Variation in the Deterioration of Fossil Resins and Implications for the Conservation of Fossils in Amber

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Variation in the Deterioration of Fossil Resins and Implications for the Conservation of Fossils in Amber

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ABSTRACT

The deterioration of fossil resins (crazing, cracking, and darkening) was investigated by comparing the effects of one year of accelerated aging—specifically intensive exposure to light, heat, and fluctuating humidity, both individually and in combination—on samples from several natural resin deposits. These included two Cretaceous ambers (from Myanmar [Burma] and central New Jersey), two Tertiary ambers (from the Baltic and the Dominican Republic), and Holocene copal from Zanzibar. The five resins were chosen for their disparate ages and botanical origins (and thus chemical and physical properties), as well as their paleontological significance. In all cases, pronounced deterioration occurred under combined exposure to light and fluctuating humidity, based on surface crazing and a decrease in absorbance of light in the UV region (360–400 nm). While crazing did not visibly occur in cases of fluctuating humidity in dark conditions, or UV exposure alone, spectrophotometric evidence indicates that some deterioration did take place. Yellowing after exposure to elevated temperatures occurred in all samples tested, with the exception of Burmese amber. All four true ambers exhibited a decrease in UV absorbance after exposure to heat (while copal actually showed an increase). The samples from the five deposits

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represent three chemical subclasses of fossil resins, and each of the resins reacted differently to the various aging conditions, with New Jersey amber particularly unstable. Based on these results, amber collections should be stored in an environment with stable humidity, relatively low heat, and minimal exposure to light. Anoxic sealing and storage, and particularly embedding amber samples in a high-grade epoxy, may be beneficial, and further investigation is indicated.

INTRODUCTION

The Division of Invertebrate Zoology at the American Museum of Natural History houses a scientifically unique collection of fossiliferous amber, including material ranging from the Early Cretaceous (145–110 Ma) to as recent as the Holocene. Ancient arthropods and other organisms preserved in over 10,000 amber samples are studied by researchers from around the globe. Significantly, the collection contains 420 holotypes, and the number of important specimens from various deposits increases yearly.

Despite the exceptional preservation of fossil resins and their organismal inclusions in deposits throughout the world, any amber or copal samples that are removed from anoxic sediments will begin to deteriorate over time. This degradation can manifest in one or more of the following ways: darkening of the amber's surface; "crazing," consisting of the development of a network of fine surface cracks; and, in the most serious examples, fracturing and cracking more deeply within or even through the piece (fig. 1). A crazed or darkened surface compromises visibility, and can also directly affect the preservation of any inclusions, setting the stage for internal cracking and deterioration. A significant crack can easily penetrate or obliterate an inclusion. Moreover, if an organism is close to the surface, repolishing may be difficult or impossible. In severe cases, oxidative damage can infiltrate amber via fine cracks (fig. 1B–E), affecting the integrity of the entire piece and any inclusions it contains. To whatever extent deterioration takes place, it puts important paleobiological data at risk (in such areas as taxonomy, systematics, taphonomy, and biogeography) in both studied and unstudied specimens.

Accelerated-aging tests involving light (UV/Vis), relative humidity (RH), and temperature have widely been used to assess the long-term stability of synthetic polymers such as plastics. Measurements are taken to assess oxidation, color change, or loss of mechanical strength to determine the mechanism of deterioration or to estimate the rate. Since amber is a highly cross-linked organic polymer, essentially a natural plastic, many of the testing parameters developed for plastics are directly applicable.

Previous studies of deterioration in amber have used accelerated aging to address similar conservation issues. Williams et al. (1990) exposed Dominican amber to an atmosphere containing formic acid, acetic acid, or hydrogen sulfide, as well as to fluctuating relative humidity and seven months of UV and natural light. Crazing and exfoliation of the surface occurred following chemical exposure, and also after sudden decreases in RH (from ≥45% RH to below 35% RH). Light caused no visible deterioration but was found to cause surface oxidation based on Fourier transform infrared spectroscopy (FTIR) analysis (Waddington and Fenn, 1988; Williams et al., 1990). The fossil resin samples in the present study were subjected to a combi-
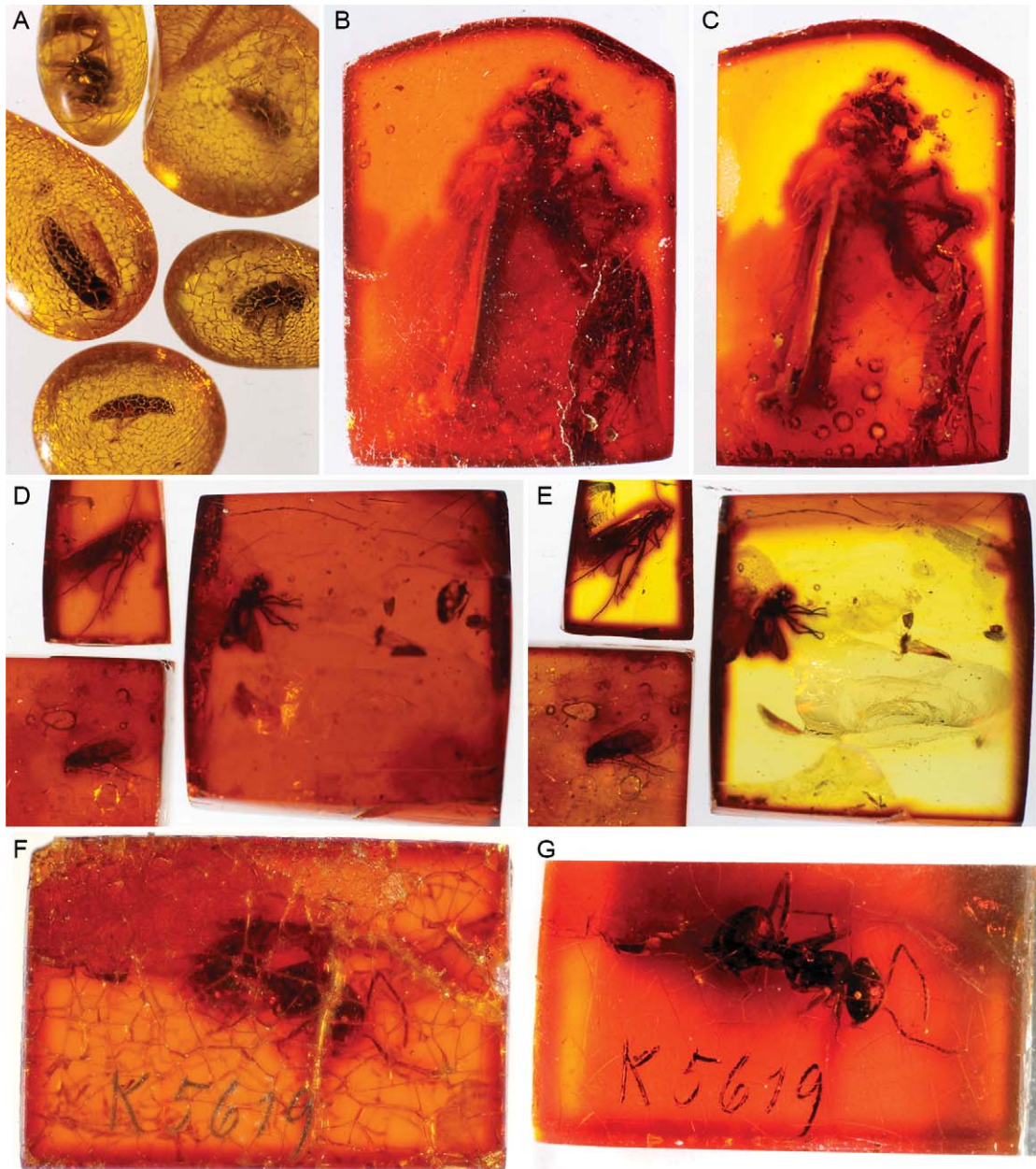
FIGURE 1. Historical deterioration of amber pieces in the AMNH collections: **A.** Crazing of several old Baltic amber specimens. **B.** Old Baltic amber piece with insect exhibiting "darkening." **C.** Same specimen after repolishing. **D.** "Darkening" of several old Baltic amber specimens. **E.** Same specimens after repolishing. **F.** Old Baltic amber piece showing overall deterioration including crazing and large crack through the insect inclusion. **G.** Same piece after embedding in a high-grade epoxy (EpoTek 301-2).

nation of UV and visible light (UV/Vis) at different levels of relative humidity, as well as to high temperatures.

Typically, museum amber collections are kept in closed cabinets, usually subject to some natural humidity fluctuations. The AMNH collection is stored in gasketed steel cabinets, and each amber piece is placed in a friction-fitting plastic box. Fossiliferous pieces of amber are typically exposed to intervals of intense light when a specimen is studied microscopically, using transmitted/reflected fiber-optic light for as much as several hours per day for several days or even weeks. UV light is known to degrade polymers through photooxidation, or chain scissioning (as well as some oxidation through the production of heat), physically manifesting as embrittlement and discoloration. The susceptibility of plastics/organics to oxidative degradation depends on many factors, but largely on a material's affinity for oxygen and the overall permeability of the polymer structure (Strong, 1996). Generally, that part of the light spectrum approaching and entering the UV region is more likely to cause damage to amber, since most fossil resins absorb light in this region (Searle, 1994; Marin et al., 1994). Oxidation of amber is believed to occur primarily in the exocyclic methylene groups (Shashoua, 2002; Thickett, 1993; Williams et al., 1990). However, because fossil resins from different deposits are known to contain different types and amounts of functional groups—unsaturated carbonyls, esters, and others (Lambert and Frye, 1982)—reactions such as oxidation or changes in unsaturation that occur during aging might be expected to show "species-specific" changes in absorption

TABLE 1. Summary of fossil resins used in present study.

Location	Age	Class[a] / Origin	Appearance	Characteristic deterioration
Myanmar (Burma)	97–100 Ma	Ib / Coniferae: *Metasequoia*?	Yellow or dark orange to russet	Apparently very durable / homogeneous[b] but can break along calcite intrusions
New Jersey	91 Ma	Ib / Coniferae: Cupressaceae	Clear yellow, yellow orange, opaque yellow or red	Friable / brittle—subject to crazing, cracking. Deep red pieces form needlelike cracks[c]
Baltic	45 Ma	Ia / Coniferae: Pinaceae or Sciadopityaceae	Clear or opaque yellow or yellow orange to ivorylike	Considered durable, but subject to "darkening" and surficial crazing over time
Dominican Rep.	17–19 Ma	Ic / Angiospermae: *Hymenaea*	Generally clear yellow, seldom opaque, oc. blue tinted or blue	Some crazing noted over time
Zanzibar, E. Africa	≤ 1000 ybp	Ic / Angiospermae: *Hymenaea*	Clear yellow	Typical polygonal crazing of surface over relatively short time

[a] Chemical resin classes based on Anderson et al., 1992, 1995, 2006.
[b] Grimaldi et al., 2002.
[c] Grimaldi et al., 1989.

for each kind of amber. If so, the stability and types of deterioration of various fossil resins should differ accordingly.

To test this, samples from five distinct Cretaceous, Tertiary, and Quaternary deposits were studied (table 1). Burmese amber is mid-Cretaceous (ca. 100 Ma) in age, uppermost Albian to earliest Cenomanian (Grimaldi et al., 2002; Cruickshank and Ko, 2003; Guanghai Shi, personal commun., 2011); New Jersey amber is slightly younger, Turonian aged (ca. 91 Ma) (Grimaldi et al., 2000). Baltic amber is dated to the Middle Eocene (ca. 45 Ma) (Engel, 2001), while Dominican amber is Miocene (ca. 17–19 Ma) (Grimaldi, 1996; Iturralde-Vinent and MacPhee, 1996). Carbon 14 dating by Grimaldi (unpubl.) indicates that Zanzibar copal is Recent (Holocene), formed less than 1000 ybp.

MATERIALS AND METHODS

A total of 11 testing conditions were prepared (table 2), and these treatments were maintained and monitored for one year. Sealed microchambers were constructed out of a UV-transparent plastic (Acrysol SUVT®, 0.125" [3.175 mm] thick cell-cast acrylic, with approximately 70% transmission at 280 nm, Spartech Corp.) and barrier film (Escal®, Mitsubishi Corp.) (fig. 2A). Relative humidity was maintained using preconditioned silica gel, and was monitored with card hygrometers. Anoxic environments were created with oxygen absorbers (Ageless® and RP System®, Mitsubishi), and were monitored with oxygen indicators (Ageless® Eye). To mitigate potential effects of pollutants or off-gassing of microchamber materials, a pollutant control sheet (Scavengel®, Art Preservation Services) was placed within each chamber. A full-spectrum fluorescent light (Life Lite, Light Energy Source, Inc.) was used for light

TABLE 2. Accelerated aging tests / fossil resin samples used.

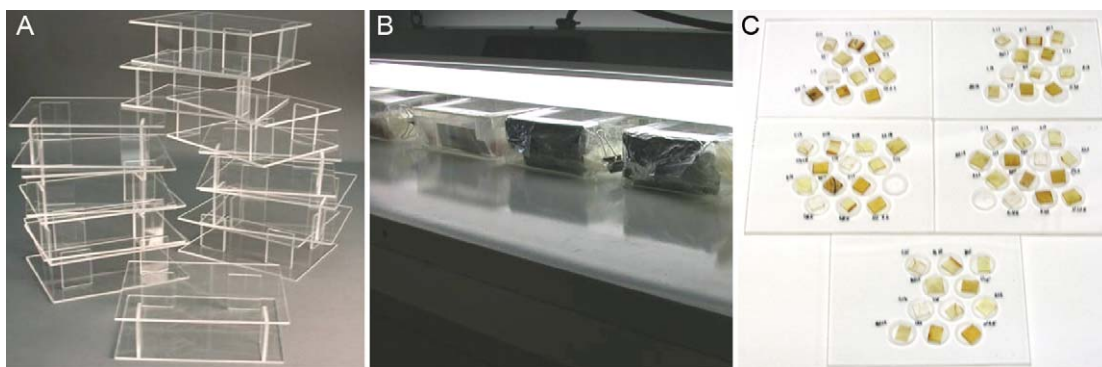| Test (no.)	Agent	RH (%)	Presence of O_2	Samples by type of resin	Additional epoxy-coated samples, Dominican and copal	Additional epoxy-coated, New Jersey samples	Totals
1	UV/Vis	0	✓	2		1	11
2	UV/Vis	50	✓	2		1	11
3	UV/Vis	0	anoxic	2		1	11
4	UV/Vis	50	anoxic	2	2	1	13
5	UV/Vis	20–70	✓	2	2	1	13
6	dark	0	✓	2		1	11
7	dark	50	✓	2	2	1	13
8	dark	0	anoxic	2		1	11
9	dark	50	anoxic	2		1	13
10	dark	20–70	✓	2	2	1	13
11	heat	10–15	✓	4	2	2	24
TOTALS				120	10	12	144

FIGURE 2. Experimental setup. **A.** Transparent UV/Vis light-transmitting plastic structures of microchambers, constructed out of Acrysol® SUVT. **B.** Complete microchambers with amber samples in the UV/Vis aging setup. **C.** Trays to hold amber samples while undergoing aging experiments.

exposure, because it has a similar spectral range to that of natural sunlight with a component of 6% UV-A and 1.2% UV-B (fig. 2B). UV-C light was not used for exposure, because such high-energy light (wavelengths below 295 nm) may cause reactions that would not normally occur under "natural" conditions (Wypych and Faulkner, 1999). The light output was 6400–8000 lux, as measured by a YF-179 Digital Light Meter (recording all light from 320–730 nm). UV levels were from 0.40 to 0.51 W/m^2 throughout the bulb, as measured by a Preservation Equipment UV 300 (peak reading at 360, 200–400 nm range). While under illumination, all samples were rotated periodically to ensure uniform exposure. Elevated temperature was achieved by a Fisher Scientific Programmable Isotemp Oven with forced-air heating at 45° C. As a rule of thumb in polymer studies, each 10° C effectively doubles the reaction rate, but at temperatures too high (approaching the glass transition temperature, Tg, which is as low as 50° C for copal [Howie, 1995]), deterioration will occur that would not normally take place (Halliwell, 1992).

Sample Preparation: Small, thin uniform slices (1.5 cm × 1.25 cm × 3 mm) of amber from each deposit were cut and polished. Where possible, these slices were produced from one or at most two large pieces of amber, in order to minimize variation within amber types. An additional set of samples from New Jersey amber, Dominican amber, and Zanzibar copal were coated with a thin layer of Buehler EpoxiCure Resin (bisphenol-A epoxy resin with N-butyl glycidyl ether and a mixture of amine hardeners), an epoxy routinely used at the AMNH to strengthen and preserve friable ambers during and after preparation of organismal inclusions (Nascimbene and Silverstein, 2000). The samples were placed in special trays while undergoing aging experiments (fig. 2C).

Analysis: Before and after aging, each sample was digitally photographed using a MicrOptics® fiber-optic flash unit with an Infinity® lens (www.microptics-usa.com). Color change in the amber was measured using an UltraScan XE spectrophotometer (Hunter Labs) with D65 illumination (daylight source) and sphere (diffuse/8) optical geometry. The instrument was calibrated with white tile and black card standards (Hunter Labs). Samples were

attached to a semimicrocell holder (10 × 20 mm cuvette), and measurements were made in transmission mode from 360 to 720 nm at 10 nm intervals. Final spectra were the average of three measurements to account for minor differences of thickness throughout the amber samples. In order to address whether aging can result in a visually perceptible color change, absorbance data were converted to CIELab color space values using Universal® (Ultrascan) software (Hunter Labs, 1985). CIELab is a system that was designed by the French Commission Internationale de l'Eclairage (CIE) in 1976 to approximate human visual perception of color. In CIELab, color is defined by three parameters, or coordinates: L is a measure of lightness (black = 0, reference white = 100); a* is a measure of redness, and ranges from

FIGURE 3. Model of CIELab Color Space: 3-D representation of perceptible color change.

green (−a) to red (+a), while b* is a measure of yellowness ranging from blue (−b) to yellow (+b) (fig. 3). The change in each of these parameters, ΔE, is calculated before and after aging to determine color change ($\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$).
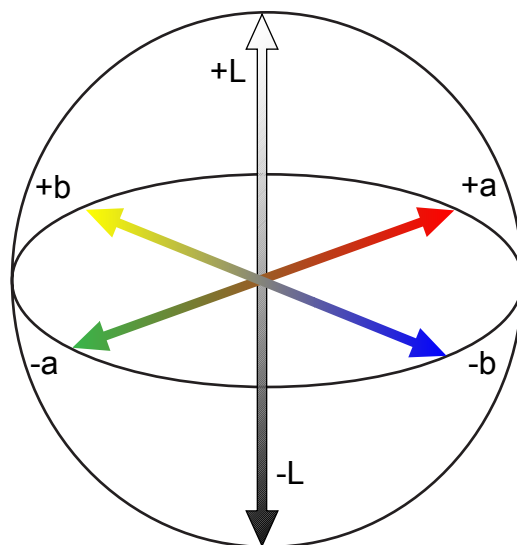
RESULTS AND DISCUSSION

The deterioration of amber was manifest in three distinct ways: as surface crazing, as a decrease in absorbance in the UV region of the spectrum, and as yellowing or darkening.

CRAZING: This type of damage was observed only when fluctuating humidity and light exposure were combined. In visual examination of all amber samples, the most pronounced crazing occurred in New Jersey amber (fig. 4A–C), which also showed a significant change in spectrophotometric absorbance.

Crazing is characterized by a dense network of fine surface cracks, generally associated with mechanical stresses applied to glassy or semicrystalline polymers. When these stresses are associated with solvents, they are referred to as "solvent crazing" (Strong, 1996; Thickett et al., 1995). Fluctuating humidity will cause many polymers to expand and contract as moisture content changes (Halliwell, 1992), thereby inducing crazing. Obvious examples are varnishes applied to wood or paintings. Crazing has commonly been observed in amber stored for decades in museum collections, as well as on ancient European amber artifacts, and has sometimes led to the formation of more serious internal cracking and surface flaking. Amber's low permeability initially limits such stresses to the material's surface. However, based on various polymer studies, craze formation will progress deeper into the material over time, ultimately resulting in complete exfoliation of the surface and crazing along any internal fractures. If an
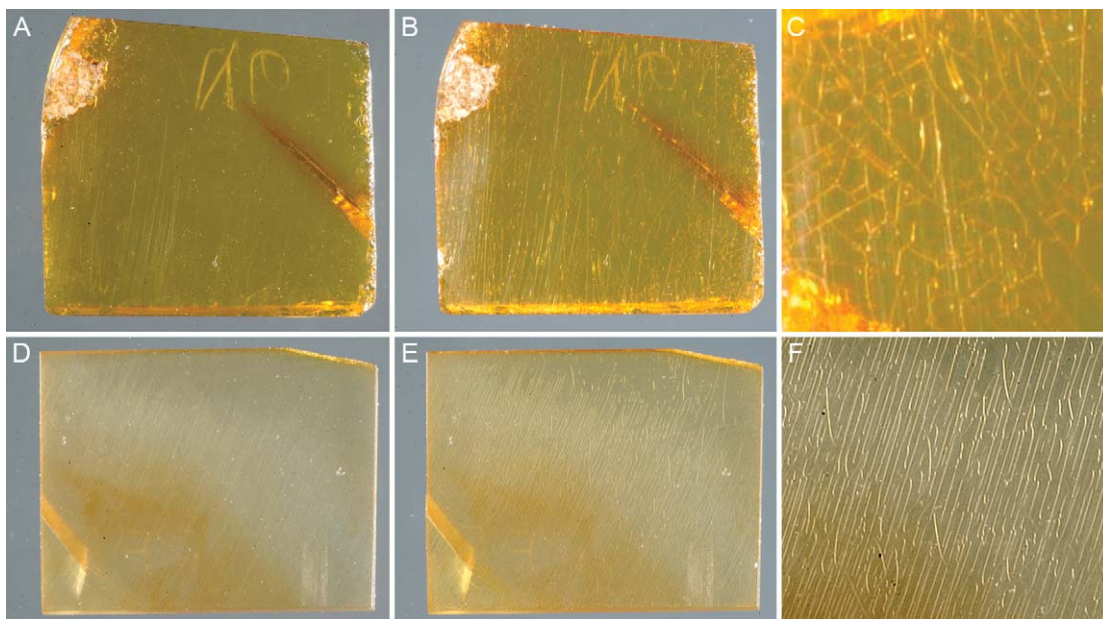
FIGURE 4. Crazing after exposure to a combination of UV/Vis and fluctuating humidity. **A.** New Jersey sample prior to treatment (size of all samples: 1.5 cm × 1.25 cm × 3 mm). **B.** New Jersey sample after treatment. **C.** Detail of crazing on New Jersey sample. **D.** Burmese sample prior to treatment. **E.** Burmese sample after treatment. **F.** Detail of crazing on Burmese sample.

internal fracture in amber reaches an arthropod or other inclusion, it can cause the entire surface of the inclusion to darken, craze, and ultimately be obliterated (fig. 1F–G). The duration of an amber piece's exposure to any particular humidity regime plays a critical role, since the polymer needs enough time to reach equilibrium with ambient conditions. Changes in RH may occur too quickly for a material to respond. Thus, test conditions in this study, in which fossil resin samples were exposed to abrupt RH changes at two-week intervals, were intentionally devised to enhance the stresses that can occur. Under these specific parameters, even Burmese amber showed some crazing (fig. 4D–F). Unstable conditions could occur in museum collections that do not have humidity controls, especially in temperate regions.

In the present study, it is notable that crazing did not occur in samples exposed to fluctuating humidity in the absence of light. This indicates that the oxidative effect of light plays a significant and possibly necessary role in crazing, friability, and embrittlement.

ABSORBANCE OF LIGHT IN FOSSIL RESINS: Spectrophotometric scans of the five fossil resins made before testing show characteristic curves in absorbance spectra, which are each distinct in intensity at the lower wavelengths (fig. 5). Peak absorbance for both the New Jersey and Burmese ambers occurs at significantly higher wavelengths than for the other fossil resins, lying further within the UV-B region (385 nm for New Jersey; 380 nm for Burmese).

Spectrophotometric absorbance values were converted to the CIELab color space system to assess color differences. Each fossil resin type studied exhibited specific characteristics in color

variability within individual samples prior to aging. Copal was found to have the most uniform coloration, and was overall the lightest, while New Jersey and Burmese ambers had the greatest variation in color (table 3). Because significant color variation existed within individual amber slices, averages between scans for each piece were used to compensate for any slight differences. However, this also resulted in a large standard deviation among measurements, particularly in the UV region. Consequently, the CIELab color data were more difficult to interpret. As such, only samples that were uniform in their coloration and did not contain cracks, inclusions, or air bubbles were assessed for CIELab color change following the aging tests.

FIGURE 5. Distinct absorbance spectra (averaged) for each of the five fossil resins before aging.

The change in CIELab color values for uniform samples before and after aging is depicted in table 4, as well as the total difference, shown as ΔE. For industrial materials like many plastics, in which samples tend to have uniform initial coloration, differences typically become visually perceptible when ΔE is greater than 5.

Yellowing: Significant color change in the form of yellowing was found only with exposure to elevated temperatures, and occurred for all ambers tested with the exception of Burmese amber (fig. 6). Yellowing is caused by an increase in absorbance in the blue region of the spectrum. This effect was most pronounced for Baltic amber (fig. 7A, B), with Dominican and copal samples also exhibiting significant yellowing, but to a lesser extent. An example of the lack of discernable yellowing in Burmese amber can be seen in figure 7C, D. While heat-aging in this study represents extreme conditions, these results are consistent with the observation that amber darkens with age, as routinely occurs in old collections of Baltic amber.

TABLE 3. Average CIELab values for fossil resin types prior to aging.

Fossil resin	L (lightness)	a (redness)	b (yellowness)
Burmese amber	72.30 ± 10.58	−0.04 ± 3.28	33.02 ± 5.86
New Jersey amber	70.50 ± 15.48	−3.33 ± 1.81	48.62 ± 14.95
Baltic amber	88.26 ± 3.37	−4.34 ± 0.89	22.68 ± 4.12
Dominican amber	84.56 ± 6.25	−2.72 ± 1.45	28.88 ± 11.56
Zanzibar copal	83.82 ± 7.09	0.17 ± 0.40	9.30 ± 3.66

TABLE 4. CIELab color change in samples with uniform coloration.

| Fossil resin	(no.)	RH	Light	ΔL	Δa	Δb	ΔE
Burmese amber	2	0	UV/Vis	0.94	0.91	1.10	1.7
	4	50	UV/Vis	−2.06	1.11	−0.59	2.4
	5	flux	UV/Vis	−0.24	0.32	−0.18	0.4
	11	0	dark	−6.69	−0.09	−2.08	7.0
	13	50	dark	3.19	−0.75	−1.32	3.5
	15	0	dark anoxic	14.56	−0.42	0.11	14.6
	17	50	dark anoxic	4.22	−0.49	−3.27	5.4
	19	flux	dark	−0.87	0.16	−0.81	1.2
	24	heat		4.32	−0.91	−0.52	4.4
New Jersey amber	1	0	UV/Vis	3.61	1.43	−3.65	5.3
	3	50	UV/Vis	−2.25	1.56	4.23	5.0
	5	flux	UV/Vis	11.27	1.11	2.11	11.5
	11	0	dark	5.72	0.17	−2.51	6.2
	14	50	dark	4.07	−0.91	−15.62	16.2
	15	0	dark anoxic	0.86	0.21	−3.13	3.3
	18	50	dark anoxic	6.30	−0.27	−2.62	6.8
	20	flux	dark	6.01	−0.71	−7.01	9.3
	22	heat		3.46	2.00	7.43	8.4
Baltic amber	1	0	UV/Vis	0.71	1.64	−1.30	2.2
	4	50	UV/Vis	−0.41	−0.15	4.04	4.1
	6	flux	Uv/Vis	−1.51	0.30	5.05	5.3
	11	0	dark	−1.15	1.07	−2.68	3.1
	13	50	dark	−1.52	0.97	−3.84	4.2
	16	0	dark anoxic	3.48	−1.38	−2.38	4.4
	18	50	dark anoxic	3.08	0.63	−6.18	6.9
	19	flux	dark	4.93	0.20	−1.82	5.3
	24	heat		−0.74	−1.04	25.57	25.6
Dominican amber	1	0	UV/Vis	−2.83	1.58	−4.02	5.2
	3	50	UV/Vis	−1.47	1.52	−6.13	6.5
	5	flux	UV/Vis	−1.31	2.13	−9.02	9.4
	12	0	dark	3.72	−1.08	7.49	8.4
	14	50	dark	0.21	0.18	−1.60	1.6
	17	0	dark anoxic	−0.78	0.81	1.69	2.0
	20	flux	dark	3.39	−0.30	0.89	3.5
	23	heat		−4.41	1.08	15.98	16.6
Zanzibar copal	2	0	UV/Vis	0.90	−0.17	−0.30	1.0
	3	50	UV/Vis	0.92	−1.33	2.73	3.2
	6	flux	UV/Vis	−3.44	−1.07	4.03	5.4
	12	0	dark	1.05	−1.31	0.98	1.9
	14	50	dark	0.31	−1.05	0.19	1.1
	16	0	dark anoxic	2.81	−0.70	−0.80	3.0
	18	50	dark anoxic	0.80	−0.85	1.11	1.6
	20	flux	dark	0.90	−1.16	2.36	2.8
	22	heat		−3.48	−3.41	11.46	12.5
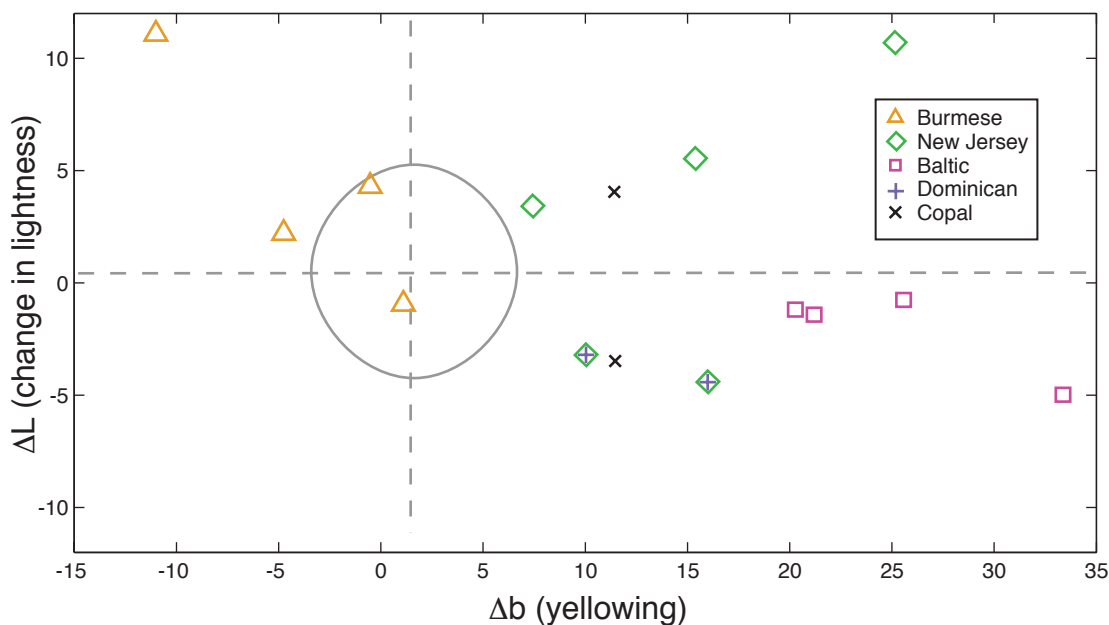
FIGURE 6. Yellowing of the five resins following heat aging, based on change in CIELab values.

Changes in UV Absorbance: The most significant change in absorbance spectra during aging occurred in the UV region that was monitored (360–400 nm). All four ambers tested showed a decrease in UV absorbance after exposure to heat, as well as light and/or fluctuating humidity. Baltic amber appeared the most stable overall, and showed little significant change in absorption, except when exposed to elevated temperature or light with fluctuating humidity. Dominican amber appeared somewhat less stable than Baltic, exhibiting significant absorbance changes from elevated temperature as well as exposure to light (UV/Vis). New Jersey amber appeared to be the most unstable of the fossil resins, showing a significant decrease in absorption in all aging conditions except dark anoxic.

Qualitative assessment of absorption spectra before and after aging demonstrates that the largest absorbance changes recorded were in the New Jersey samples, followed by the Burmese samples. This was expected, as both New Jersey and Burmese ambers absorb more light in the UV portion of the spectrum, indicating a greater susceptibility to UV deterioration (Strong, 1996). Interestingly, copal samples showed an *increase* in absorbance in the UV range with exposure to heat, light, and fluctuating humidity, which probably reflects the extent of crosslinking in resins that have barely matured.

A general trend noted is that the greatest differences in UV absorbance were seen with light exposure, particularly when combined with fluctuating humidity. However, in almost all tests involving RH, such changes in UV absorbance were less pronounced in dark-aged samples of comparable humidity, which is evidence that exposure to light (visible and ultraviolet) plays a significant role in the deterioration of fossil resins. In fact, dark-aged samples often showed little change in absorption regardless of humidity.
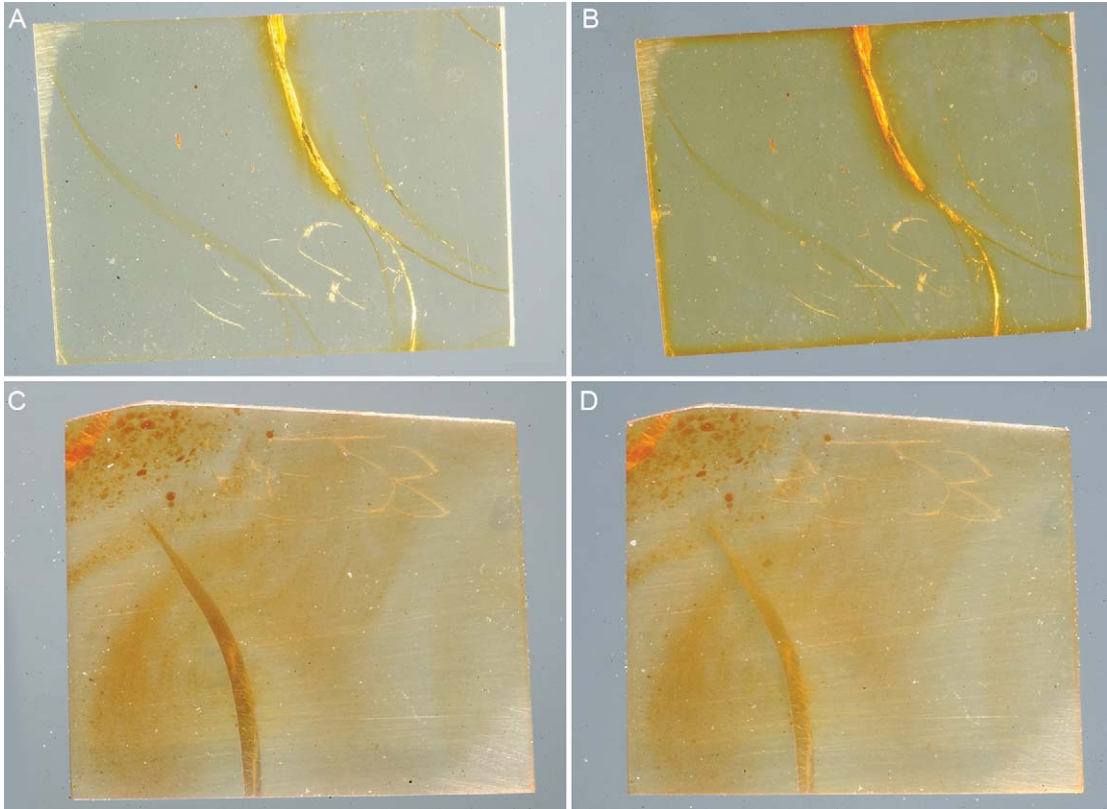
FIGURE 7. Images showing effects of heat on amber samples. **A.** Baltic sample prior to treatment. **B.** Yellowing of Baltic sample due to heat exposure. **C.** Burmese sample prior to treatment. **D.** No discernible yellowing of Burmese sample after heat exposure.

HUMIDITY: The trends for the effect of humidity itself are more difficult to interpret. Qualitatively, there is a trend for increased deterioration with the presence of moisture, in both light and dark-aged samples. The role of moisture in deterioration is expected of organic materials and has been found in accelerated aging tests of Baltic amber (Shashoua, 2002). However, the differences between aging at 0% and at 50% in this study were not conclusive, and no optimal humidity level was determined. In other studies, both excessively low and excessively high humidity (above 50%) have been linked to the deterioration of particular amber types. For example, low relative humidity is detrimental to Dominican amber (Williams et al., 1990), while Baltic amber is adversely affected by both high and excessively low humidity (Shashoua, 2002).

No studies have determined the optimal storage humidity for different fossil resins, and there are numerous and often divergent storage protocols at various institutions, from high to low humidity, with and without anoxic conditions. The results of this study and others taken together suggest that a stable RH environment is critical. Collection policy should also be taken into consideration—RH fluctuations imposed by frequent removal of specimens from the microclimate(s) of that collection's storage facility during research could be more detrimental

to the amber (particularly in conjunction with periods of exposure to intense light) than long-term storage at a humidity level that does not match the museum's ambient conditions.

Further study is indicated to address any interactions between fluctuating temperature and humidity that may apply to stored collections (specifically to what extent crazing or other deterioration can be influenced by such interactions). This would, however, require the use of special environmentally controlled chambers.

ANOXIC STORAGE: It is notable that for New Jersey amber, significant deterioration or change was avoided only under anoxic conditions, and that, overall, the five fossil resins showed the least change in absorbance when this treatment was imposed. However, further study is warranted regarding the benefits of anoxic storage, since oxygen-free conditions were not maintained during light exposure (anoxic environments in the UV/Vis tests failed over the course of the study).

MATURITY AND FRAGILITY IN FOSSIL RESINS: The general increase in fragility and suscep-tibility to degradation in older ambers is probably due to several factors. First, these resins are physically and chemically more mature. Ragazzi et al. (2003) found a significant correlation ($r = 0.7$, $p < 0.01$) between the age of amber deposits and the thermal behavior (i.e., tempera-ture of dissociation) of the ambers. The oldest ambers they studied, from Triassic and Creta-ceous deposits, generally had the highest thermogravimetric values, while Tertiary ambers and Holocene copals showed lower values. The age of various fossil resins likewise is correlated with hardness (Nascimbene et al., unpubl.). Age is therefore a significant variable in the polymeriza-tion, cross-linking, and isomerization (collectively, the "maturation") of fossil resins. This may help explain the general trend we found between UV absorbance and amber age, in which the more mature, older resins tested show a higher absorbance, while the youngest ones show the least (see fig. 5).

New Jersey amber was produced by coniferous trees of the cedar family Cupressaceae (Anderson, 2006; Grimaldi et al., 2000). According to the molecular classification of natural resins proposed by Anderson et al. (1992) and Anderson and Crelling (1995) (see table 5), and based on a recent study by Anderson (2006), New Jersey amber is designated as Class Ib. Class Ia Baltic amber (given the Ia designation because it was the first amber studied) contains the cross-linking agent succinic acid, and is from a coniferous tree probably of the family Pinaceae. Class Ia and Ib ambers are labdanoid diterpenes having a "regular" stereochemistry. Class Ic fossil resins, in contrast, are labdanoids with an "enantio" configuration. These include, but are not restricted to, relatively recent resins derived from broadleaf trees of the genus *Hymenaea* (Leguminosae) (Nascimbene et al., 2010). Species of *Hymenaea* produced the ambers from the Miocene of Mexico and the Dominican Republic, as well as the copals from Colombia and eastern Africa. Although the tree that produced the mid-Cretaceous Burmese amber is as yet undetermined, it is certainly coniferous and likely taxodiaceous/cupressaceous. Recent chemi-cal testing by Anderson reveals that, like the New Jersey amber, the Burmese amber is Class Ib (Anderson, personal commun.).

Baltic amber may be naturally durable because of extensive cross-linking with succinic acid (and the apparent durability of Burmese amber may also be due to a strong cross-linking agent,

TABLE 5. Chemical classification of fossil resins (Anderson and Crelling, 1995).

Class	Description	Examples
I	Most known ambers: macromolecular structures derived from polymers of labdanoid diterpenes, including labdatriene carboxylic acids, alcohols, and hydrocarbons	
Ia	Regular configuration, normally including communic acid, communol, and succinic acid	Baltic amber
Ib	Regular configuration, often including communic acid, communol, and biformene. Succinic acid not present	New Jersey and Burmese ambers
Ic	Enantio configuration, including ozic acid, ozol, and enantio biformenes	Dominican amber, Zanzibar copal
II	Derived from polymers of bicyclic sesquiter-penoid hydrocarbons, such as cadinene and related isomers	(Lower Eocene) Indian and Arkansas ambers
III	Natural fossil polystyrene	(Tertiary) German and New Jersey resins (rare)
IV	Nonpolymeric, including sesquiterpenoids based on the Cedrane carbon skeleton	Moravian "amber"
V	Nonpolymeric diterpenoid carboxylic acid, including abietane, pimarane and iso-pimarane carbon skeletons	Retinites in European brown coal

as yet unidentified). Geological age and molecular composition together generally appear to have the greatest effect on how amber matures. However, depositional factors and geological processes may also play a significant role.

MOISTURE AND ANAEROBIC SEDIMENTS: One factor when considering relative humidity for storage is the degree of moisture in sediments where amber or copal is found. There is mounting evidence that most if not all amber deposits are significantly preserved by anoxic conditions due largely to the presence of moisture for at least part of their history (Gomez et al., 2002; Grimaldi et al., 2000; Iturralde-Vinent, 2001). The amber-bearing sediments were in many cases initially deposited in a nearshore marine environment, such as a delta or estuary. In fact, New Jersey amber occurs in damp to wet lenses of soft lignite overlain by unconsoli-dated layers of sand and clay (Grimaldi et al., 2000). Though the sediments are acidic and sulfurous, the clay functions as a chemical buffer as well as a physical barrier to atmospheric exposure, protecting especially deep layers with stable moisture. It is interesting to note that Copper Age Baltic amber jewelry that was buried in peat bogs with corpses is remarkably well preserved, far better than that of later Roman and Middle Age pieces that were exposed to atmospheric conditions in tombs (Grimaldi, 1996). Just as taphonomic conditions like the presence of moisture appear to play a major role in the preservation of amber, similar condi-tions can presumably be mimicked in collections of amber.

Coating or Embedding Amber: In this study, close visual examination of the surfaces of amber samples that were coated with epoxy did not reveal any noticeable deterioration following accelerated aging. However, the surface of the epoxy finish itself did show some degradation after three months exposure to UV light (yellowing, minor crazing), similar to that of uncoated amber pieces subjected to the same conditions. In this case, one advantage of sealing (coating or embedding) amber samples is that any compromised epoxy can be ground and polished further or even removed completely. Notably, long-term observation and regular examination of embedded AMNH amber pieces suggest that an epoxy seal successfully protects such specimens from exposure over time to fluctuating humidity or the full oxidative effects of light and heat, especially if specimens are stored in a dark, stable collections environment.

Although no longer a common practice, it should be mentioned that storing fossil resin specimens in solutions like mineral oil is highly discouraged, because the oil will interact with the amber, and will also make further preparation difficult or impossible. Class II ambers (like Indian amber or amber from Arkansas) are particularly susceptible.

Amber Collections and Exhibitions: The need to protect amber specimens from deterioration applies not only to paleontological collections, but also to stored archaeological collections containing amber artifacts, as well as to excavated amber samples awaiting preparation. Unprepared samples are often stored in less than ideal conditions over several years before they are eventually processed. Also, amber pieces in exhibitions (whether paleontological or archaeological) are often subject to inadequate conservation, and some exhibitions are permanent. As an example, a long-term exhibition in the Museo Geominero in Madrid housed numerous Dominican amber pieces with insects, and for the first several years the specimens were kept in poor conditions leading to significant deterioration (crazing, darkening, etc.). Fortunately, necessary changes were finally instituted with respect to temperature, RH, and UV light, and the display case containing the amber was henceforth environmentally monitored (Baeza et al. 2007).

CONCLUSIONS

Results of the present study reveal that amber is best housed in closed storage or sealed containers to minimize exposure to light, with maintenance of stable humidity. Though this was not tested, it is assumed that storage in cooler temperatures (e.g., ca. ≤21° C) is also beneficial. For all fossil resins tested, the least deterioration took place in dark storage with stable humidity. Although an optimal humidity level was not determined, our results indicate that stable RH is critically important. Similar results were obtained in other studies using Baltic and Dominican amber, but which also suggested an optimal humidity in the range of 35%–45%. There appears to be considerable variation in the effects of humidity among amber types, and New Jersey amber in particular is the most susceptible to damage from exposure to light, heat, and fluctuating humidity, even in mild conditions.

The need to seal amber specimens to protect them from damaging exposure was known as early as the mid-19th century, beginning with the practice of embedding small pieces of Baltic amber containing fossils in a natural modern resin (Canada balsam), stored within glass wells.

Amber preserved this way in several European museums shows no crazing or darkening. One important disadvantage of the technique, though, is that further preparation of the piece is very difficult to impossible without damaging the amber; and unfortunately, without subsequent preparation, details of the inclusions are usually compromised for viewing by modern systematists. Also, embedding amber pieces in Canada balsam is highly impractical for collections with thousands of pieces, and for the larger (ca. >2 cm diameter) pieces that may actually be the most valuable ones.

For fossil collections, the present method of choice is to embed amber pieces in a high-grade epoxy (Corral et al., 1999; Nascimbene and Silverstein, 2000; Hoffeins, 2001), which is more efficient than using balsam and also allows preparation to be done multiple times. The epoxy strengthens and clarifies friable amber specimens, enabling the close preparation required to view details of inclusions, and also preserves the amber pieces for long-term study. Epoxies, however, have limitations similar to amber (Down, 1984, 1986), and some of them yellow over time even when only minimally exposed to light and heat. As noted earlier, the amber samples that were coated with the Buehler epoxy for this study showed some surface deterioration of the epoxy (yellowing, minor crazing) within three months of accelerated UV aging; however, no visible changes were seen to the epoxy-coated amber itself.

The conservation effects of the various epoxies used for embedding or coating amber specimens is a subject for further investigation.

ACKNOWLEDGMENTS

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APPENDIX

Full Summary of Treatments for Fossil Resins

Fossil resin	Sample (no.)	Treatment	Fossil resin	Sample (no.)	Treatment
Burmese	1	UV with 0% RH	Burmese	15	Dark anoxic / 0% RH
Burmese	2		Burmese	16	
Burmese	7		Burmese	17	Dark anoxic / 50% RH
Burmese	8		Burmese	18	
Burmese	3	UV 50% RH	Burmese	19	Dark 20%–70% RH
Burmese	4		Burmese	20	
Burmese	9		Burmese	21	Accelerated temp.
Burmese	10		Burmese	22	
Burmese	5	UV 20%–70% RH	Burmese	23	
Burmese	6		Burmese	24	
Burmese	11	Dark 0% RH	New Jersey	1	UV 0% RH
Burmese	12		New Jersey	2	
Burmese	13	Dark 50% RH	New Jersey	7	
Burmese	14		New Jersey	8	

Fossil resin	Sample (no.)	Treatment	Fossil resin	Sample (no.)	Treatment
New Jersey	3	UV 50% RH	Dominican	1	UV 0% RH
New Jersey	4		Dominican	7	
New Jersey	9		Dominican	8	
New Jersey	10		Dominican	3	UV 50% RH
New Jersey	5	UV 20%–70% RH	Dominican	4	
New Jersey	6		Dominican	9	
New Jersey	11	Dark 0% RH	Dominican	10	
New Jersey	12		Dominican	5	UV 20%–70% RH
New Jersey	13	Dark 50% RH	Dominican	6	
New Jersey	14		Dominican	11	Dark 0% RH
New Jersey	15	Dark anoxic / 0% RH	Dominican	12	
New Jersey	16		Dominican	13	Dark 50% RH
New Jersey	17	Dark anoxic / 50% RH	Dominican	14	
New Jersey	18		Dominican	15	Dark anoxic / 0% RH
New Jersey	19	Dark 20%–70% RH	Dominican	17	Dark anoxic / 50% RH
New Jersey	20		Dominican	18	
New Jersey	21	Accelerated temp.	Dominican	19	Dark 20%–70% RH
New Jersey	22		Dominican	20	
New Jersey	23		Dominican	22	Accelerated temp.
New Jersey	24		Dominican	23	
Baltic	1	UV 0% RH	Dominican	24	
Baltic	2		Copal	1	UV 0% RH
Baltic	7		Copal	2	
Baltic	8		Copal	7	
Baltic	3	UV 50% RH	Copal	8	
Baltic	4		Copal	3	UV 50% RH
Baltic	9		Copal	4	
Baltic	10		Copal	9	
Baltic	5	UV 20%–70% RH	Copal	10	
Baltic	6		Copal	5	UV 20%–70% RH
Baltic	11	Dark 0% RH	Copal	6	
Baltic	12		Copal	11	Dark 0% RH
Baltic	13	Dark 50% RH	Copal	12	
Baltic	14		Copal	13	Dark 50% RH
Baltic	15	Dark anoxic / 0% RH	Copal	14	
Baltic	16		Copal	15	Dark anoxic / 0% RH
Baltic	17	Dark anoxic / 50% RH	Copal	16	
Baltic	18		Copal	17	Dark anoxic / 50% RH
Baltic	19	Dark 20%–70% RH	Copal	18	
Baltic	20		Copal	19	Dark 20%–70% RH
Baltic	21	Accelerated temp.	Copal	20	
Baltic	22		Copal	21	Accelerated temp.
Baltic	23		Copal	22	
Baltic	24		Copal	23	