Copal vs. amber

Maggie Campbell Pedersen and Bear Williams investigate the infrared and optical characteristics of treated and natural ambers and copals.

Part I: Observation and simple gemmological tests

The correct identification of ambers and copals can be extremely difficult. Not only are we expected to be able to differentiate between them, but we are also expected to be able to recognize and identify all of the treatments given to them. Unfortunately these are constantly increasing in number and complexity. One treatment that is appearing more and more is autoclave-treated copal (including the greened variety), yet still many misunderstandings remain about this material.

When identifying ambers by sight we have a few basic rules from which to start. Fortunately, we know that green is not a natural amber colour (unless it is the result of fluorescence), and so when we come across green resin we know that it is either plastic or a natural resin that has been treated in some way.

Baltic amber is probably the most visually recognizable of all the well-known ambers in its natural form, but it is also the most versatile when it comes to treatments. With heat and pressure it can be clarified or totally re-constituted from powder or chips. Simple heat-treatment can darken the surface or produce discoidal stress fractures (the so-called 'sun spangles') inside the material. Like many other resins it can be turned green through a series of treatments in an autoclave. Greened Baltic amber may retain the amber's characteristic swirls of opaque and clear material, making it easy to recognize.

Discoidal stress fractures rarely occur naturally and so their presence suggests heat-treated Baltic amber — other ambers are seldom, if ever, treated this way. This is because they are too rare and expensive, and, secondly, the younger ambers such as those from Mexico or the Dominican Republic have a lower melting point than Baltic amber and would melt if heated to the high temperatures necessary to produce the fractures. However, nowadays we are seeing copals treated in an autoclave to produce sun spangles.

It is becoming more and more necessary to carry out tests on the resins we come across, and not just to rely on recognition by sight. The question of whether a resin is natural or treated, and whether it is amber or copal, can have a big influence on the value of the finished item. For example; greened, 40 million year-old Baltic amber is more valuable than greened, 300 year-old Colombian copal, and clarified and heat-treated Baltic amber would be more valuable than heat-treated copal used in imitation of Baltic amber.

The normal gemmological tests are not very useful for resins. We know that all ambers float in saturated salt water, but so do natural or treated copals, as well as pressed amber. In general, specific gravity tests can therefore only differentiate between natural resins and their simulants, but not identify them.

Gemmological tests that are reserved more for organics can give us some clues, although they too are only rough guides. For example, the hot point test may give us some idea of the nature of the resin,

1: Treated Colombian copal. Photo © Maggie Campbell Pedersen.

Organics

2: Pendant with greened Baltic amber.
3: Typical Baltic amber rough (left), and Colombian copal rough (right).
Photos © Maggie Campbell Pedersen.

but it is vague at best. As a rule the older and more 'mature' the resin (i.e. the more stable it becomes through the evaporation of the volatiles, and the cross-linking and polymerizing of the chemical components), the lower its melting point and the more rapidly a hot point will melt the surface of the resin. In addition, the more fragrant the smell emitted by melting, the younger the resin is likely to be. However, when copal is treated and 'artificially aged' in an autoclave, the hot point test gives an incorrect result as the surface has been 'matured'.

The same principle applies to testing with solvents. While Baltic amber is almost inert to solvents, some of the younger ones such as Dominican amber will soften slightly. Untreated copals will soften very quickly, but autoclave-treated ones will again give misleading results due to the artificial aging of the material.

Natural resins from various localities will react very similarly under crossed polars, although there is evidence that treated ones may react differently (see part 2 xx).

Under UV light, ambers from different localities may fluoresce different colours; for example, Baltic amber fluoresces a paler, chalkier colour than many others. Treated materials tend to fluoresce less strongly. However, fluorescence is always strongest in freshly cut material and often tends to fade or change colour with time, so the results are not clear enough to draw anything but vague conclusions.

However, we still need to know what the materials are, as well as which treatments they may have undergone, both for academic purposes and to ensure that the general public are not being cheated. It used to be simple; Baltic amber could be identified by sight — the treatments used on it were well-known and easily recognized — whilst other ambers were rare, looked different and were never treated. Copals were pale yellow and never treated. Today, while we may be able to recognize some of the resins by sight and have a 'gut feeling' about others, we often need the help of more sophisticated equipment found in specialist laboratories.

Over the past couple of years I have constantly come up against resins that need verification; most recently these include examples of greened materials that were thought to be Colombian copal and Baltic amber. To confirm my identifications, they, along with other samples, have been tested with great patience by Bear and Cara Williams at Stone Group Laboratories in Missouri, USA.

Maggie Campbell Pedersen

Part II: Use of FTIR, Raman and crossed polars

Introduction

Careful observation is necessary with natural resins, due to both the delicate nature of these materials as well as the fact that they are commonly cabbed or are in the form of beads, thus limiting certain testing methods. Whenever possible, visual observations should be confirmed with non-destructive advanced testing methods. For this research project, three testing methods — FTIR (Fourier transform infrared) spectroscopy, Raman analysis, and crossed polarizers — were employed to gain insight into the nature of autoclave-treated greened copal and its natural copal counterparts, in order to better identify and confirm treatments. The copals were then compared against treated Baltic amber and its natural counterpart. A total of 63 treated and natural ambers and copals were used in this investigation. For the purposes of clarity, any references to 'amber' in this article are those of Baltic origin. As is the case with copal, amber treatments can include pressing, heating or autoclave (heat with pressure). The copals in this test came from various origins, primarily Colombia and Madagascar.

FTIR

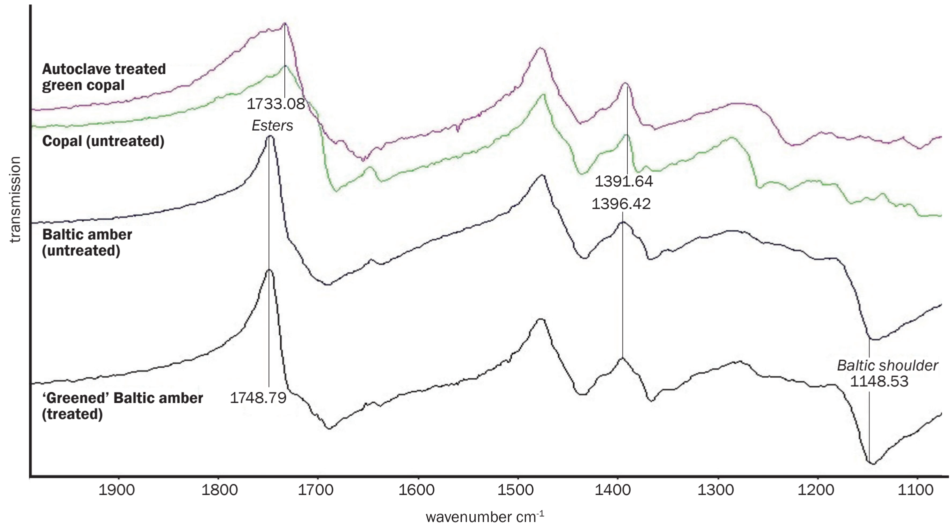
Tests were performed using a Perkin Elmer Spectrum 100, with a Pike Technologies Upward Looking Diffuse Reflectance attachment. As previous studies have shown, due to the organic nature of these materials, FTIR spectroscopy is one of the clearest methods of making distinctions between amber and copal. The FTIR observations here may introduce new information for those freshly discovering infrared techniques in testing. In (**1**), four representative resins were tested to determine the similarities and differences in the labelled spectral ranges.

FTIR discussion

(**1**) In the two upper lines (green and red), significant similarities are seen between the natural copal and the greened copal treated in the autoclave (heat with pressure). These copals, whether treated or natural, showed ester level absorptions at 1733 cm^{-1}.

In the lower two lines, the spectrum of the greened Baltic amber does not vary from the near-precise match to the spectra seen in those of the natural ambers. An ester peak is seen at 1748 cm^{-1}, indicating a clear distinction from the copals or younger resins. This peak remains consistent even if the amber is treated, melted and/or pressed.

"As an organic gemstone, fine amber is highly prized. As we study these resins in gemmology, we want to remember we are not dealing with crystalline materials, but a complex group of organic molecules. Terminology and testing methods must look to organic chemistry in order to understand the complex variations due to natural and artificial aging, as well as the impact of various treatments."

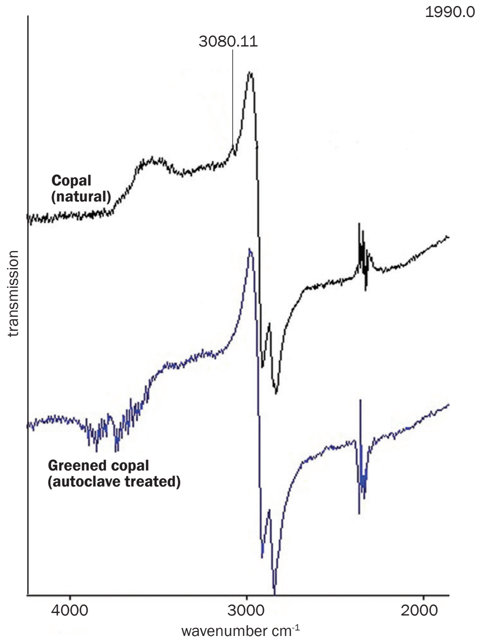


1: FTIR (absorption mode) shows differences between treated and natural Baltic amber and copal.

Within the infrared region, observations are broken into two sections: the fingerprint and the functional group bands. The fingerprint group is the unique character area and covers the range from 400 to 1000 cm^{-1}. The functional group sees chemical reactions that operate outside of the far infrared, and these bands cover the range of 1000 to 4000 cm^{-1} and beyond.

Differences between copal and Baltic amber are clearly evident in other areas seen in (**1**) as well. The 'Baltic shoulder' recorded in the range between 1185 — 1148 cm^{-1} is seen clearly in both the conventionally heated Baltic amber, as well as the non-treated material. According to these results, the treatment does not change the basic structure in a way that would make treated Baltic recognizable from its natural counterpart. This must be done by the traditional observation techniques discussed in Part I, or as we will cover later. The region between 1245 — 1010 cm^{-1} is that of C-O molecular bonds[1] and the amber peaks shown in (**1**) are characteristic of Baltic succinate resins. It is within these functional group bands that the Baltic peak is seen, particularly in the slope that goes from 1181 to 1147 cm^{-1}, which remains diagnostic of Baltic amber. This is consistent, even in the case of heat treatments or pressing.

All copals we have tested to date do not exhibit the Baltic shoulder, and their ester level absorption peak will consistently appear

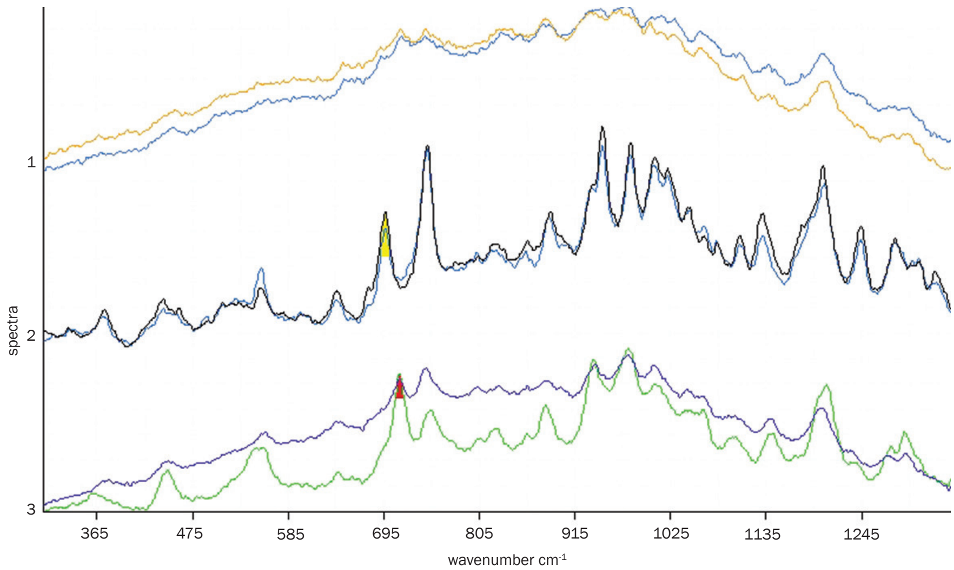


2: In this FTIR (mid-infrared) reading , the area above 3000 cm^{-1} is known to be related to the molecular bonding of hydrogen to carbons. In this case it is a higher than normal C-H stretch and is peculiar to aromatic hydrocarbons[2]. After treatments the 3080 alkene peak disappears.

at 1733cm^{-1} , rather than at 1748cm^{-1}, as seen in ambers. Based on these markers, we can separate amber from copal, whether treated or not.

We were further able to separate natural and treated copals by studying where changes occur within the functional groups

Organics



3: Raman spectroscopy of study group representatives.
Spectra 1: Autoclave treated and natural Baltic amber.
Spectra 2: Madagascan and Colombian copals — both untreated.
Spectra 3: Colombian and reportedly Madagascan greened copals, autoclave treated.

in the infrared and by making comparisons before and after treatment. Natural copals show what can be described as exocyclic methylene groups[3] that were destroyed during treatments. There is evidence of this (**2**), seen at 3080 cm^{-1} in the natural copal. After autoclave treatments this absorption peak disappears.

The aromatic hydrocarbon peak is almost always present in the more resinous types of copal, and the advent of heat/pressure treatments will initiate the devolatilization or artificial aging process. Mostly all resins and copals contain higher levels of the volatile organic compounds (VOCs) than those of naturally aged and fossilized ambers.

By this method, we can conclude that a treated copal (whether greened or golden) cannot be artificially transformed into amber as it will leave evidence of its more recent past. It is also apparent that FTIR testing can show clear evidence of the differences between copal and amber, and without the need for destructive tests.

Raman spectroscopy

Raman spectroscopy can interpret these chemical changes in a different manner. The equipment used is an Enwave Optronics Raman with a 785nm laser. The Raman data (**3**) shows three groups of two readings each. These graphs are overlaid for comparison references and are representative of six different readings grouped by the following three spectra:

Spectra 1: the heated vs. natural Baltic ambers show near identical results. Of note is the softened peaks of their readout, suggesting that the volatile organic compounds have effectively leached out through millions of years.

Spectra 2: shows untreated copals from two countries. These also show a very close match, in this case suggesting possible similarities in tree resin type. Also note the higher levels of VOCs indicated by the sharper and higher peaks. However, the main import here is the frequency peak marked in yellow on the graph, centered at 696.2 cm^{-1}.

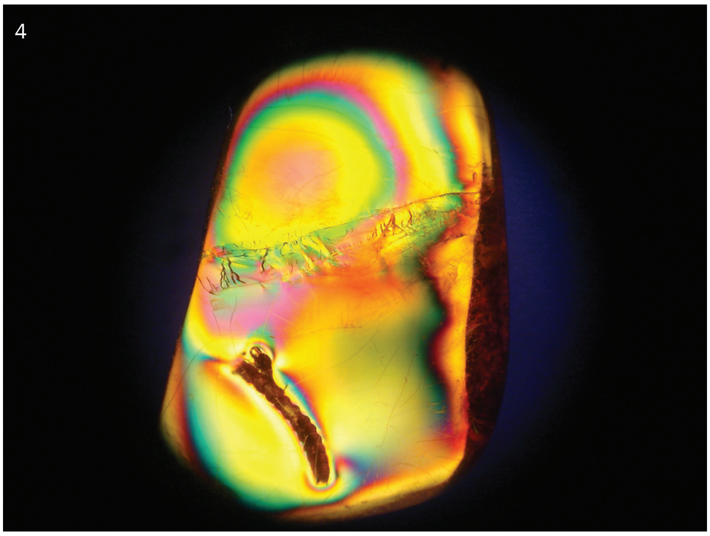
Spectra 3: After autoclave treatments these copals showed peak shift changes. Indicated in red, this shift shows evidence of the artificial aging process, and it now manifests itself at 712.45 cm^{-1}. The 696 cm^{-1} peak has not only experienced a slight shift, but the treatment has also somewhat softened the height of the peaks and caused the spectra to more closely emulate amber readings. This smoothing effect on the peaks might also be considered a function of the extent or number of treatments, as VOCs are driven out during the autoclave process.

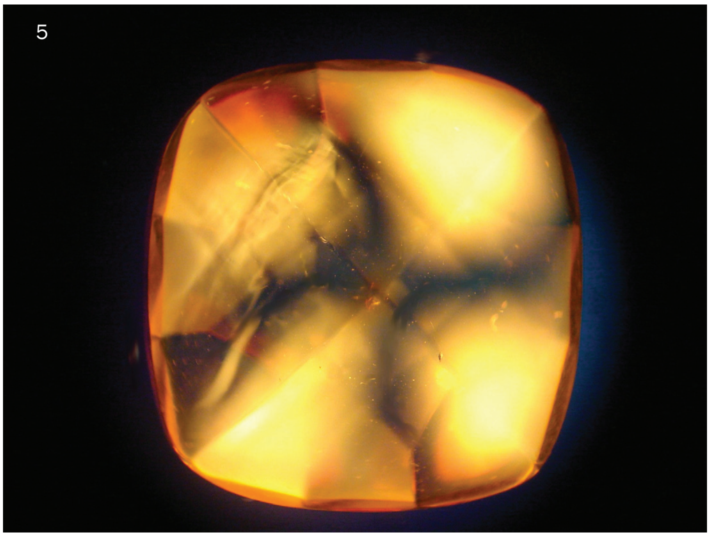
Non-destructive tests through the use of Raman spectroscopy can give evidence that greened copals have undergone autoclave enhancement. Coupled with FTIR readings, it is possible to determine whether a resin is amber or copal and better establish the nature of the material.

Immersion under crossed polarizing filters

While FTIR and Raman testing are currently limited to advanced testing labs, all gemmological labs have a polariscope. For resins; clean, room-temperature water makes a good immersion fluid. As with all young resins or amber, outer surfaces harden more quickly while the inner parts cure more slowly. This can create enduring areas of strain and internal pressures in ambers and copals as they fully cure. This strain mechanism exhibits itself as multicolour interference patterns under

> "Esters are organic compounds which form when natural acids and alcohols interact. Interestingly, esters containing simple hydrocarbon groups are volatile fragrant substances[4]. The differing (copal vs. amber) esters (1733 vs 1748 cm^{-1} respectively) in the infrared, may well be indicative of our olfactory-sensed variations in odour between the two, that are produced during hot point tests."





4: Concentric rings of colour interference caused by internal pressures and straining shown in this beetle larva bearing natural Baltic amber.
5: A heated and pressed golden Baltic amber relieved of its tensional strain, shows an ADR-like optical phenomenon. Photos © Bear Williams.

polarizing filters (**4**). Foreign particles trapped within can also create strain and colour effects can be seen surrounding the inclusion. Most natural ambers and copals will show these multi-hued patterns in crossed filters.

In our observations using this technique, none of the pressed or autoclave treated materials, whether amber or copal, exhibited any colour interference patterns. Amber transitions into a plastic state when heated to 1700°C[5]. It can then be formed, or pressed into one larger piece from various smaller components. Similar results are produced in autoclave treatments where clarity enhancement or the greening effect is induced. We can theorize that when the material is brought to a softened plastic phase, that it would release the inner pressures and strains while allowing the cooling amber/copal to re-form into a more evenly distributed structure of tensile cohesion.

This strain relief and the re-organizing to a more consistent internal structure is seen repeatedly in treated resins viewed under polarized lenses. It appears as a dark, wavy, pseudo-birefringent (false optic figure) cross effect as the sample is rotated. The observed phenomenon is similar to the strain patterns seen in many artificial glasses and plastics and can sometimes also be seen as dark web-like patterns. The treatment also eliminates any of the interference colours in tested samples.

Conclusion

Analysis with FTIR and Raman spectroscopy can give consistent indicators of whether a resin is amber or a much younger copal; and if copal, whether it has been treated. The Baltic shoulder as well as 1748cm^{-1} FTIR absorption peaks can identify a material as being a Baltic succinate, either treated or natural; while the 1733cm^{-1} FTIR peak is consistent with copals, either treated or natural. The Raman shift from 696cm^{-1} to 712cm^{-1} is indicative of autoclave treatment, while the greater height and sharper angles of all peaks throughout the spectrum can indicate a higher concentration of volatile compounds, typical of younger, untreated copals. A final look through crossed polars can aid observation techniques and give gemologists a good clue as to whether a natural resin is treated or not. The process of first classifying the material, then determining treatment will produce good diagnostic results.

Bear Williams

SGL extends gratitude to all of our advisers for their feedback. I would especially like to acknowledge Maggie Campbell Pedersen's dedication to finding the truth, educating the industry, and always being careful to state those things we do not know, avoiding misinformation or advocating false testing. She has generously provided amber samples of known provenance from her collections that have been authenticated and dated. We believe our studies complement each other, as amber is a valued and delicate gem material, and benefits from both careful observation as well as advanced spectroscopy methods.

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