Original article

Aging and yellowing of triterpenoid resin varnishes — Influence of aging conditions and resin composition

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Abstract

The aging of natural triterpenoid resins used as varnishes on paintings is still insufficiently understood. Although progress has been made, questions concerning the aging pathways in light vs. darkness, or the correlation of oxidation with yellowing, remain open. The influence of aging conditions, primarily the amount of light, but also resin composition, on the aging process were investigated. The aging reactions are followed using a variety of mass spectrometric and spectroscopic techniques. Aging processes in dammar and mastic varnishes are shown to be more dynamic and extensive than had generally been believed. In unaged bulk resins, large quantities of radicals develop within weeks after application as a varnish, due to the greatly increased surface-to-volume ratio. This is true for all aging conditions, including aging in darkness, and is accompanied by considerable oxidation as well. After a few months, most of the initial triterpenoids are oxidized. Natural aging in light and darkness leads to the same main aging products. All these findings point to the conclusion that aging largely proceeds by the same pathways in both light and darkness, mainly autoxidation. Without light, enough radicals are formed to maintain extensive autoxidation, although more slowly. Thus, differences between light and dark aging mechanisms are much smaller than often believed. In mastic, the absence of the polymeric constituents is found to enhance oxidation, but reduce yellowing. It appears that the polymer acts as a natural radical stabilizer, favoring the pronounced intrinsic yellowing tendency of mastic. The manipulation of resin composition might lead to improved aging properties of triterpenoid resin varnishes.
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Keywords: Natural resins; Triterpenoid resins; Varnish; Aging; Mass spectrometry of resins; Electron paramagnetic resonance spectroscopy of resins

1. Research aims

The natural triterpenoid resins, dammar and mastic, have long been used as varnishes for paintings, and remain widely used today [1,2]. Their main drawback is that they deteriorate rather quickly. A major problem is the pronounced yellowing of thick layers of varnish, which can significantly change the appearance of a painting. In addition, brittle cracking degrades both the optical properties of the varnish and its protective function. Concomitant with these effects is a marked change in solubility. Old natural varnishes must usually be removed with rather polar solvents, which has significant potential to damage the painting by swelling and leaching of paint components [3–5]. Clearly, both for the long-term survival

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and an improved visual appearance of valuable works of art, it is desirable to better understand the aging behavior of these resins.

2. Introduction

Various authors have studied the aging of triterpenoid resins, with the goal of understanding and slowing their deterioration [6−15]. The main degradation pathway is autoxidation, an oxidative radical chain reaction [16,17]: after the chain is initiated by formation of a radical (step 1), oxygen from the air is inserted (step 2). The resulting peroxy radical abstracts a hydrogen atom from another molecule, leading to a hydroperoxide and a new radical that propagates the chain reaction (step 3). Recombination of two radicals terminates the chain (step 4). However, the homolytic cleavage of peroxide bonds formed in the process leads to two new radicals (branching of the chain, step 5), allowing autoxidation to proceed despite some degree of recombination. The cleavage of peroxide bonds can be induced both thermally and by light [16,17].

In pioneering work, De la Rie monitored the changes in solubility, oxidation and yellowing of dammar artificially aged by exposure to light and heat, and the influence of added stabilizers [18−20]. He found that in the presence of light, extensive oxidation proceeded by autoxidation, but yellowing was limited. Yellowing was explained as a secondary non-oxidative thermal process which takes place among autoxidation products. It was found to be particularly strong when photoaged varnishes were subsequently thermally aged [18]. Van der Doelen et al. focused mainly on the study of naturally aged dammar and mastic varnishes from paintings and followed their degradation by identification of individual oxidation products on a molecular level [21−24]. She identified differences in aging pathways under natural and artificial aging conditions. Varnishes aged in a xenon-arc weatherometer revealed extensive A-ring oxidation by a Norrish-type reaction that did not occur during natural aging [23].

Zumbühl et al. applied graphite-assisted laser desorption/ionization mass spectrometry (GALDI-MS) to the study of light-induced aging of dammar and mastic varnishes [2,25]. This new method allowed sensitive detection of a very wide variety of oxidation products, especially in the early stage of aging. It was demonstrated that aging of a single triterpene compound results in literally hundreds of oxidation and aging products, and up to seven oxygen atoms can be incorporated into a single triterpenoid molecule [26]. Additionally, it was demonstrated that oxidation also takes place in darkness, and on a relatively short timescale, within weeks and months, rather than years and decades [10,27,28].

Application of electron paramagnetic resonance spectroscopy (EPR) to the problem revealed rather large quantities of radicals in all dammar and mastic varnishes, regardless of the aging conditions to which they had been exposed [27]. The combined facts that oxidation proceeds in darkness and radicals are present under all conditions led to the conclusion that autoxidative radical chain reactions also take place in darkness

and are not dependent on continuous exposure to light. It might have been expected that without continuous light exposure, the radical termination rate (step 4 of autoxidation) exceeds the radical formation rate (steps 1 + 5) since light is supposed to be the main source of radicals (step 1). In that case, autoxidation would almost drop to zero in darkness. This study thus suggested that aging pathways in light and darkness are actually quite similar, in contrast to earlier assumptions.

The similarities and differences between the aging pathways in light and darkness are addressed in more detail in this work. New data from aging studies and an investigation of radical kinetics give deeper insight into the aging processes and dynamics. Additionally, the resin composition and its influence on aging properties is examined. The importance of composition emerged from a study of mastic harvested on the island of Chios, Greece. In this work, the resin exuding from the trees was protected from sunlight irradiation during harvest. This dark harvested mastic was shown to be devoid of a polymer fraction and, in bulk form, contains only very low amounts of radicals [29]. Photoaging of the dark harvested mastic resulted in significant oxidation, but markedly reduced yellowing. This led to the conclusion that the mastic polymer might play an important role in the pronounced yellowing predisposition of mastic.

3. Experimental part

3.1. Methodologies

Several triterpenoid resins were naturally aged in darkness, under museum conditions (low levels of light without UV at the Art Museum Zurich) and in a window (high light intensities with UV). Changes over time were monitored using a variety of analytical methods: infrared spectroscopy (FTIR), GALDI-MS, EPR, ultraviolet/visible spectroscopy (UV/VIS) and gas chromatography-mass spectrometry (GC-MS). FTIR spectroscopy was performed with a Perkin-Elmer System 2000, equipped with an i-Series IR/VIS microscope. UV/VIS measurements were performed on an Uvikon 940 spectrophotometer (a 2-beam instrument), Kontron Instruments (Watford, Herts, UK). GC-MS analysis is described in detail elsewhere [29], GALDI-MS and EPR spectroscopy in [14,27].

3.2. Materials

The influence of resin composition was studied by aging 6 different resins: dammar, commercial mastic as used by restorers, the best commercially available mastic, mastic harvested in the absence of sunlight, mastic harvested after 4 days in sunlight, and mastic without polymer.

As used by restorers, conventional mastic resin is typically many years old and extensively oxidized and yellowed [27]. "Batavia" dammar and conventional commercial mastic were obtained from Kremer Pigmente (Aichstetten, Germany). Both resins were stored in a cabinet for several years prior to use. Fresh commercial mastic (Large Tears No. 1 and No. 3) was obtained directly from the Chios Gum Mastic Growers

Association (Chios, Greece) [30]. It is only 1–2 years old, and the small surface-to-volume ratio of the large beads minimizes oxidation of the resin during storage [29]. "Best commercially available" mastic corresponds to fresh Large Tears No. 1. For polymer removal, Large Tears No. 3 were dissolved in dichloromethane and precipitated with methanol three times.

Harvesting of mastic without sunlight exposure results in suppressed radical and polymer formation [14,29]. In such samples, light-induced radical autoxidation has not been initiated, so oxidation of the resin could be expected to be slower. Mastic harvested in darkness was collected near Pyrgi during two visits on the island of Chios in September 2000 and October 2001, immediately before the start of the aging study. The branches of the trees were wrapped in aluminum foil to protect the resin from sunshine. The resin was transferred to sealed containers in the early morning or late evening to avoid any exposure to direct sunlight (see [29] for more details). Freshly harvested mastic is colorless and oxidation is minimal.

The resins were dissolved in a Shellsol T/ethanol (20 vol%) mixture. Shellsol T was obtained from Kremer Pigmente, and ethanol puriss p.a. from Fluka (Buchs, Switzerland). The solutions were sprayed on anodized aluminum plates and dried for 19 days in a room without artificial light and only a small amount of UV-free daylight prior to aging. Natural aging was carried out simultaneously in darkness (in a drawer), under museum conditions (exhibition room, Art Museum Zurich) and in daylight through window glass. Aging under daylight conditions took place in a northwest-facing window, with several hours of direct sunlight irradiation in summer. A large glass facade opposite the window reflected sunlight throughout the day.

Samples from the varnishes were taken by scraping an area of ca. 50 cm^2, which resulted in about 20 mg of sample, thus indicating that the dry varnish thickness was around 4 μm. The ca. 20 mg powder was placed in an EPR tube, and the EPR analysis carried out as soon as possible. The content of the tube was then dissolved in 5 ml of freshly distilled THF (Fluka) for UV/VIS analysis. Special care was taken to use freshly distilled THF and collect spectra without any delay after preparation of the solutions. UV/VIS spectra were normalized to a concentration of 4.0 mg/ml for direct comparison.

4. Results

The key results on the influence of conditions and resin composition on aging and yellowing of triterpenoid varnishes are presented here. The complete set of analytical data obtained from all resins in all experiments may be found in the thesis of Dietemann [14].

4.1. Oxidation

Oxidation proceeded very rapidly in all of the resins investigated, and under all aging conditions, including in darkness. This can easily be seen by GALDI-MS (Fig. 1), and also by GC-MS (Fig. 2). In GALDI-MS, analytes are desorbed
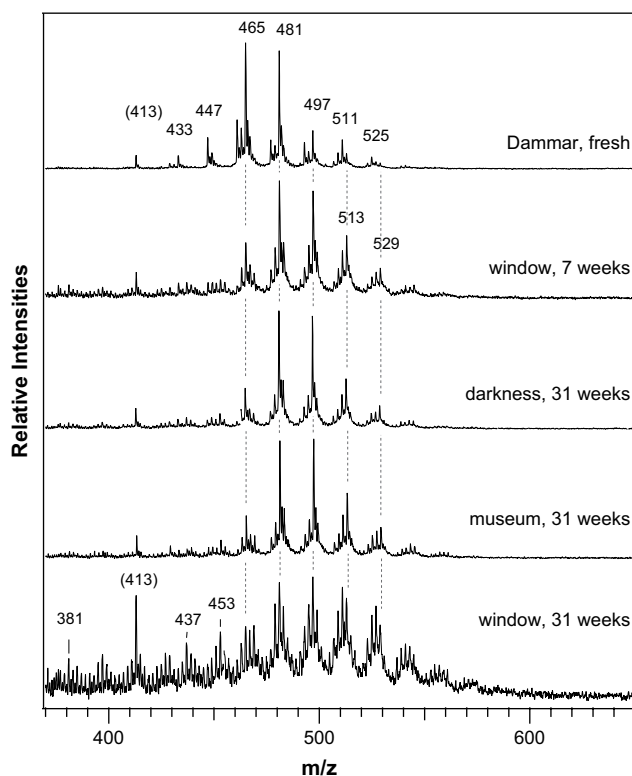

Fig. 1. GALDI mass spectra of films of dammar (triterpenoid part): fresh (upper), naturally aged for 7 weeks in a window (2nd), and aged for 31 weeks in darkness (3rd), under museum conditions (4th), and in a window (lower). Strong oxidation after a short time is revealed by mass shifts towards higher masses, while further oxidation leads to degradation products with lower masses than the initial triterpenoids. The degree of oxidation is similar after 7 weeks in intense light with UV (window) and 31 weeks in darkness or moderate amounts of light without UV (museum conditions). The similarity of the spectra suggests that aging pathways are similar in light and darkness. (The signal at m/z 413 is a contaminant in the spectrometer.)

without fragmentation and detected as sodium adducts, due to added sodium chloride. Thus, each analyte only results in one signal at an m/z value corresponding to $(M + Na)^+$ [26,27], see Table 1. Oxidation of a pure triterpenoid compound results in a wide variety of products with mass increments of 14 and 16 Da [26]. These increments are explained by incorporation of oxygen atoms (16 Da) and simultaneous loss of hydrogen atoms. Allylic oxidation of a double bond, for example, results in a mass increment of 14 Da (+O −2H). Comparison of Figs. 1 and 2 reveals that many more aging products are formed than detected and identified by GC-MS. GC may suffer from low sensitivity or insufficient resolution of some substances, or lack of volatility of polar compounds.

In Fig. 1, the degree of oxidation is similar after 7 weeks in light and 31 weeks in darkness. Furthermore, the similarity of the spectra suggests that aging pathways are similar in light and darkness. The main aging pathways as reported by Van der Doelen et al. [23] are **5 → 15**, **16**, or **8 → 17**, **19**, **14** (numbers refer to components in Table 1). It is evident that after only a few months, the main components of the resins are at least 50% oxidized. FTIR spectroscopy reveals that oxidation under museum conditions is not much more pronounced than in
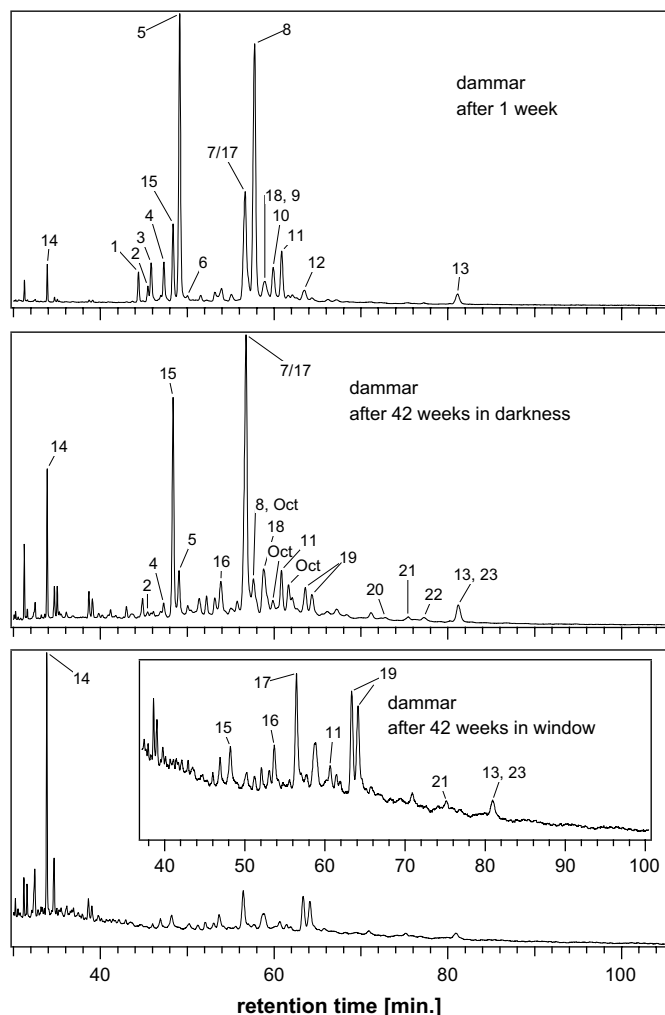
Fig. 2. Gas chromatograms of films of dammar, naturally aged for 1 (upper) and 42 weeks in darkness (middle) and in a window (lower, inset: magnification). The initial triterpenoids are oxidized to a large extent even after 42 weeks of dark aging. After 42 weeks of natural aging in a window (high light intensities), even the primary oxidation products are further decomposed (low intensities in GC). The labels refer to Table 1.

Table 1
Compounds identified in fresh and aged dammar by GC-MS. Compounds marked with * were methylated prior to analysis. The m/z values correspond to sodium adducts as detected in GALDI-MS.

Label	Compound name	MW [Da]	m/z (M + Na)+
In fresh resins (unoxidized compounds)			
1	Dammaradienone	424	447
2	nor-β-Amyrone	410	433
3	Dammaradienol	426	449
4	nor-α-Amyrone	410	433
5	Dammarenolic acid*	458	481
6	α-Amyrin	426	449
7	Oleanonic acid*	454	477
8	Hydroxydammarenone	442	465
9	Oleanonic aldehyde	438	461
10	Dammarenediol	444	467
11	Ursonic acid*	454	477
12	Ursonic aldehyde	438	461
13	Hydroxyhopanone	442	465
Oxidation products			
14	Hexakisnor-dammaran-3,20-dione	358	381
15	20,24-Epoxy-25-hydroxy-3,4-seco-4(28)-dammaren-3-oic acid*	474	497
16	3,4-Seco-2-carboxy-25,26,27-trisnor-4(28)-dammareno-24,20-lactone*	430	453
17	20,24-Epoxy-25-hydroxy-dammaran-3-one	458	481
18	20,24-Epoxy-25-hydroxy-dammaran-3-ol	460	483
19	3-Oxo-25,26,27-trisnordammarano-24,20-lactone	414	437
20	17-Hydroxy-11-oxo-nor-β-amyrone	440	463
21	11-Oxo-oleanonic acid*	468	491
22	17-Hydroxy-11-oxo-nor-α-amyrone	440	463
23	11-Oxo-ursonic acid*	468	491
Oct	ocotillone type oxidation products		

darkness (Fig. 3), confirming the GALDI-MS results in Fig. 1. This demonstrates that moderate amounts of light without UV (museum conditions) only slightly enhance the oxidation compared to that occurring in darkness. In contrast, intense direct sunlight through a window (up to 30,000 lux [14]), results in much stronger oxidation, as expected. The presence of large amounts of degradation products (m/z < 460) may be characteristic for aging under high light intensities.

The fact that the same aging products are identified by GC-MS under all aging conditions is a further indication that the aging processes in both light and darkness are basically the same, although the reaction rates may differ. This was true for all the resins tested [14]. Notable by their absence are Norrish-type aging products that develop from photolytic UV cleavage of C–C bonds in α-position to ketones. These compounds are characteristic for xenon-arc weatherometer aging, but were not reported by Van der Doelen et al. [23] in naturally aged

varnishes from paintings. They thus concluded that UV light should be excluded to accurately simulate natural aging. The present study shows that Norrish-type aging products are also absent from samples naturally aged under harsh conditions with very high light intensities including the UV component transmitted by window glass. Presumably a glass-filtered xenon-arc weatherometer generates too much light at wavelengths of 320–350 nm and thus does not simulate even harsh natural window-filtered daylight due to overproportional acceleration of UV-induced photolytic reactions. This would explain the difference in the amounts of Norrish-type products.

The Norrish reaction is an example of a *photolytic* reaction, in which a molecule dissociates directly after absorption of light. In contrast, Feller distinguishes a *photochemical* reaction as proceeding by secondary processes after excitation of a molecule by light [17, p. 47/48]. An example would be the decomposition of peroxides by a sensitized mechanism [31]: the sensitizer molecule, such as a ketone, absorbs light and transfers the energy to an acceptor, the peroxide. The peroxide would decay, but the sensitizer itself is not altered. The absence of products that are characteristic of photolytic reactions in naturally light aged samples supports the hypothesis that aging processes in both light and darkness are similar. Light can accelerate the process by increasing the
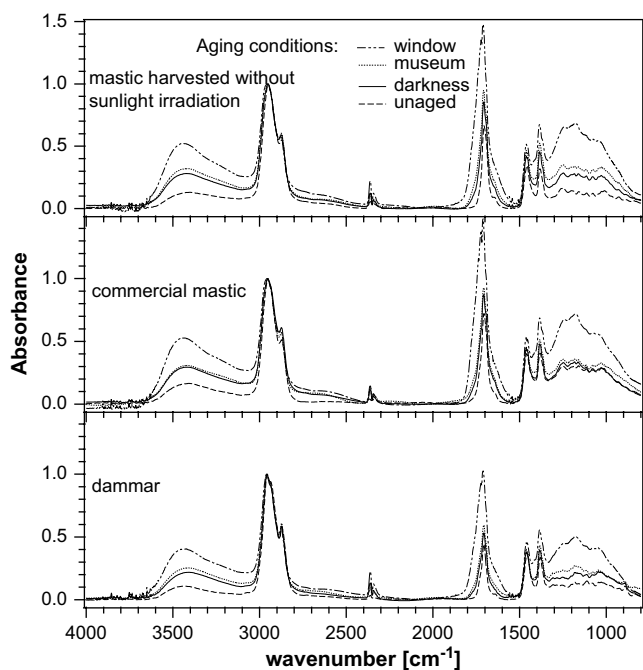
Fig. 3. FTIR spectra of mastic harvested in darkness (upper), commercial mastic (middle) and dammar (lower), unaged and aged for 42 weeks in darkness, under museum conditions and in a window. Resins aged in darkness are considerably oxidized after 42 weeks (increased absorbance at 3600–2500 cm^{-1} (OH), 1800–1600 cm^{-1} (C=O) and 1500–800 cm^{-1} (C–O)). A similar degree of oxidation can be seen in varnishes aged in darkness and in a museum, but aging in a window (high light intensities with UV) considerably enhances oxidation. Differences between the various mastic resins are rather small for a given aging condition. Spectra were normalized to an absorbance of 1.0 at the C–H stretching vibration band (2950 cm^{-1}).
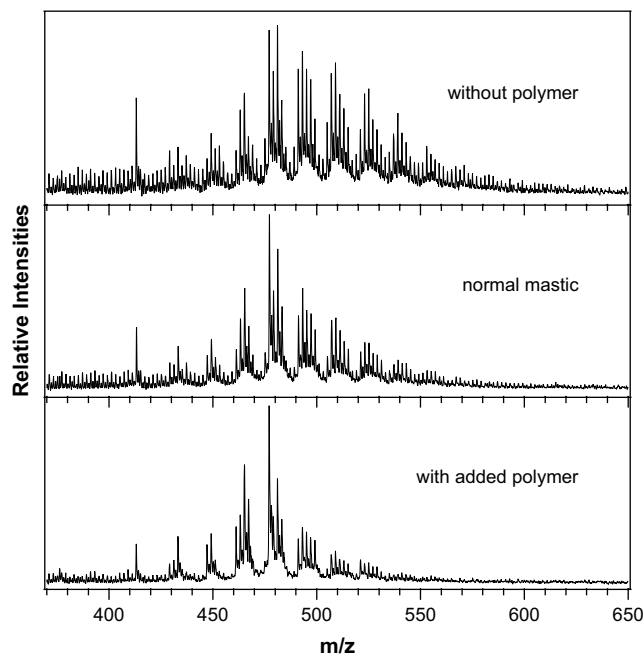

Fig. 4. GALDI mass spectra of mastic films with variable amounts of polymer, artificially photoaged for 880 h. Oxidation and decomposition are enhanced with lower amounts of polymer, suggesting that the mastic polymer retards oxidation of the triterpenoids.

4.2. Radicals in natural aging of varnishes

Extensive, rapid oxidation has a strong positive correlation with radical concentrations in natural resin varnishes, regardless of storage conditions [27,29]. This indicates that the main oxidation pathway is the autoxidative radical chain reaction, both in light and in darkness. This view is also supported by the results of the natural aging study and the kinetics of radical formation and decay (Section 4.3, see below).

Fig. 5 depicts the development of radical concentrations during natural aging. Few radicals (2–5 nmol/g) were observed in the 19-day drying period after applying the resins as varnishes. During that time, the varnishes were stored in a room with very low light levels without UV. The end of this drying period was then taken as the origin of the time axis in Fig. 5. When the films are subsequently stored in darkness, the radical content does not drop to zero, as could be expected if photochemical initiation reactions are necessary, but instead increases steadily to ca. 10 nmol/g (Fig. 5, lower). During storage in light, the radical content increases more rapidly, to ca. 15–20 nmol/g (museum conditions), or 30 nmol/g (window). These are very large values which are probably explained by the very high surface-to-volume ratio of the ca. 4 μm-thick films. Lower concentrations reported earlier, ca. 5 nmol/g of radicals in darkness and ca. 15 nmol/g in light (in a window), were obtained from thicker films of 15–25 μm [27].[1] The strong influence of the surface-to-volume ratio on

concentration of primary radicals that can also be formed thermally (see Sections 4.2 and 4.3).

The differences in oxidation of resins aged under the same conditions were rather small. Especially notable is that the initial degree of oxidation of the bulk material had little effect on aging of the film. Both, mastic with small surface-to-volume ratio (Large Tears No. 1) and mastic harvested without sunlight irradiation, were minimally oxidized at the time of varnish film preparation, but subsequently aged in a fashion similar to the lower quality materials. Thus, suppressing the beginning of the degradation chain in the bulk resin (step 1 of autoxidation) cannot slow the degradation process down once a thin film with large surface-to-volume ratio is formed. This confirms the findings of a previous study [29].

The presence or the absence of the mastic polymer fraction had a clear effect on oxidation in varnish films. When this fraction is removed, oxidation is faster and more extensive. This was apparent in the naturally aged samples, but even more pronounced in artificially aged samples described elsewhere [14]. Fig. 4 shows both enhancement of oxidation when the polymer fraction is removed from commercial mastic, and decreased oxidation when polymer is added. All three samples derive from the same mastic sample. One aliquot was used as an unaltered control while the polymer fraction of the second aliquot was removed and added to the third.

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[1] The results reported in [27] were too high by a factor of 5, due to a calibration error. The values given here are corrected.
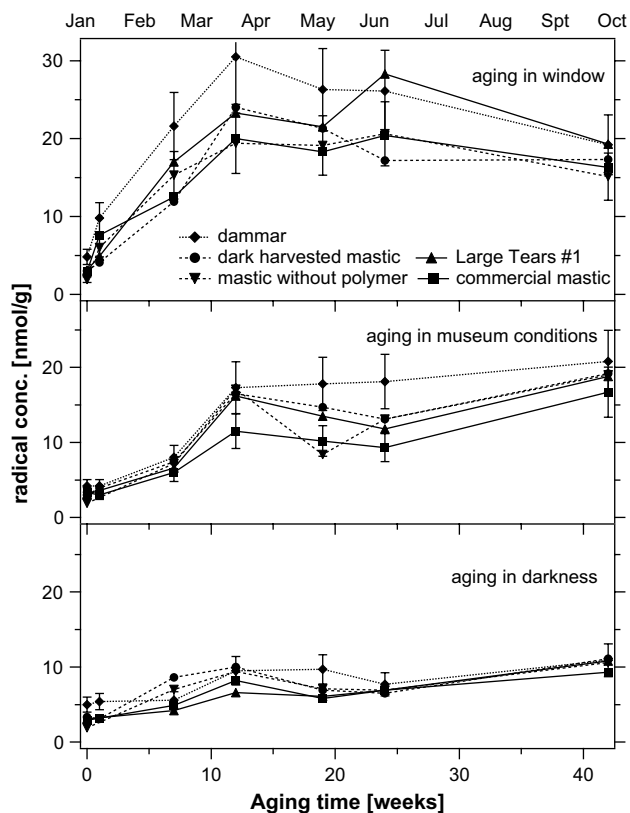
Fig. 5. Radical concentrations in naturally aged varnishes. Samples were aged in darkness (lower), under museum conditions (UV-free light of moderate intensities, middle) and in a window (high light intensities with UV, upper). The radical concentrations in the window are also influenced by the amount of sunlight, i.e. time of the year (top of graph). Error bars indicate the estimated error of 20%.

Table 2

Development of radical content [nmol/g] in films of dammar (film thickness ca. 6 μm) after a change in the illumination conditions. Films stored for 3 years in darkness were exposed to artificial indoor light (fluorescence tubes), and films of the same series, aged for 3 years in a window, were put into darkness. For each data point, a new sample of varnish was taken immediately before the measurement. The strong influence of light on radical formation in dark aged varnishes is emphasized by bold numerals.

time [hours]	Darkness –> light	Light –> darkness
0	**8.8**	20.9
1.5	**16.9**	16.4
3.5	17.3	17.3
7	15.8	14.2
24	21.6	15.3
101	24.8	17.5

day than measured in the morning and depicted in Fig. 5. Second, radical concentrations of 30 nmol/g are very high; it is possible that recombination kinetics limit the maximum concentration that can be sustained.

Differences in radical concentrations in the different resin materials are rather small, but some trends are apparent. Dammar often contains the most radicals, and mastic with polymer contains less than the corresponding resin without polymer. From this, and keeping in mind the lesser oxidation in mastic with polymer, it is very likely that the polymer functions as a radical scavenger.

4.3. Kinetics of radical formation and termination in varnishes

In Fig. 5, some of the fluctuations in radical content could be related to changes in solar irradiation due to seasonal or daily weather variations. To find out how quickly the varnishes respond to changes in illumination conditions, the kinetics of radical formation and termination were studied. It is also useful to correlate the radical kinetics with other changes in the varnishes. In general, varnishes are well known to react very sensitively to changes in illumination conditions, e.g. yellowed varnishes stored in darkness bleach after only a few hours of light exposure [7,9].

Table 2 shows the radical concentrations in thin (6 μm) films of dammar before and after a change of illumination conditions. Dammar aged in darkness reacts strongly to light; the amount of radicals almost doubles within 1.5 h of exposure. Illumination conditions were quite moderate: 270 lux artificial indoor light with 60 μW/lm in the UV. The radical content further increased over the following days, but the main increase took place within a few hours.

In contrast, the dammar films aged in a window and then put into darkness exhibited only a ca. 20% drop in radical content after 1.5 h, followed by a much slower decrease over the following days. Radical concentrations remained very high after several days.

Fig. 6 shows more detailed radical decays of resins in darkness [14]. In addition to dammar, dark harvested and commercial mastic were also studied. These samples were taken from the natural aging series after 12 weeks, and stored

radical concentration is also known from mastic beads [29]. Further, these results correlate well with the observation of De la Rie and Theodorakopoulos that photoaging degradation products are formed only in a surface layer of <8 μm [18], or 7–15 μm [15,32], respectively.

While always positively correlated, radical content and oxidation are roughly proportional only early in the aging process [27]. Although the amount of radicals in the samples aged in the museum is double as high as in the dark aged samples, the amount of oxidation judged by FTIR or MALDI-MS is only slightly higher. The amount of light in the window is 10–100-fold higher than in the museum, and the oxidation is much more progressed. Nevertheless, the radical concentrations in all the window aged samples is only less than 50% higher. For the latter, two explanations are possible. First, the amount of radicals measured could be lower than the actual values due to an artifact of the sampling procedure: samples of the window aged varnishes were scraped off the substrate in the morning hours, to minimize large fluctuations caused by recent weather conditions. Thus, all of these samples were taken after a dark period of several hours that allowed the radical concentrations to drop to some extent (see radical kinetics below, Table 2). In other words, radical concentrations in the window aged samples are probably higher during the
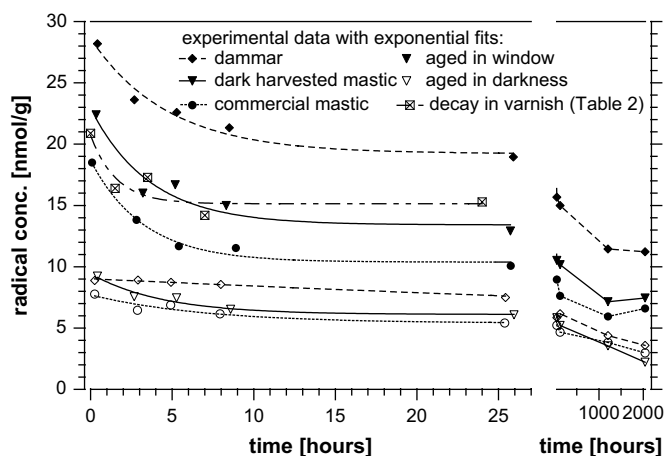
Fig. 6. Decay of radical content in pulverized dammar and mastic samples in EPR tubes. Samples were taken from varnishes aged for 12 weeks in sunlight (solid symbols) or darkness (open symbols) and subsequently stored in darkness. For comparison with the situation in an intact varnish, the data of the last column in Table 2 are also depicted. The lines are single exponential fits to the data.
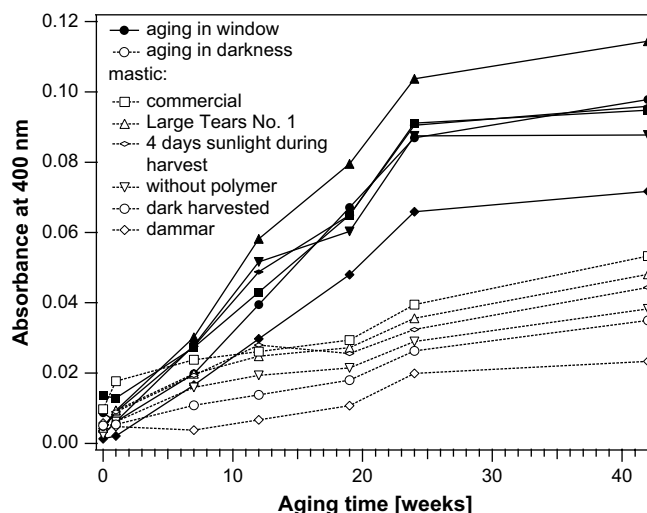

Fig. 7. UV/VIS absorbencies at 400 nm of varnishes aged for 42 weeks in a window (solid symbols) and in darkness (open symbols). Yellowing is more pronounced in light aged samples at this stage of aging. Despite stronger oxidation, the samples without mastic polymer are clearly less discolored, although differences are still relatively small after 42 weeks.

in darkness after the first EPR measurement, in the quartz EPR tubes. They were thus dark aged in pulverized form with high surface area. By contrast, the data in Table 2 were obtained from intact varnishes, from which a new sample was scraped off the substrate for each measurement. The most important result to note here is that radical decay kinetics are similar regardless of prior light exposure (although the curves obviously start from different initial values). This suggests chemical similarity of the radicals under both light and dark aging conditions. The rate of decay is high (decay constant = 3−5 h) during the first day, then slows by at least a factor of 10 over the remainder of the study period. By comparison with the data in Table 2, the pulverized samples reveal a larger initial decrease than the intact varnish, which is probably due to the increased surface area.

4.4. Yellowing

The relationship between yellowing and oxidation is somewhat complex. Varnish yellowing is most dramatic after initial light-induced oxidation and subsequent long-term dark storage [18]. This seems to show that oxidation products enhance or lead to yellowing, but that coloration often does not monotonically increase with aging because yellow compounds can be bleached by visible light. Thus, the degree of yellowing does not necessarily correlate with the degree of oxidation or age of the varnish. Over the time period of this study, yellowing and oxidation were found to be positively correlated. Continuous aging led to a monotonic increase of oxidation products and of yellowing, as seen in the mass spectra shown above (Fig. 1) and from UV absorbance measurements (Fig. 7). The more oxidized samples (aged in the window) were also the most yellow after 42 weeks. Oxidation in these varnishes is so advanced that sufficient yellowing precursors are available to compete with the simultaneous bleaching in light. For varnishes aging in

darkness, more time is clearly needed to oxidize sufficiently to become more yellow than the light aged varnishes, as should eventually occur.

More interesting are the differences between the different resin materials. Although still similar after 42 weeks, some trends appear in the varnishes aged in darkness (Fig. 7) and under museum conditions (not shown, see [14, p. 195]). As expected, dammar shows the smallest degree of yellowing. Despite stronger oxidation, the mastic samples without polymer (mastic without polymer and dark harvested mastic) are less discolored than the polymer-containing mastics. The differences in absorbance in the samples aged in the window are less distinct than for those aged in darkness and under museum conditions, but similar trends can be seen nevertheless. Large Tears No. 1 is most yellow, while mastic without polymer and dammar are less yellow, although the differences between mastic without polymer and other mastic qualities are quite small after 42 weeks of aging at very high light intensities.

5. Discussion and conclusions

Our data show that the stages in the life of a mastic varnish can be described as in Fig. 8. The four stages represent distinctly different chemical compositions, but the autoxidation process is the same throughout, regardless of storage conditions. The first significant change occurs shortly after the resin comes into contact with the air, as it is exuded by the tree. Mastic then consists of mono- and triterpenes, but contains almost no radicals and is absolutely colorless [29]. The sunlight drying process during mastic harvest results in a dramatic increase in the radical content. During drying the monoterpenes polymerize or evaporate. The radicals start autoxidation, which completely dominates all subsequent aging. During storage as resin beads, the triterpenes on the
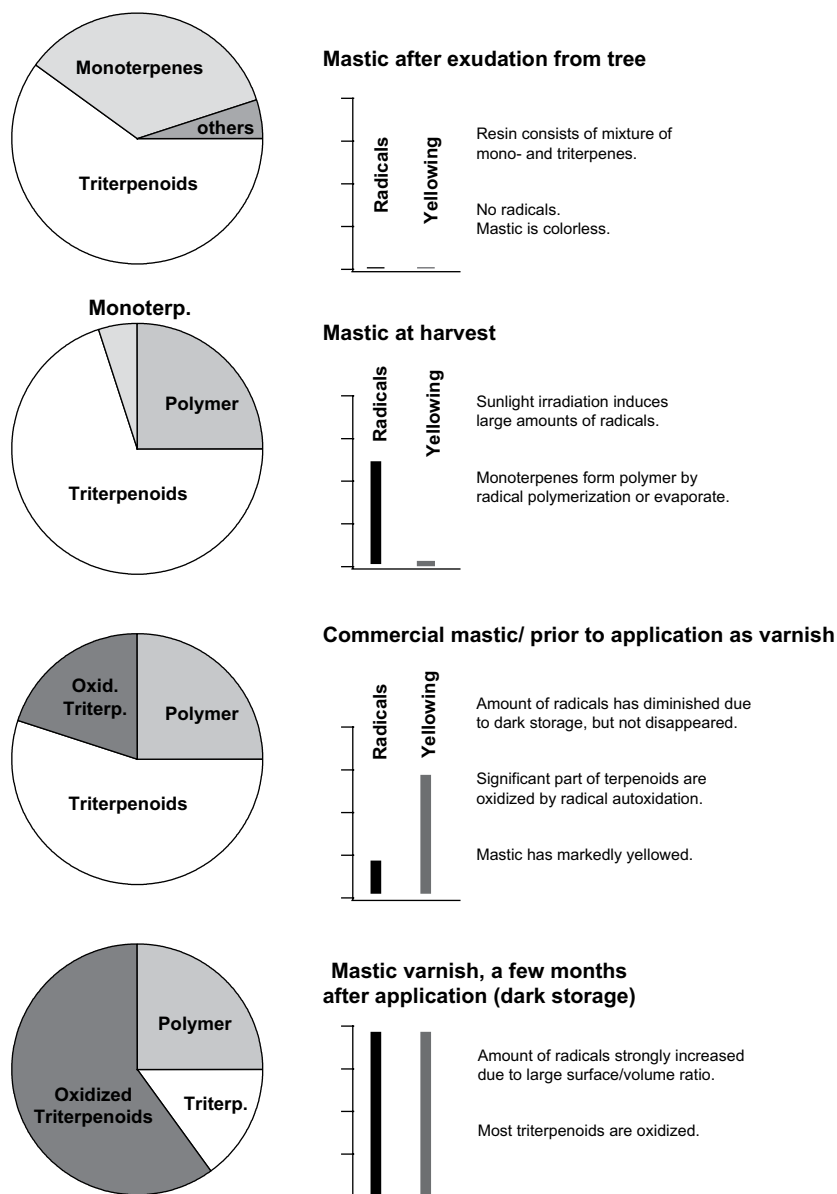
Fig. 8. Stages in the life of a mastic varnish. The ratios of components in the pie charts are rough estimations and should not be considered precise.

surface degrade quickly. The main characteristic of this stage is the degree of yellowing, which becomes extensive in darkness. After application as a varnish, the substantially increased surface-to-volume ratio results in a further large increase in radical content, and oxidation proceeds even more rapidly, regardless of storage conditions. After a few months, most of the triterpenoids are oxidized.

5.1. Influence of aging conditions

In both light and darkness, the same aging products are identified by GC-MS or GALDI-MS, and these are fully consistent with autoxidative pathways. Fast oxidation of the triterpenoids corresponds to rather large amounts of radicals under all storage conditions, and radical kinetics reveal dynamic processes. The data unambiguously lead to the conclusion that aging conditions merely alter the initiation

rate, but not the reaction pathway. Although this is not unusual (many materials age similarly in light and darkness [17,33]), it is in contrast to some conventional views of aging of these resins.

The belief that aging is fundamentally different in light and darkness may simply be a misunderstanding. Thomson stated that deterioration of a varnish is mainly a matter of photochemical oxidation because the energy for the chemical reactions is most likely to come from light [28]. De la Rie et al. drew similar conclusions, since in their studies considerably more degradation occurs in dammar during aging in light than during thermal aging [18,19]. However, the amount of photolytic reactions (like Norrish reaction) appears to be minimal, and realistical, moderate light levels enhance autoxidation only to a limited extent (Figs. 1 and 3) and mainly indirectly, presumably by homolytic cleavage of peroxides (step 5 of autoxidation) by sensitizing mechanisms

[31]. Since peroxides are readily cleaved thermally [17], the absence of light does not change the oxidative pathways in darkness, only the rate is lower. Light is clearly not necessary for autoxidative pathways in darkness (oxidation also proceeds in a previous heat aging study, see Figs. 1 and 8 in Ref. [18]). It is therefore misleading to consider the deterioration of resins as mainly photochemical oxidation, since the same processes take place without light, although at slightly lower rates. The more pronounced degradation during artificial light aging studies can be readily understood as reflective of an extremely high rate of autoxidation initiation under the extreme irradiation of those studies. It can also be stated that the museums' efforts to protect varnishes from too much light or UV is truly useful to slow down the degradation process as much as possible.

Of course Thomson's statement is correct to the extent that adding light to heat cause more chemical bonds to be broken, and more radicals to be formed. However, this does not mean that the autoxidation initiation rate drops to zero if no light is present, nor is light necessary for radical initiation in these materials. Even mastic that was strictly protected from any sunlight during its whole lifetime contains small amounts of radicals [29], and varnishes made of this material have as many radicals as non-protected resins when dark aged (Fig. 5). Obviously there are other, currently unknown, initiators, possibly atmospheric compounds such as SO_2 or NO_x. Another interesting possibility is that minor components in the resin might be involved. For example mastic has been reported to contain about 1 ppm of Mn [34], and Mn^{2+} was detected in mastic by EPR [29]. It might well act as a catalyst for radical formation, as it does when used as a drying agent in oil paints [33].

More work will be needed to elucidate the influence of such minor compounds or atmospheric pollutants on the beginning of the autoxidation chain. Once radicals are formed, formation of peroxides will take place immediately, and autoxidation is promoted further by (thermal) cleavage of peroxide bonds. Significant oxidation can then take place within few weeks, even if the varnishes and the resins prior to varnish application are strictly protected from light.

5.2. Yellowing

Yellowing of varnishes on paintings is usually more pronounced in darkness. Since oxidation was believed to be of minor importance under these conditions, De la Rie suggested that yellowing is a thermally activated, non-oxidative secondary reaction following photochemical oxidation [18]. The yellow substances proposed are unsaturated ketones, formed by aldol condensation and dehydration reactions. Ketone and hydroxy functional groups introduced by preceding autoxidation therefore enhance yellowing.

This model has been recently revised to take into account the fact that autoxidation occurs under all aging conditions [27], not only in light. Radical oxidation alternating with condensation and dehydration reactions gives a straightforward explanation for the formation of unsaturated ketones or quinones, by allylic oxidation of double bonds or by introducing hydroxy and ketone groups at suitable positions for subsequent yellowing (Fig. 9). De la Rie's model of yellowing puts emphasis on the non-oxidative character of yellowing reactions, although these *secondary* reactions are only possible after initial oxidation (*primary* reaction). In our model, however, radical oxidation, dehydration and aldol condensation are considered to be of equivalent importance. This puts more emphasis on yellowing being a *consequence* of oxidation. A differentiation between primary and secondary reactions then becomes useless, since oxidation could equally be interpreted as a secondary reaction following primary thermal reactions due to formation of double bonds that enhance autoxidation.

Despite stronger oxidation occurring in light, yellowing is usually less pronounced in light aged films than in dark aged films, very probably due to simultaneous bleaching. In relatively fresh varnishes, however, the extent of oxidation can limit yellowing, and the more strongly oxidized varnishes aged in light may be more yellow than aged in darkness (Fig. 7). In previously photoaged varnishes, enough oxygen is incorporated in the form of ketones and hydroxy moieties that the same yellow substances develop even under a nitrogen atmosphere, as in De la Rie's heat aging study [18]. Under normal
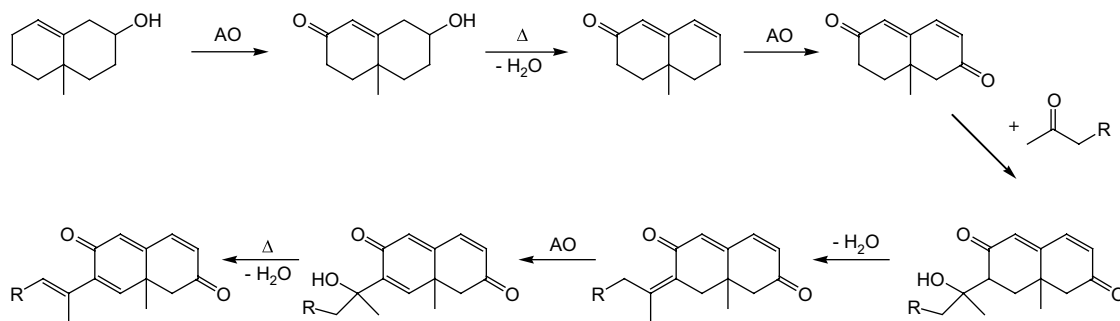

Fig. 9. Autoxidation occurring in darkness gives a straightforward explanation for yellowing. Allylic oxidation (AO) alternating with non-oxidative dehydration or condensation reactions (△) leads to large unsaturated systems causing yellowing. Autoxidative introduction of hydroxy groups followed by elimination of water can enlarge pre-existing unsaturated systems. The example shown is speculative; it is thought to demonstrate the principle of how large unsaturated systems might be formed from single ketones and double bonds.

conditions, however, autoxidation continues and enhances yellowing in both light and darkness.

It is interesting to note that bleaching of dark aged yellowed varnishes takes place on a similar time scale [7 (p. 70),9] as the increase in radical content (Table 2), that is within a few hours after change of illumination conditions. It might thus be that bleaching proceeds by disruption of delocalized chromophore systems by radical attack. Yellow compounds could also absorb visible light and destroy peroxides in their vicinity by sensitizing mechanisms [31], the resulting radicals attacking the delocalized systems.

5.3. Influence of resin composition

Mastic is known to yellow more than dammar. It might be concluded that dammar is more stable than mastic, but Figs. 5 and 6 show that dammar usually contains more radicals than mastic, and oxidation proceeds very rapidly (Figs. 1 and 2). Thus it seems reasonable that particular components of mastic are responsible for its pronounced yellowing predisposition, and not simply the disposition to radical oxidative degradation.

The possible yellowing influence of individual triterpenoid compounds, especially those with a polypodatriene structure, has been discussed elsewhere [29]. The present natural aging study did not provide new information about such compounds, but rather suggests that the mastic polymer is important in yellowing: mastic with the polymer fraction removed and mastic harvested in darkness, which also lacks polymer, contain more radicals and oxidize more quickly, but are less yellow than polymer-containing mastics. This is a new finding and counterintuitive, because one would expect a higher degree of oxidation to result in stronger yellowing under the same aging conditions. Thus, the polymer seems to enhance the pronounced yellowing predisposition of mastic, presumably by acting as a radical scavenger. Since the polymer is highly unsaturated [35], formation of delocalized chromophores by allylic oxidation is expected to rapidly lead to strong yellowing. Additional data from artificial aging studies show that pure polymer isolated from mastic yellowed strongly within a short time, while traces of triterpenoids remaining in the polymer were very resistant to oxidation (data not shown).

5.4. Outlook

Harvesting of mastic without exposure to light was not successful in reducing or limiting oxidative degradation during aging as a varnish, which shows that light is not required for radical initiation. On the other hand, removal of the polymer might be a simple and straightforward way to obtain an improved mastic varnish material, at least as far as yellowing is concerned. The associated enhanced oxidation could be compensated by other means, for example by addition of photostabilizers such as hindered amine light stabilizers (HALS). These have been shown to work well only if UV light is excluded [9,19]. It might be that the breakdown of HALS in the presence of artificial UV light is an artifact, as with the

formation of large amounts of Norrish-type aging products (see above), and that HALS are able to function in natural aging with UV. This was already indicated by Carlyle et al. [9]. However, more work has to be done to evaluate the value of such modified varnish materials for their use on real paintings, including, for example, the effect of polymer removal on the mechanical properties of the varnish.

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