyde may pose a potential problem if not analyzed properly.

The application of standard gemological testing methods allows the unambiguous distinction of most tortoise shell from its imitations, which

Figure 16. During several centuries of popularity, a wide variety of objects were crafted from tortoise shell. The carved box at the bottom is approximately $10.5 \times 6.5 \times 2.5$ cm; the book is approximately $12 \times 8.5 \times 1.5$ cm. The book and carved box are from Mona Lee Nesseth, Custom and Estate Jewels, Los Angeles; courtesy of Tricia and Michael Berns. The chain is courtesy of Elise Misiowski. Photo © Harold & Erica Van Pelt.



include semisynthetic and synthetic plastics. However, the identification of objects made of blond tortoise shell and the precise determination of a particular plastic require the use of more sophisticated laboratory techniques. Of the meth-

ods tested, the technique determined to be most versatile and useful for this purpose is specular reflectance IR spectroscopy. The results of this study can also be applied to plastics used to imitate other gem materials.

ABOUT THE AUTHORS

Mr. Hainschwang (thomas.hainschwang@gia.edu) is a research gemologist at GIA GemTechLab in Geneva, Switzerland. Miss Leggio is working on her Diplôme d'Université de Gemmologie on sea turtles, tortoise shell, and imitations of tortoise shell at the University of Nantes, France.

ACKNOWLEDGMENTS: The authors thank Christian Bonnet (eyeglasses manufacturer, Sens, France) and Jacques Fretey

(International Union for the Conservation of Nature and Natural Resources [IUCN], Paris) for their advice, loans, and donations of tortoise shell samples; and Jean Lescure (Laboratoire de Zoologie [Reptiles et Amphibiens], Muséum National d'Histoire Naturelle, Paris) and George Balazs (Pacific Islands Fisheries Science Center, Honolulu, Hawaii) for fruitful discussions. The authors also thank Jacques Meynier, Meynier et Fils S.A., Lavans Les St. Claude, France, and Gérard Piassale, Plastimod S.a.r.l., Yonnax, France, for supplying plastic imitations for this study.

REFERENCES

- Adamo I., Pavese A., Prosperi L., Diella V., Merlini M., Gemmi M., Ajo D. (2005) Characterization of the New Malossi Hydrothermal Synthetic Emerald. *Gems & Gemology*, Vol. 41, No. 4, pp. 328–338.
- Animal products in ancient Egypt (2005) http://nefertiti.iwebland.com/animal_products/ [accessed Feb. 9, 2006].
- Bariand P., Poirot J.-P. (1998) *Larousse des Pierres Précieuses*. Larousse Bordas, Paris, 284 pp.
- Bloomfield A. (2000) *How Things Work: The Physics of Everyday Life*, 2nd ed. John Wiley & Sons, Chichester, UK.
- Buist J.M. (1986) Resume—the origins of polymers and their cellular derivatives. *Progress in Rubber and Plastics Technology*, Vol. 2, No. 3, pp. 17–30.
- Coates J. (2000) Interpretation of infrared spectra, a practical approach. In R.A. Meyers, Ed., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Chichester, UK, pp. 10815–10837.
- Daley R.E., Daley S.J. (1996) *Organic Chemistry*. WCB, Boston, pp. 1186–1238.
- Farrar W.V. (1968) Formaldehyde: The centenary of a simple molecule. *Chemistry in Britain*, Vol. 4, No. 11, pp. 500–502.
- Gibbs S. (1977) People and polymers. A brief history of the accidental progression of the plastics industry. *Plastics and Rubber International*, Vol. 2, No. 5, pp. 221–224.
- Hendrickson J.R., Wood J.R., Young R.S. (1977) Lysine:histidine ratios in marine turtle shells. *Comparative Biochemistry and Physiology, Part B: Biochemistry & Molecular Biology*, Vol. 57, No. 4, pp. 285–286.
- International Instruments and Marine Turtle Conservation (2002) Special issue of the *Journal of International Wildlife Law and Policy*. Vol. 5, No. 1–2.
- Karl S.A., Bowen B.W. (1999) Evolutionary significant units versus geopolitical taxonomy: Molecular systematics of an endangered sea turtle (genus *Chelonia*). *Conservation Biology*, Vol. 13, No. 5, pp. 990–999.
- Kiefert L., Hänni H.A., Chalain J.-P., Weber W. (1999) Identification of filler substances in emeralds by infrared and Raman spectroscopy. *Journal of Gemmology*, Vol. 26, No. 8, pp. 501–520.
- Langenheim J.H. (2003) *Plant Resins: Chemistry, Evolution, Ecology, Ethnobotany*. Timber Press, Portland, OR.
- Natural plastics (2005) <http://www.plastiquarian.com/naturals.htm> [date accessed: 10/19/05].
- Naumann D. (2000) Infrared Spectroscopy in Microbiology. In R.A. Meyers, Ed., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Chichester, UK, pp. 102–131.
- Pedersen M.C. (2004) *Gem and Ornamental Materials of Organic Origin*. Elsevier Butterworth-Heinemann, Oxford, UK, 268 pp.
- Perrine D. (2003) *Sea Turtles of the World*. Voyageur Press, MN.
- Sears J.A. (1977) Polymer pioneers. *Chemistry*, Vol. 50, No. 7, pp. 6–10.
- Spotila J.R. (2004) *Sea Turtles: A Complete Guide to Their Biology, Behaviour, and Conservation*. John Hopkins University Press, Baltimore, MD.
- Van der Vegt A.K. (2002) *From Polymers to Plastics*. Delft University Press, Delft, The Netherlands. Internet edition NUGI 831; <http://mail.vssd.nl/hlf/Polymers.pdf>.
- Voet D., Voet J.G., Pratt C.W. (2005) *Fundamentals of Biochemistry: Life at the Molecular Level*. John Wiley & Sons, Hoboken, NJ.
- Webster R. (1994) *Gems, Their Sources, Descriptions and Identification*, 5th ed. Rev. by P. G. Read, Butterworth-Heinemann, Oxford.
- White W.B. (1974) The carbonate minerals. In V. C. Farmer, Ed., *The Infrared Spectra of Minerals*, Mineralogical Society, London, p. 232.