Influence of Sunlight during Harvest on the Oxidation and Yellowing of Natural Mastic Resins Used as Varnishes on Artwork

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Abstract: The natural resin mastic, composed largely of triterpenes, is used as a varnish on artwork. This study investigates the influence of light on the autoxidation and yellowing of mastic, both during harvest and after application as a film. The nature of photoinitiation reactions is considered, as is the propagation of oxidative processes in both light and darkness. Oxidation, radical content and yellowing were studied by graphite-assisted laser desorption mass spectrometry, EPR and UV/VIS spectrometry, respectively. Exposure to sunlight during harvesting is found to strongly affect the resin. The radical content increases dramatically, and oxidation is accelerated. These differences are also observed during artificial aging under a range of conditions. Mastic that is harvested without exposure to sunlight deteriorates less quickly in all respects. This is attributed to lack of sunlight-generated radicals and/or labile radical precursors, which are very long-lived in the viscous resin or solid film. Remarkably, radicals are found to be nearly as prevalent in dark-aged films as those aged in light. Oxidation in the dark is also nearly as fast as with continuous light exposure. These results suggest that dark and light aging are not fundamentally different, in contrast to the conventional model.

Keywords: EPR · MALDI · Oxidation · Resin · Terpenes.

1. Introduction

Many paintings are varnished with the triterpenoid natural resins dammar or mastic [1]. Initially these varnishes saturate and brighten the colors and give a smooth, glossy appearance to the painting. With time they yellow, become brittle and crack. Yellowing may change the subjective impression of a painting significantly (see Fig. 1). It is often the main reason for replacement of a varnish. Because removal can damage the painting [2–4], various authors have studied the aging behavior of varnishes, with the goal of understanding and slowing their deterioration [1][5–16]. Although progress has been made, the problem remains unsolved. Synthetic varnishes and multilayer synthetic/natural coatings have been introduced [17–20], but these are also not entirely satisfactory, and the search continues for the optimum artwork varnish.

Dammar and mastic consist mainly of triterpenoids, with lesser amounts of hydrocarbon polymers and sesquiterpenoids [1][21][22]. Deterioration of these materials proceeds *via* radical chain reactions (autoxidation), as summarized in Eqns (1)–(5) [13][23][24]:

Initiation *via* UV excitation of keto groups followed by alpha cleavage (Norrish reaction) has been proposed as a major initiation step [5][14]. The peroxyl radicals are relatively stable, thus step (3) is probably rate determining. Hydroperoxides are homolytically cleaved by heat or light (4), and the chain is branched and propagated.

In addition to the reactions shown, others proceed in parallel. Alkoxy radicals RO• can react to alcohols, ethers or ketones. Addition to double bonds may compete with abstraction in step (3) [23][24]. Products like hydroperoxides also undergo non-radical reactions. As a result, many of the known aging products of dammar and mastic varnishes are not expected to form directly by reactions (1)–(5), but nevertheless result from
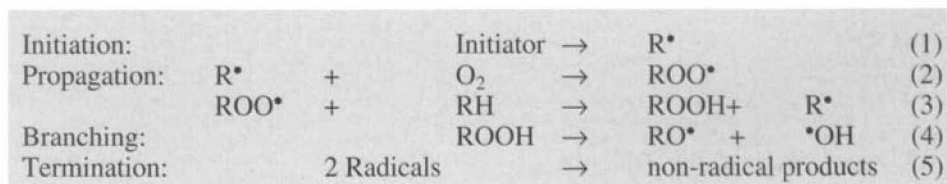
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Initiation:			Initiator $\rightarrow$	R•		(1)
Propagation:	R•	+	O_2 $\rightarrow$	ROO•		(2)
	ROO•	+	RH $\rightarrow$	ROOH+	R•	(3)
Branching:			ROOH $\rightarrow$	RO• +	•OH	(4)
Termination:		2 Radicals	$\rightarrow$	non-radical products		(5)

Fig. 1. Painting before (left) and after (right) replacement of its strongly yellowed varnish. With the yellowed varnish, the colors are brownish and the painting appears flat. With a clear varnish, the contrast between the pale walls and the now blue sky, as well as the more pronounced shadows, lead to a much more vivid, plastic, and three-dimensional painting. (Wilhelm Meyer, Duel scene in front of church ruin, 1831. © Swiss Institute for Art Research.)

these primary events [9][10]. Components of resins also polymerize and decay again with progressive aging [6][16][21].

Radical oxidation in darkness was believed to be of minor importance in varnishes because of rapid termination and insufficient initiation rates [6]. While intuitively reasonable and true for other materials used in artwork, such as oils [25], evidence for this was marginal. One indication was the solubility of photoaged varnishes in polar solvents, *versus* that of thermally aged varnishes in less polar solvents [5]. The trend was believed to correlate with the degree of autoxidation [6][7], but this assumes that oxidation always leads to strongly polar products that are insoluble in apolar solvents. This is not necessarily true because photoaging results in enhanced formation of acids compared to thermal aging [6], which strongly decreases solubility in apolar solvents. This is especially the case if UV-rich light sources such as xenon-arc lamps are used [11]. Dark autoxidation is a known phenomenon in general (*e.g.* drying of oils or synthetic polymers), and was recently also report-

ed for polyterpenes [26]. Absence of light does not alter the propagation pathways (reaction steps (2) and (3)), but decreases the initiation rate (reaction step (1)) [24].

However, our prior work proved that dark oxidation takes place in resins and resin varnishes [16]. Oxidation was easily followed by graphite-assisted laser desorption/ionization mass spectrometry (GALDI-MS). Commercially available resin was found to be in an advanced stage of oxidation, although considered 'fresh' [14][16]. With this technique, analytes are desorbed from 2-μm graphite particles and detected as sodium adducts.

Electron paramagnetic resonance spectroscopy (EPR) revealed that considerable amounts of radicals are present in varnishes stored in darkness. This suggests that dark oxidation also proceeds by radical chain reactions, as in light. However, an important question remained: how are the radical reactions initiated without light? The only possibility for thermal initiation seemed to be the homolytic decay of labile peroxides, but they are only produced by the autoxidative processes themselves.

To explain this body of data, oxidation and deterioration of the resins was postulated to be initiated when drying in the sunlight on the trees [16]. To test this and find out more about the influence of sunlight during harvest on the deterioration of the resulting varnish, mastic resin was collected on the island of Chios, Greece, with and without exposure to sunlight. These samples, along with commercial mastic, were then aged under different conditions, to investigate their long-term stability.

2. Experimental

The 'Chios' commercial mastic was obtained from A. Grogg Chemie (Bern, Switzerland). The fresh mastic resin was harvested near Pyrgi on the island of Chios, Greece. The branches of the trees were wrapped in aluminum foil to protect the resin from sunshine, see Fig. 2. The resin was collected for several days, and transferred to sealed containers during early morning or evening, so as to avoid any exposure to direct sunlight.

Fig. 2. Harvest of mastic resin protected from sunlight. After cutting the bark of the mastic trees, the colorless resin oozes out within minutes. Traditionally it is left on the tree to dry for about two weeks. For this study, some branches of the trees were wrapped in aluminum foil immediately after cutting to protect the resin from direct sunlight.

dry on the sample tip. A THF solution of the resin was pipetted onto the graphite and also allowed to dry. The sample quantity was varied empirically for best signal and resolution. The analytes were detected as alkali metal adducts. To avoid spectral confusion, sodium adduct formation was enhanced by addition of a small amount of NaCl to the graphite/ methanol slurry. Residual contamination of the spectrometer with diffusion pump oil led to signals at m/z 413, 469, 483 and 507 (marked with asterisks in the Figs) which interfered with the signals of the triterpenes. These signals appeared immediately after sample insertion, and grew with time.

The cw-EPR spectra were recorded on a Bruker spectrometer (ESP 300 E, microwave frequency 9.4 GHz). The magnetic field was determined by a NMR Gaussmeter (ER 035 M, Bruker, Fällanden, Switzerland). The concentration of radicals in the pulverized resin samples were determined by comparing the integral of the absorption line with the linear regression of a series of four standard samples with known radical concentrations. The standard was the fourth line in the spectrum of $VO(acac)_2$ (Acros Organics, Basel, Switzerland, purity: 99%), dissolved in water-free toluene. Due to physical differences between the calibration standard (toluene solution) and the resin samples (powder), the remaining uncertainty in radical concentration is estimated to be ±20%. The absolute radical concentrations reported previously [16] are too large by a factor of 5 due to subsequently discovered calibration problems. Nevertheless, the relative proportions are correct and therefore also the conclusions drawn from the data.

UV/VIS-spectra were collected with a Uvikon 940 spectrophotometer (a 2-beam instrument), Kontron Instruments (Watford, Herts, UK). Samples of ca. 10 mg resin were dissolved in 5 ml freshly distilled tetrahydrofuran and measured in quartz cuvettes.

The varnish sample from the painting 'Damenportrait' (18th century, artist unknown) was provided by the Swiss Institute for Art Research. It was removed with isopropanol during its restoration.

The samples for artificial aging were prepared as follows: the resin was dissolved in a commercial hydrocarbon solvent (Dottisol D40, 1:3 wt%) and filtered. Aliquots were pipetted onto glass microscope slides. Artificial aging was carried out under daylight-simulating lamps (Power Twist True Lite, 'Duro Test' 20TH12 TXC) in an oven at 60 °C. The samples were protected from direct irradiation by the glass window of the oven. For aging without UV, an additional commercial UV-filter (cut-off at 410 nm) was placed between the lamps and the samples.

The graphite-assisted laser desorption/ionization experiments were performed on a home-built 2 m linear time-of-flight mass spectrometer. Resolution was improved by delayed extraction to ca. 600 at m/z 500. Ions were extracted using a 21 kV acceleration voltage and a delay time of 180 ns. Desorption was performed using the 337 nm output from a nitrogen laser (VSL-337ND-T, Laser Science Inc., Franklin, MA/USA).

The samples were prepared for mass spectrometry as follows: A suspension of 2-µm graphite particles (Aldrich, Buchs, Switzerland) in methanol was allowed to

3. Results and Discussion

3.1. *Unaged Mastic Resins*

The mastic beads or 'tears' which are commercially available are at least six months old. Harvesting and processing on the island of Chios, followed by packaging and transport are responsible for this delay. Most mastic used on paintings is, however, older since it is rarely, if ever, purchased on a 'just-in-time' basis. As a result of these factors, what a restorer applies to a painting is quite different from what came out of the tree. This is already apparent to the naked eye – the exudates on the tree are crystal-clear, while commercial mastic beads are usually distinctly yellow.

To follow the process of aging from the beginning, samples of mastic were collected on Chios, both in the traditional way involving two weeks of drying in the sun on or under the tree, and under exclusion of light with no drying period. A nice overview of mastic collection methods is given in [27]. In this study, traditionally collected samples were studied without the usual processing with sea water and soap.

As seen in the mass spectra of Fig. 3, there is a dramatic difference in the composition of the truly fresh resin *vs.* commercial resin. Initially, it shows two dominant group of peaks, at m/z 461–467, and m/z 477–481. These correspond to the expected main components of mastic [9][12][16]. In contrast, the commercial 'fresh' samples are highly oxidized. A typical series of oxidative peak groups begins to become apparent, at m/z 493, 509, *etc.* Also one begins to observe degradation products at m/z values below that of the parent compounds.

Equally dramatic is the difference in radical content of mastic collected or stored for short periods under different conditions, as seen in Fig. 4. A few days of sunlight during harvest increases the
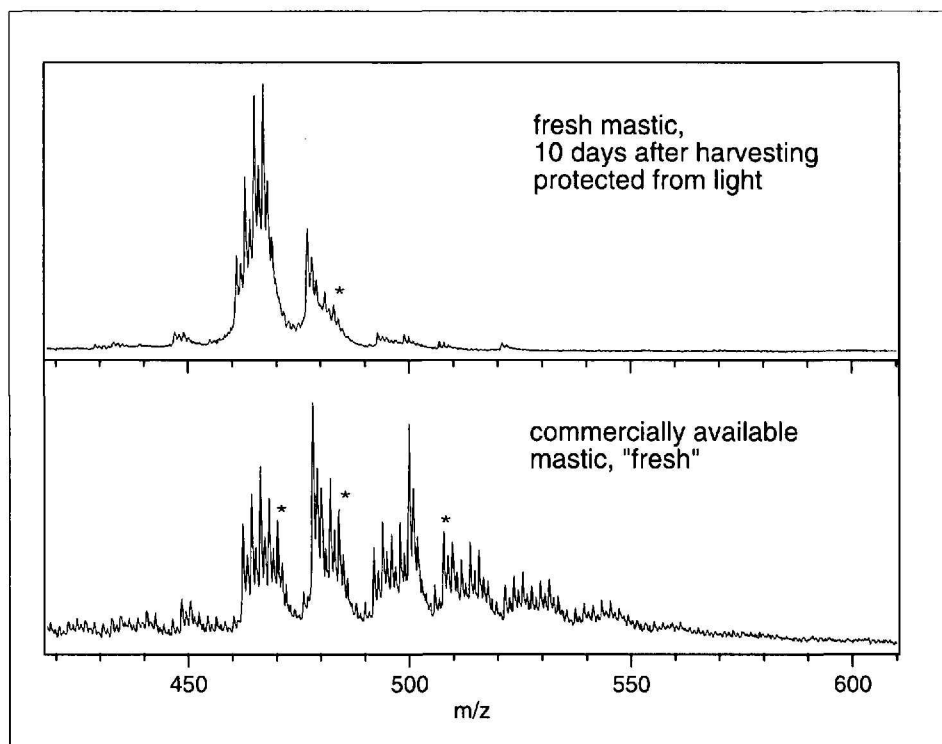

Fig. 3. Triterpenoid mass range of GALDI mass spectra of absolutely fresh (upper) and commercial mastic (lower). The commercial resin, usually considered 'fresh', is obviously in an advanced stage of oxidation and degradation, since most of the signals above m/z 490 are oxidation products and not found in the truly fresh resin. Also degradation products are visible at m/z values lower than the initial compounds. Signals marked with asterisks are contaminants in the spectrometer.
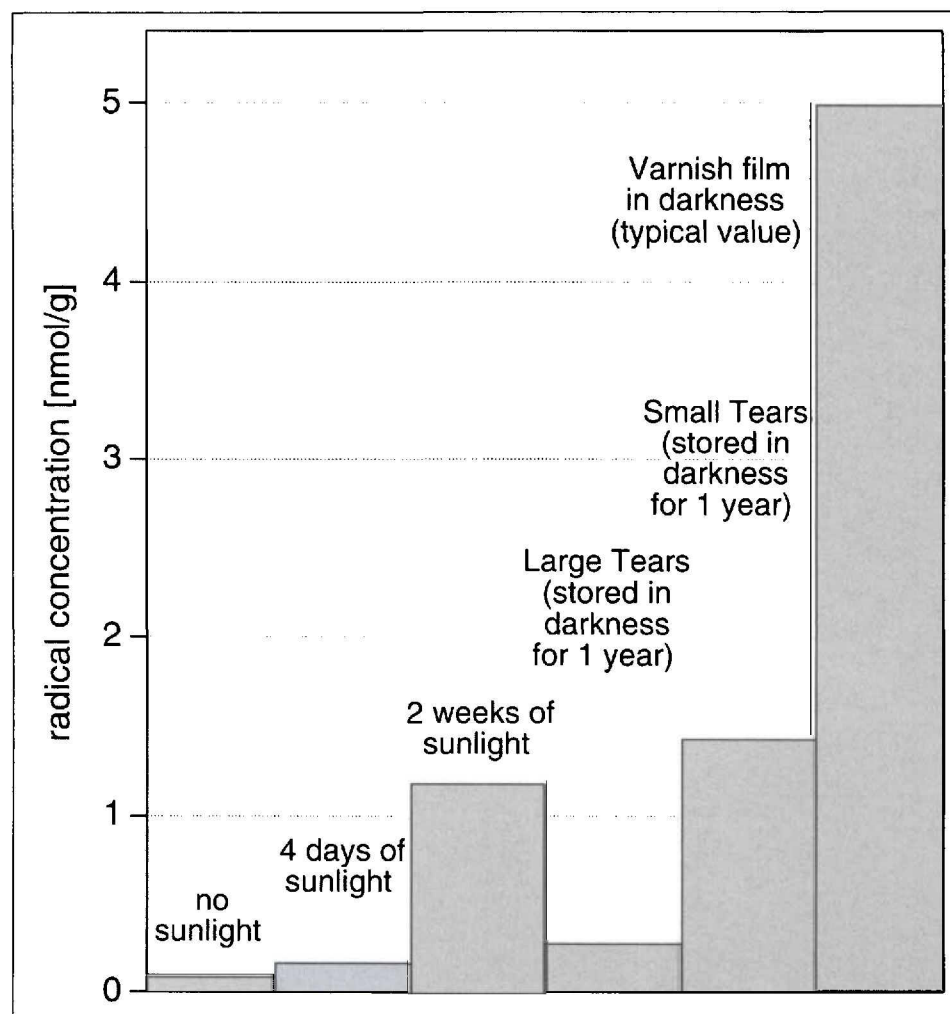
Fig. 4. Radical concentrations in different mastic samples. Harvesting of resin with protection from sunlight irradiation resulted in very low radical content. Irradiation for only four days led to almost twice the amount of radicals, and conventional drying in the sun for about two weeks increased the radical content by more than ten times. These results show a clear effect of sunlight irradiation during harvest on the amount of radicals. This is a probable cause of subsequent oxidation and degradation of the resin. Radical contents also seem to be strongly influenced by the surface/volume ratio, since small beads (tears) contain much more radicals than large pieces, but still much less than a varnish film.

radical concentration significantly. In commercial mastic, large beads (tears) contain fewer radicals than small tears, presumably an effect of surface/volume ratio. Similarly, a varnish film contains many more radicals than a resin bead. Storage in darkness decreases the radical concentration, but it soon reaches a constant level and does not decrease further.

3.2. Aged Mastic Resins
3.2.1. Effect of Indoor Sunlight Aging

As seen in Fig. 5, the difference in the mass spectra between aging with and without indoor sunlight is small. Although oxidation is stronger with light, exposure to air as a thin film is clearly a more important factor in the oxidative changes that occur.

The peak groups that develop on aging are spaced by 14–16 mass units, corresponding to incorporation of oxygen, or oxidation with associated unsaturation. This is consistent with the formation of multiple oxidation products from each component of the fresh resin. Identical aging behavior has been observed for

pure triterpenes such as hydroxydammarenone (dipterocarpol) [15], a major component of both mastic and dammar.

With increasing number of incorporated oxygens, the probability of polymerization also increases, thus further oxidation leads to more polymerization products, while the pattern in the triterpenoid mass range stays more or less the same (Fig. 5). Polymerization products also decay again, resulting in more decomposition products at low masses [16].

3.2.2. Effect of Sunlight During Harvest on Aging

Two mastic resins were artificially aged: one collected under complete exclusion of light ('protected'), and the other collected in the traditional manner with sunlight exposure ('exposed'), but not processed (e.g. washed) in any other way. Artificial aging was carried out both with and without the UV component of the spectrum (wavelength <410 nm). This was compared to aging in darkness.

As seen in Fig. 6, the mastic collected with exposure to sunlight is already sig-

nificantly oxidized compared to the protected sample. It is not as dramatically altered as a commercial sample, but lies somewhere in-between. This sample was dried in the sun and kept in darkness for only two months. The presence of new compounds that are not exuded by the tree means that initiation of decomposition processes has occurred. Since the energy-rich compounds formed via photolytic oxidation propagate the autoxidation process, it was predicted that the exposed sample would age more rapidly than the protected sample.

This was found to be the case, as shown in Fig. 7 and Fig. 8. Both with and without UV exposure, the exposed sample was more heavily oxidized, at all stages of artificial aging. The peak groups corresponding to sequential oxidation extend to higher masses and are more intense. In the protected sample the singly oxidized group (m/z 481, from m/z 465) remains the most intense, while it is the doubly oxidized group (m/z 507, from m/z 477) that is the maximum of the distribution for the exposed sample.
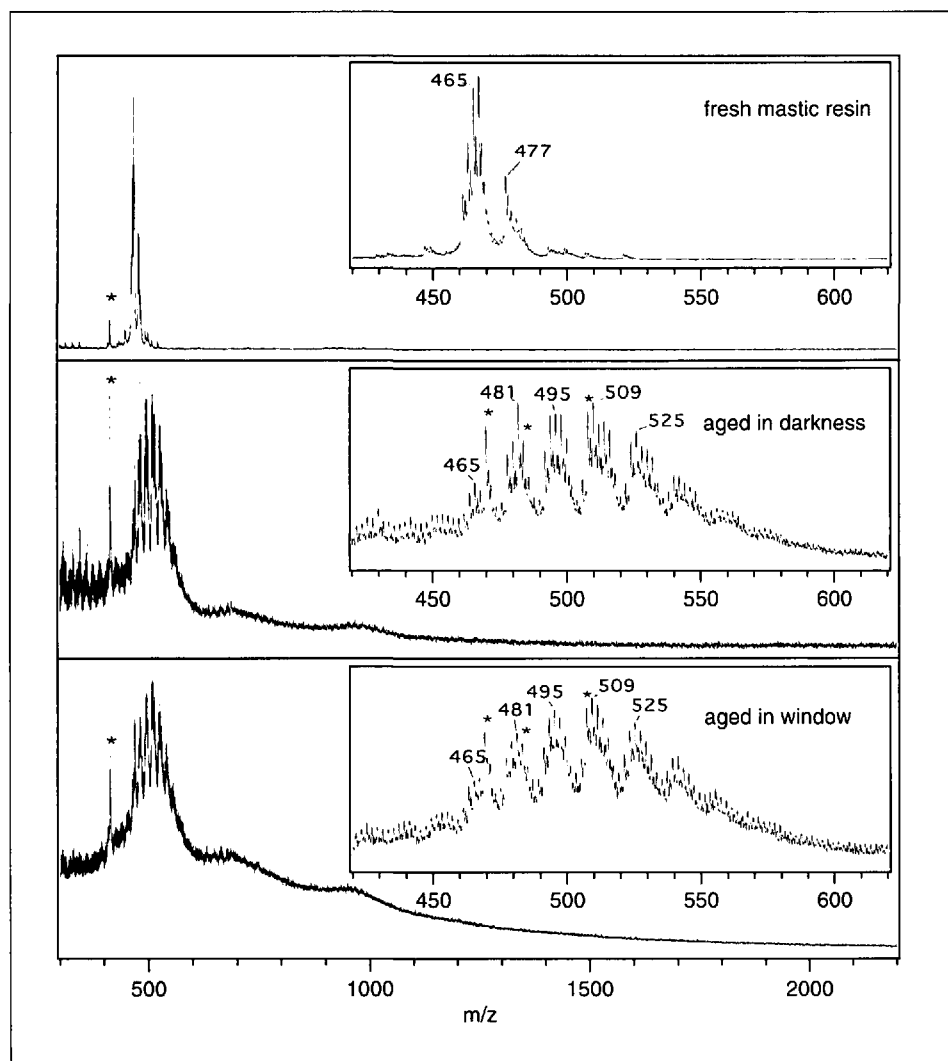

Fig. 5. Effect of light during aging on oxidation of mastic films. Depicted are the GALDI-MS of mastic films stored for only one year in a south-facing window (lower), and in darkness, respectively (middle). For comparison, the spectrum of fresh mastic resin is also shown (upper). The mass spectra of the aged films are very similar, and it is obvious that strong oxidation took place in both cases. Thus, oxidation is stronger in light, leading mainly to more polymerization and decomposition, but these processes also proceed in darkness. Exposure to light is obviously not as important as being exposed to the air as a thin film. Signals marked with asterisks are contaminants in the spectrometer.
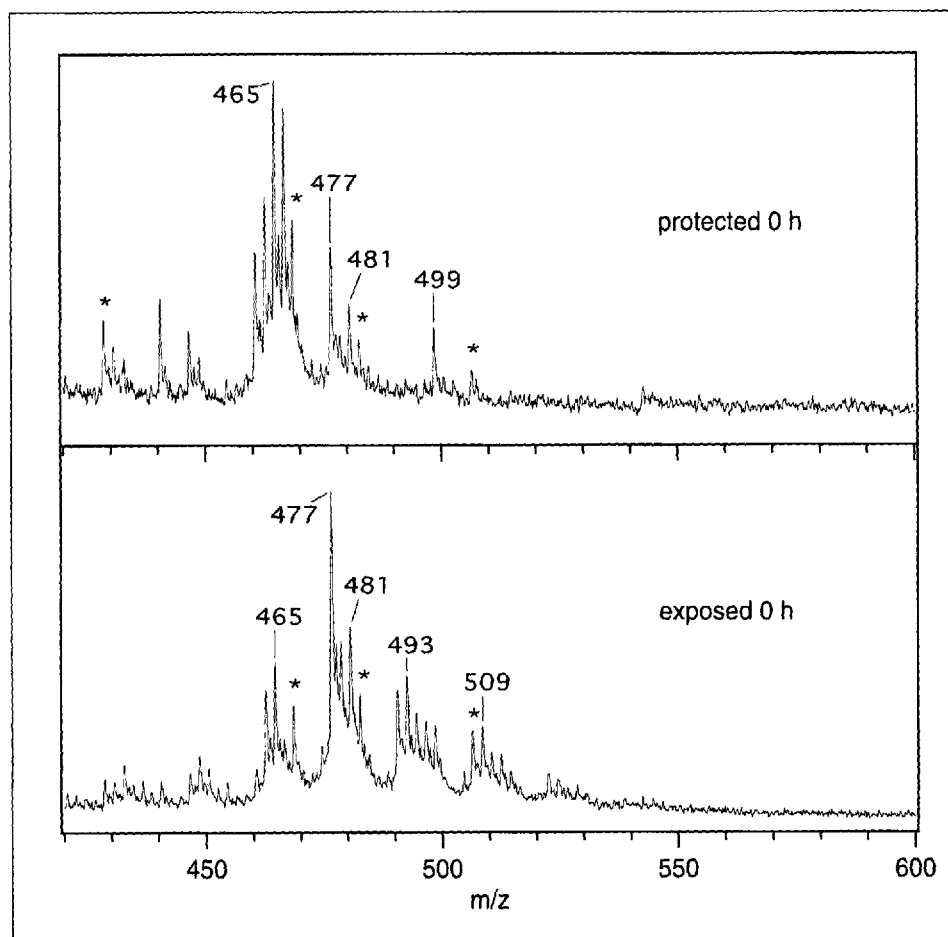
Fig. 6. GALDI-MS of the unaged mastic resin films for artificial aging. Protected from sunlight during harvest (upper) and conventionally dried in the sun for two weeks (lower). A difference in degree of oxidation stage already visible. Signals marked with asterisks are contaminants in the spectrometer.
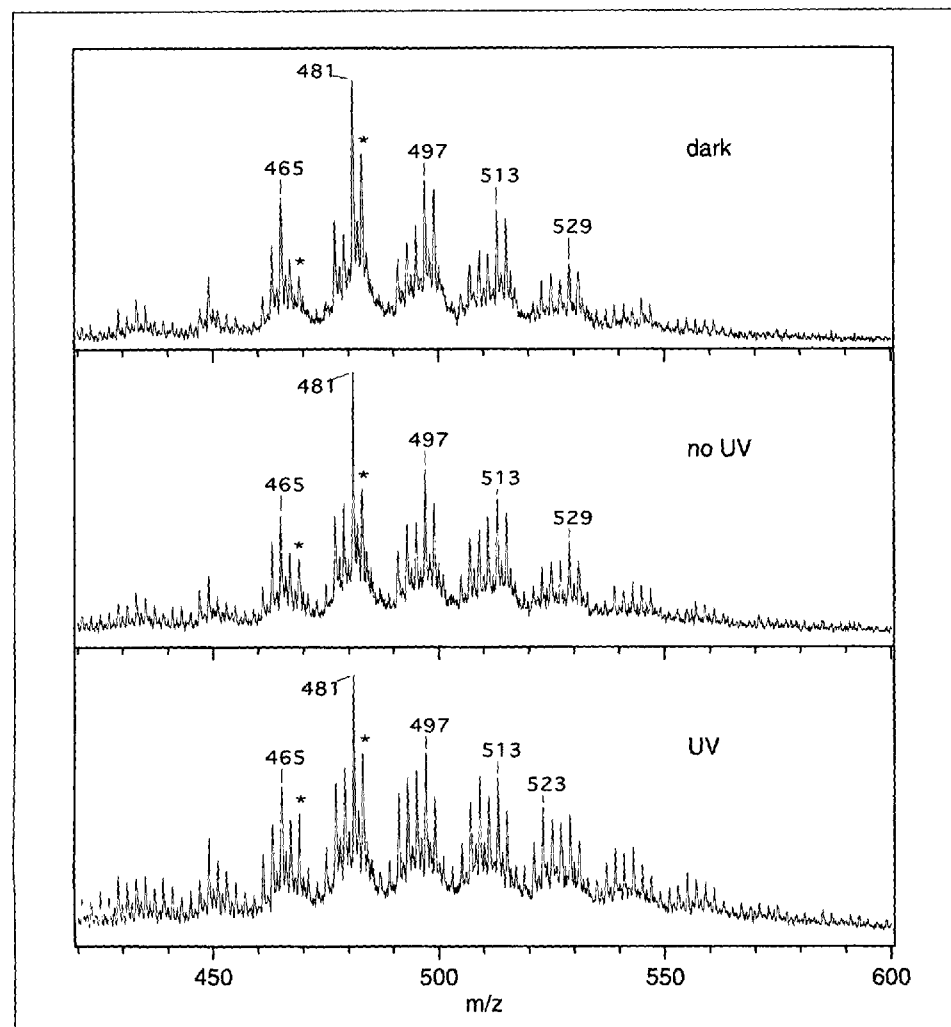

Fig. 7. GALDI-MS of films of mastic (protected from sunlight during harvest) after 300 h of artificial aging. Strong oxidation occurred under all aging conditions, demonstrating that the effect of light during aging is rather small and strong oxidation also takes place in darkness.
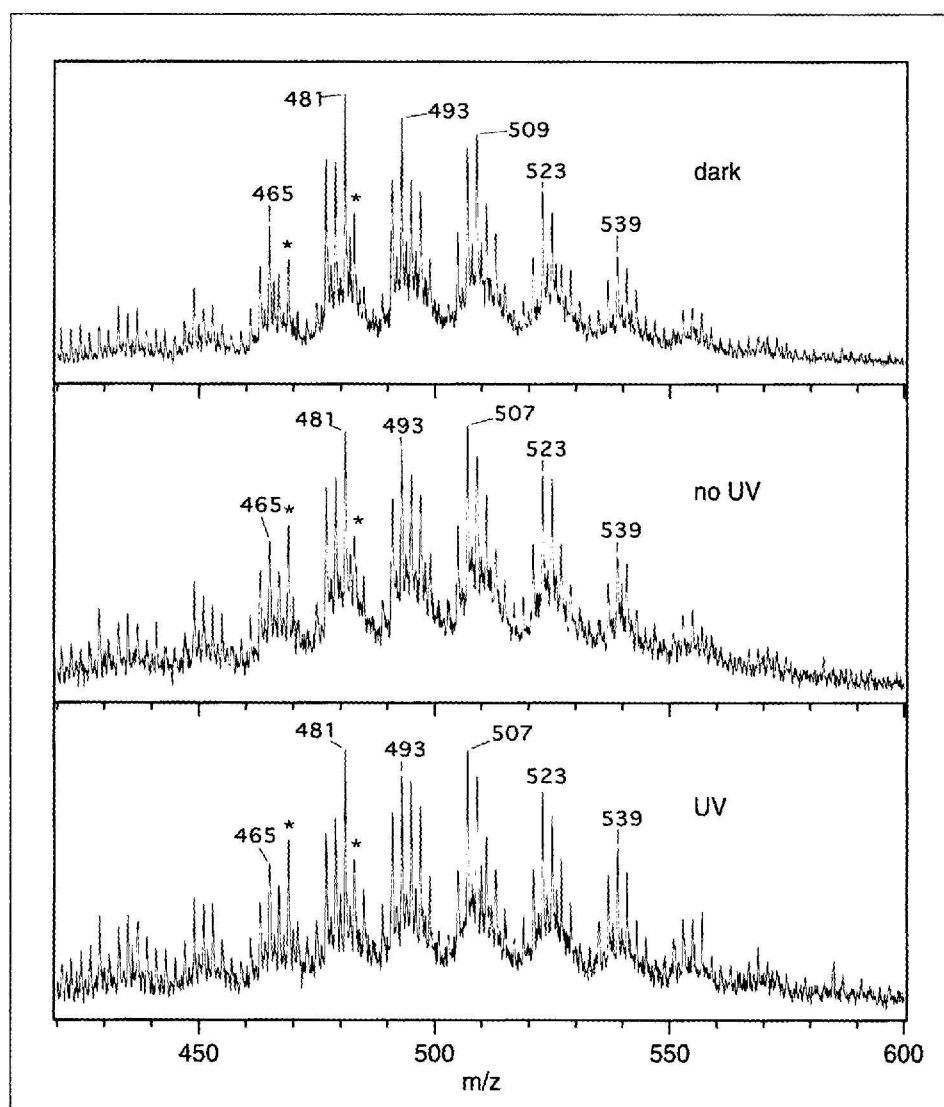
Fig. 8. GALDI-MS of films of mastic (conventionally dried in the sun) after 300 h of artificial aging. Strong oxidation occurred under all aging conditions, and again the differences in the mass spectra are rather small. Compared to the aged films of 'protected' mastic (Fig. 7), oxidation is stronger: the peak groups corresponding to sequential oxidation extend to higher masses and are more intense. This is true even if one keeps in mind that the initial composition of the samples was different. The exposed sample contained more triterpenoids appearing at m/z 477 (mostly isomeric acids [9]), containing one oxygen atom more than the prevalent triterpenoids in the protected sample (appearing at m/z 465/467 in the mass spectrum). However, this is not due to a larger degree of oxidation in the fresh resins but to natural variation in the composition of unoxidized triterpenoids.

As found for unaged resins and also reported earlier [16], application as a thin film with a large surface/volume ratio is probably more important for degradation processes in varnishes than exposure to light. The mass spectra of samples aged in darkness and exposed to simulated daylight without UV show a quite similar degree of oxidation. Exposure to some UV (simulated daylight through window glass) does have some effect on the mass spectra, but not a large one. The distribution of peak groups extends typically one increment further to the high mass side for samples that were both protected or exposed during harvest.

The effects seen in the mass spectra during aging are reflected in the EPR results (see Table). The fresh protected sample had an unmeasurably low radical content, the exposed sample already contained a substantial amount. Aging increased the radical concentration in all cases, but the protected sample was less affected. Again the presence of initiator

compounds in the exposed sample appears to sensitize the resin to further autoxidation.

Table 1. Radical concentrations in artificially aged mastic samples [nmol/g].

	Aging time		
	0 h	50 h	300 h
protected, dark	–	2.4	4.8
protected, no UV	–	3.3	8.8
protected, UV	–	4.0	NA[a]
exposed, dark	5.3	4.8	7.2
exposed, no UV	"	3.3	10.2
exposed, UV	"	7.2	17.9

[a] not analyzed

As noted in the introduction, one of the most important aspects of aging from the viewpoint of art conservation is yellowing, a consequence of oxidation. Here

too a clear difference was found between the protected and exposed samples during artificial aging. Samples protected from sunlight during harvest yellowed significantly less, as could easily be observed with the naked eye. As shown in Fig. 9, the absorption at the blue end of the spectrum was lower for the protected samples throughout the aging process. The harvesting method was clearly more important for the yellowing behavior than the nature of the aging conditions.

Also notable is the fact that aging in complete darkness is rapid, as also reported before [16]. This was found in the mass spectra, EPR, and yellowing studies. It is also known among restorers that paintings kept in darkness yellow significantly, although the color bleaches somewhat on reexposure to light. Oxidative radical chain reactions proceeding in darkness support the hypothesis of unsaturated ketones being the cause of yellowing [16]. Although oxidation occurs at a higher rate in light, yellowing is
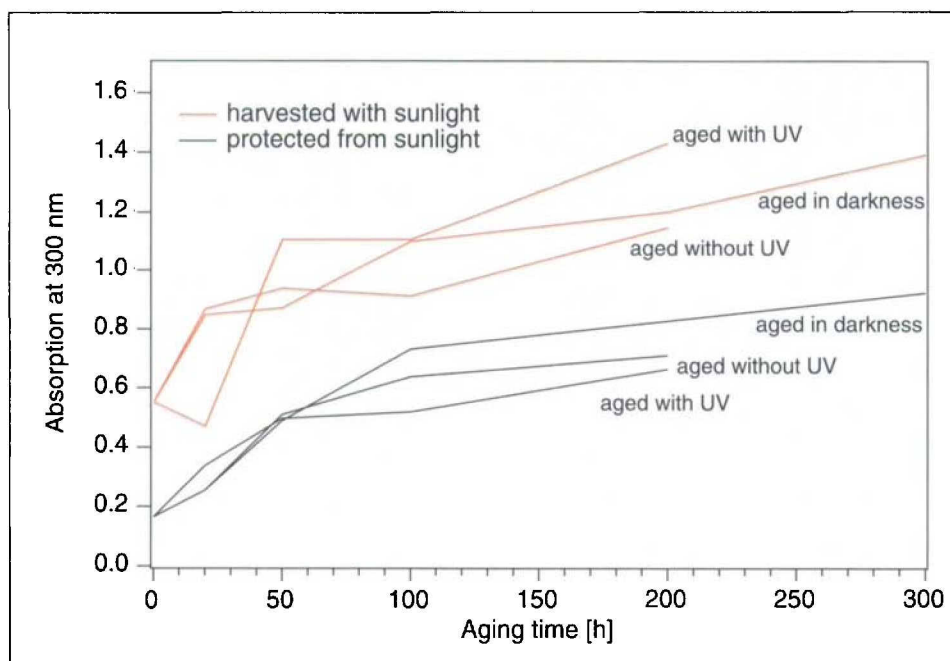
Fig. 9. Development of absorption at 300 nm during artificial aging of mastic films. The resin protected from sunlight during harvest yellowed significantly less than the exposed resin, independent of aging conditions. Even after 300 h of aging, its absorption at 300 nm is still in the range of the exposed sample after only 50 h of aging. Yellowing can be substantially reduced by protection of the resin from direct sunlight during harvest.

thought to be stronger in darkness only because the colored compounds are not simultaneously photobleached.

The great similarity of all measured parameters between light and dark aging, along with the clear influence of light exposure during harvest strongly suggests that autoxidation is a process which proceeds indefinitely after initiation. Continuous or repeated light exposure is not needed to promote it.

3.3. Naturally Aged Varnishes from Artwork

An example of a naturally aged varnish from a painting is depicted in Fig. 10. The painting was restored and its varnish replaced because of the strong yellowing. In the GALDI-MS, the same oxidation and degradation pattern is visible as in the artificially aged samples, but is even more advanced: the signals of the initial compounds and primary aging

products are smaller compared to degradation products at m/z <460, and the peak groups are less distinct than in the beginning of oxidation. This is a typical phenomenon of progressive aging since new compounds with more or less than 30 carbon atoms (thus with masses between these of triterpenoids) can be formed by continued polymerization and degradation [16].
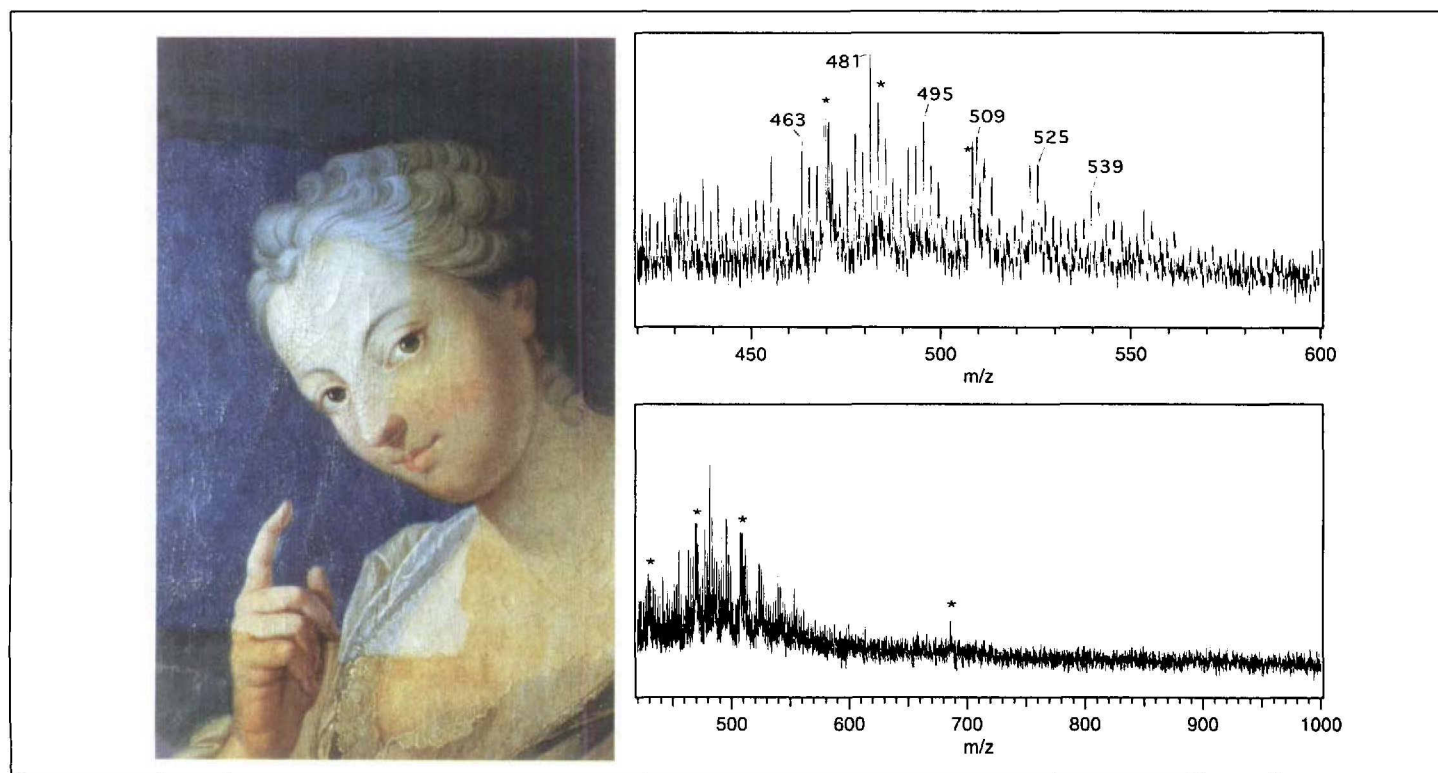

Fig. 10. Painting with partially removed varnish and its GALDI-MS. The triterpenoid (upper) and oligomeric mass ranges are shown (lower). Although oxidation and degradation are very advanced, it is still recognizable as a triterpenoid varnish, probably mastic. Signals marked with asterisks are contaminants in the spectrometer. (Portrait of a Lady, 18th century, artist unknown. © Swiss Institute for Art Research.)

4. Conclusions

Truly fresh mastic resin was collected with and without the traditional exposure to sunlight. Both these resins were found to be much less oxidized and yellowed than commercially available mastic. However, the protected samples contained far fewer radicals and were less oxidized than the exposed samples. Application as a varnish film significantly increased the rate of deterioration of all samples. The differences between samples observed at harvest persisted during artificial aging with light and/or heat. The samples protected from sunlight during harvest were in every respect more stable, including yellowing, one of the most important aspects for artwork conservation.

Radical initiation in mastic resins appears to occur during harvesting and processing. Thereafter, autoxidation can no longer be stopped, and natural mastic varnishes deteriorate relatively quickly on paintings regardless of the care taken in storing or exhibiting them. Dark and light aging of mastic varnishes are therefore essentially the same process. Samples of varnishes removed during restoration of paintings are consistent with this and with the results of artificial aging.

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