

THE IMPACT OF ORGANIC ACIDS ON VARNISHES IN MUSEUM ENVIRONMENTS

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ABSTRACT

The role played by indoor environmental pollutants on the degradation of natural and synthetic resins has been investigated in the EC MEMORI project. The purpose is to understand the protection offered by exhibition and storage spaces in museum environments, investigating the effects of acetic acid and formic acid on varnishes in particular. For this purpose, mass spectrometric techniques, GC-MS, ESI-MS, MALDI-TOF, were applied together with dynamic mechanical analysis (DMA). The morphological and chemical behaviour of mastic, dammar, Laropal A81 and Regalrez1094 resins on glass and steel substrates was evaluated after exposure to different levels of volatile organic acids in the laboratory, and at sites in museums where monitoring of the level of the organic acids was performed. The effects of acetic acid have been reported in the previous PROPAINT project, but this is the first time that studies conducted with the use of formic acid are reported. The replicas were analysed periodically to verify the degradation of the varnishes occurring over one year after the acid exposure. The results revealed that organic acids had an oxidising action. The ESI-MS data highlights that both acetic and formic acids cause oxidation of natural resins, and oxidation takes place on both glass and stainless steel as substrate. By measuring and estimating the oxidation state of dammar in the model systems containing a layer of dammar and a layer of Regalrez, under exposure to acetic acid, it is also possible to observe that although the resin is oxidised by exposure to acetic acid when on glass support, no effect is observed on stainless steel substrate. Indications are that the organic acids have an oxidative and cross-linking effect, and their presence enhances the damage caused by inorganic pollutants and light. The challenge is to evaluate dose-response functions for the varnishes and lowest levels at which damage occurs.

Keywords

Natural varnishes, organic acids, museum environments, organic pollutants

1. Introduction

The study of the generic damage effects over time of the gaseous content inside enclosures on cultural heritage objects

lacks detailed research. With regards to the trapping of internally generated pollutants, the most damaging species is predicted to be the organic acids. It is well known that wood and a range of other materials used in the construction of enclosures and also the enclosed cultural heritage objects themselves can emit acetic, formic and other organic acids [1]. High and potentially damaging concentrations of the organic acids and other emissions can accumulate in the relatively small volumes of the enclosures [2], [3], [4]. For example, the binding media and varnishes of paintings can emit organic gaseous pollutants.

Organic acids may act as hydrolysing agents, modifying the molecular weight distribution of the resin components, and consequently the varnish solubility. Chemical deterioration that may be observed as a colour change, usually yellowing, of the varnish often happen together with physical deterioration that can be seen as loss of transparency, cracking, pulverising, shrinking or wrinkling [5]. Rene de la Rie (1987) states that: "The varnish problem" is perhaps the most important one in painting restoration since it is the rapid degradation of varnishes that induces most restorations."

When a painting is restored, the old varnish is commonly removed or thinned. When the restoration process is finished a new varnish is applied. Common varnishes are natural (mainly dammar and mastic) or synthetic resins dissolved into a suitable solvent. Although the painting should be relocated into the frame only when the evaporation process is complete, it can happen that this rule is not fully respected. In the PROPAINT (FP6 SSPI no 044254) project it was demonstrated that the evaporation process of the solvents used for the preparation of MS2A, a ketone resin, takes more than two years [6], [7]. If the paint is relocated into the protective enclosure, the solvent is trapped inside it, compromising the conservation not only of the varnish layer, but of the paint binders as well. The solvent can penetrate the paint layers and partially dissolve the binder. High concentrations of organic acids are often measured inside microclimate frames for paintings [2], [3], in showcases and storage rooms [8]. Damage effects of acetic acid vapour has been observed on varnishes [9]. In particular glacial acetic acid has been shown to have a strong oxidising effect on natural resins, such as dammar and mastic. Glacial acetic acid successfully destroyed the protective effect of Tinuvin 292, which was used as light stabiliser to prolong the life of a dammar resin film [10].

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Because exposure to glacial acetic acid does not represent realistic conditions in the EC MEMORI project particularly, the effect of a lower concentration of acetic acid and formic acid (1%) on varnishes was investigated.

2. Experimental

2.1 Sample

Varnish replicas natural resins mastic, dammar, and synthetic resins Laropal A81 and Regalrez 1094 were prepared on steel and glass substrates (Figure 1).

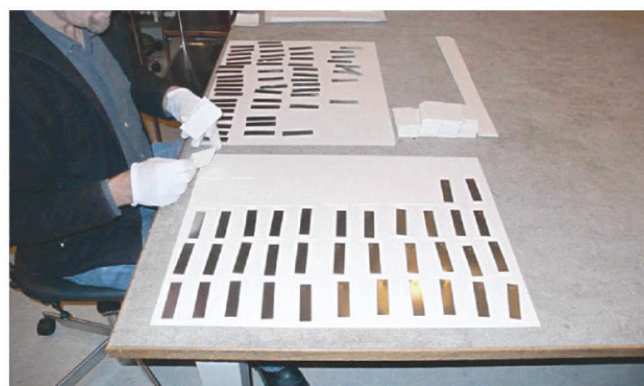
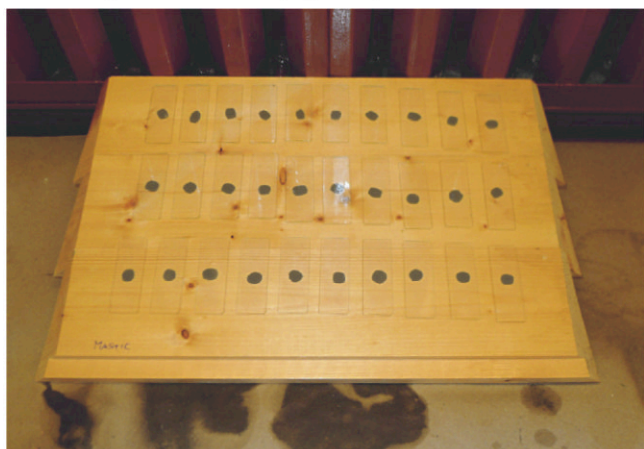


Figure 1 Varnish replicas of mastic, dammar, Laropal A81 and Regalrez 1094 prepared on steel and glass substrates.

The chemical composition of dammar and mastic used for the preparation of the model samples was in agreement with what has been reported in the literature [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [10]. A model systems containing a layer of dammar and a layer of Regalrez was investigated.

2.2 Artificial ageing

Varnish replicas were artificially aged under acetic acid and formic acid; the samples were exposed in four different closed glass vessels conditioned to RH = 75% with a saturated salt solution consisting of 150 mg NaCl (analytic grade) soaked with 30 ml 1% acetic acid (100%, analytic grade) solution, at the temperature of 23-24°C. The exposures were started at different times to obtain the same end time for all the four sets of samples / exposure times (3 days, 1,2,3,4 weeks)

2.3 Instrumentation

Gas Chromatography Mass Spectrometry (GC-MS) - 6890N GC System Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a 5975 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer equipped with a PTV injector.

Py-GC-MS Analyses were performed using a pyrolyzer Pyrojector SGE Analytical Model 5000 series Pyroprobe CDS, coupled with a gas chromatograph combined with a 6890 Mass Selective mass spectrometer 5973 single quadrupole (Agilent Technologies, Palo Alto, CA, USA).

ESI-MS (Electrospray Ionization - Mass Spectrometry). A HPLC 1200 Infinity (Agilent Technologies, Palo Alto, CA, USA) coupled to a High Resolution Jet Stream ESI-Q-ToF detector (6530 Infinity, Agilent Technologies).

MALDI-MS (Matrix-Assisted Laser Desorption/Ionization - Mass Spectrometry). All MALDI spectra were recorded on an Applied Biosystems (Framingham, MA, USA) Voyager TOF mass spectrometer equipped with a nitrogen laser (337 nm).

DMA. Dynamic Mechanical Analysis: Measurements were made in bending mode (free length of 5 mm) from 30 to 200°C with a heating rate of 3C min⁻¹ and a frequency of 1 Hz, using a Rheometric Scientific Analyser (DMA) Mark 3

2.4 Site exposure

Two sites were selected for exposure of the varnish replicas: The Conservation Department at Tate (UK) and Chesters museum (English Heritage)

3. Results and discussion

3.5 Analysis of the artificially aged samples

3.5.1 GC-MS and ESI-MS results for natural resins

GC-MS was used to evaluate the oxidation level of the natural varnishes exposed to acetic acid[10]. To understand the oxidation, compounds identified in each resin they were grouped according to their structure. Dammar oxidation compounds were divided into: dammarane, oleanane and ursane type compounds. Mastic oxidation compounds were divided into dammarane, oleanane, masticadienoic and isomasticadienoic type compounds. The relative amount of each compound in each subset of compounds was multiplied with a calculated oxidation state, based on the number of oxygen and unsaturations, and subsequently normalized for the sum of the relative content of the compounds of each subset. The higher the oxidation the higher the number obtained. The results show oxidation for dammar, both on glass and steel under exposure to acetic acid, while dammar with Regalrez does not really show any oxidation. Mastic shows a relative increase of the oxidation level of isomasticadienoic type compounds under exposure to acetic acid. As far as exposure under formic acid is concerned, oxidation is more clearly observed for dammar with Regalrez on both glass and steel, as well as mastic on glass, while dammar on both substrates and mastic on steel appear less affected. Figure 2 shows the data obtained for ursane type compounds of dammar resin, dammarane compounds of dammar with Regalrez 1904 replicas and isomasticadienonic type for mastic resin, from ageing with acetic acid.

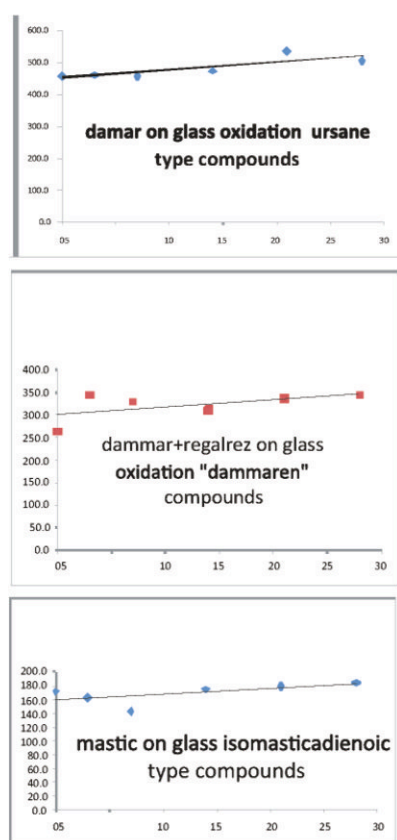


Figure 2 Oxidation of the model varnishes (dammar, mastic and dammar with Regalrez) under exposure to acetic acid.

To better interpret the oxidation of these resins under exposure to organic acids, ESI – MS analyses have been performed.

Oxidation of dammar resin under exposure to acetic acid is present with both substrates. Moreover dammar on glass seems less oxidised than dammar on steel, both unaged and aged, suggesting that steel catalyses oxidation. Mastic is also oxidised by acetic acid, and both model systems on glass and steel show an oxidised profile with respect to the raw resin. Dammar with Regalrez seems much more stable to ageing and the mass spectra are extremely similar to that of the unaged raw dammar. Oxidation is clearly observed by the increase of the relative abundance of m/z higher than 500, ascribable to highly oxidised compounds. Figure 3 shows an example of ESI-MS spectra in which model samples of dammar on steel exposure to acetic acid for 0 and 28 days are compared.

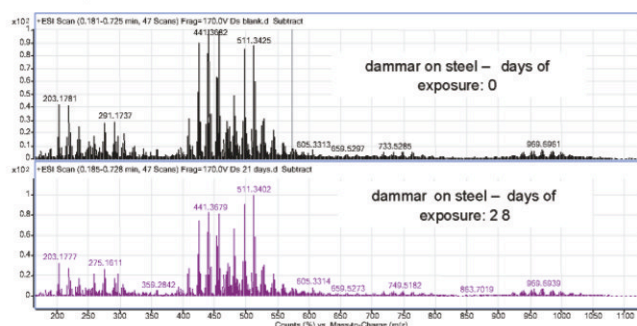


Figure 3 ESI-MS spectra of model samples of dammar on steel under exposure to acetic acid.

Under exposure to formic acid both dammar and dammar with Regalrez are oxidised, while nothing is really clearly observed for mastic resin. The high molecular weight fractions of the resins, both dammar and mastic, do not seem to show any significant trend or behaviour under exposure to the organic acids.

3.5.2 MALDI-TOF, DMA and micro-thermal analysis results for natural resins

The oxidising power of both acetic and formic acid is also confirmed by MALDI –TOF[10]. Spectra are shown in Figure 4 Dammar, solid state, aged 2 months glacial acetic acid (upper) and 98% formic (lower), M-matrix peaks. In the lower spectrum the region between 700-900 m/z is more pronounced. 4 for dammar aged 2 months in glass vessels containing glacial acetic acid and 98% formic acid.

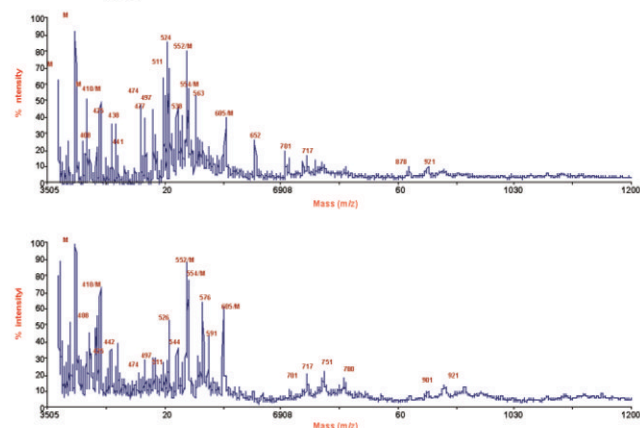


Figure 4 Dammar, solid state, aged 2 months glacial acetic acid (upper) and 98% formic (lower), M-matrix peaks. In the lower spectrum the region between 700-900 m/z is more pronounced.

Despite the fact that oxidation is less clearly observed in mastic resin, crosslinking is clearly taking place under artificial ageing. Physico chemical techniques were also used to understand changes in the physical properties of the resins under exposure to the organic acids. Figure 5 shows the tan delta values plotted against temperature for resin mastic samples (control and 4 weeks). As for dammar varnish there is a shift to higher temperatures of the onset of resin mastic softening and this is accompanied by a change in the shape of the tan delta curve. This indicates an increase in the glass transition temperature (T_g) of the resin mastic.

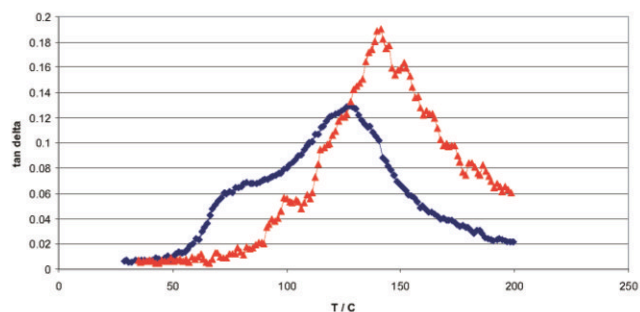


Figure 5 Effect of acetic acid on resin mastic: Control (dark blue) and 4 weeks (red). Shift of peak to higher values indicates higher value of T_g (glass transition temperature).

Additional micro-thermal analysis of the varnishes, reported elsewhere (MEMORI deliverable), showed that the T_g of the surface of the dammar was already high in the region of 100°C even before dammar exposure to acetic acid.

3.5.3 GC-MS and ESI-MS results for synthetic resins

During the aging in acetic and formic acids the multi-analytical procedures based on mass spectrometry [10] (GC/MS, Py-GC/MS) do not reveal changes of the chemical structures of the Regalrez 1094 [27], [28], [29], [30], [31] and Laropal A81 [32], [33], [34]. Figure 6 shows the chromatograms obtained by GC/MS of the extracted fraction of Regalrez 1094 at t₀ and after four weeks in acidic environment.

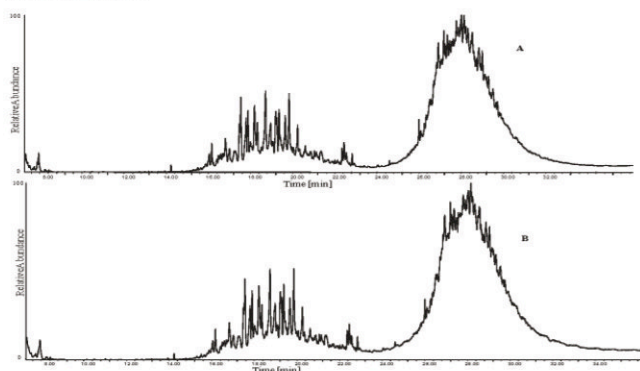


Figure 6: Comparison between the t₀ chromatogram of extracted fraction of Regalrez 1094 on steel (A) and the chromatogram of extracted fraction of Regalrez 1094 on steel after four weeks on aging in acetic acid (B).

The chromatograms of Regalrez 1094 obtained by Py-GC/MS confirms the GC/MS results. The chemical structures of the polymer and the products of analytical pyrolysis during the aging in acetic acid and formic acid are the same as the raw material. In particular, during the monitoring of the aging in the polymer there aren't oxidation products. Furthermore, there aren't differences between the Py-GC/MS profile of the polymer on steel and on glass.

3.5.4 DMA results for synthetic resins

Dynamic Mechanical Analysis (DMA) was used to measure the viscoelastic properties of the varnish coatings on steel in terms of the glass transition (T_g) and viscoelasticity of varnish films.

For Regalrez 1094 the effect of acetic acid on onset temperature is insignificant but there are changes in the shape of the tan delta peaks (of the glass transition (T_g) and viscoelasticity of varnish films). Figure 7 shows tan delta peaks for the control, 3 days exposed, 1 week and 3 weeks replicas.

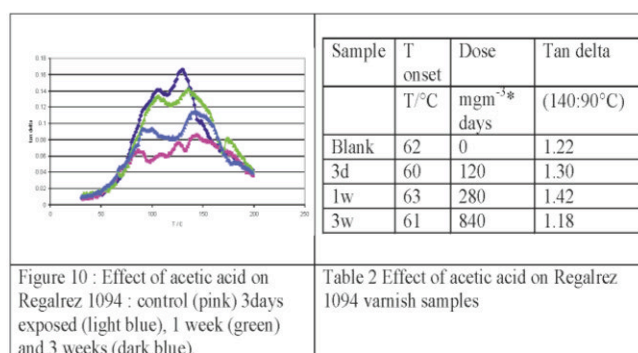


Figure 10 : Effect of acetic acid on Regalrez 1094 : control (pink) 3days exposed (light blue), 1 week (green) and 3 weeks (dark blue).

Table 2 Effect of acetic acid on Regalrez 1094 varnish samples

Figure 7 Effect of acetic acid on Regalrez 1094: control (pink) 3 days exposed (light blue) 1 week (green) and 3 weeks (dark blue).

Change is most pronounced after 3 week exposure as there is a shift to lower temperatures of the main peak. The 3 week aged sample shows a decrease and this is more pronounced in the 4 week exposed sample where the value of the tan delta ratio falls to about 0.5. This may be due to plasticisation of the sample as ageing was performed at 75% RH or some processes occurring leading to formation of lower molecular weight material. In the case of formic acid a similar effect occurs except there is a shift in onset temperature and shape change in tan delta occurs already after 2 weeks.

For Laropal A81 ageing with acetic acid change of the tan delta curves occurs after 3 weeks exposure. With formic acid there is already a change in the 2 week aged sample. So formic acid is slightly more damaging to Laropal A81 than acetic acid.

3.6 Analysis of model system exposed in museum locations

The molecular analysis of natural resins under exposure on site gave similar results as those obtained from physical techniques: That is, changes observed are higher than those observed for artificial ageing under organic acids only. As an example the ESI-MS spectra obtained for the natural resins exposed at Tate and Chesters are shown in Figure 8 and Figure 9.

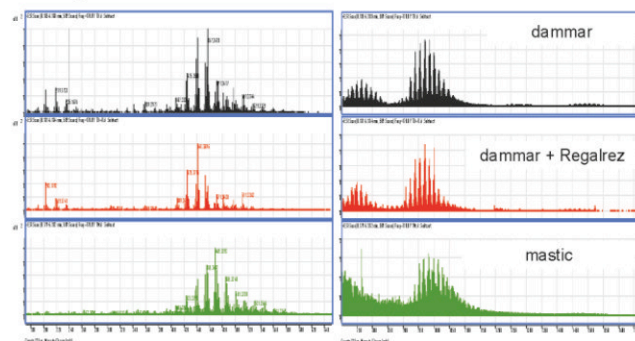


Figure 8. ESI-MS spectra of model varnishes on steel exposed in mc-frame in Conservation Dept., Tate.

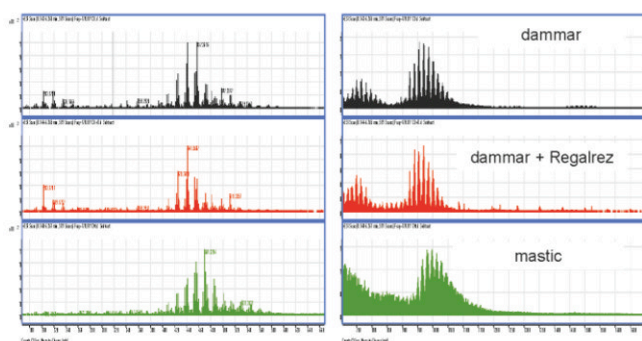


Figure 9 ESI-MS spectra of model varnishes on steel exposed at Chesters museum.

In both cases dammar under the layer of Regalrez is less oxidised than dammar alone.

The mass spectrometric analysis of synthetic resins showed chromatographic profiles in accordance to those obtained for the model systems, but, as already highlighted previously, physical changes can take place in these varnishes that cannot be observed by the mass spectrometric techniques.

4. Conclusion

The results revealed that the organic acids have an oxidative and cross-linking effect, and their presence enhances the damage caused by inorganic pollutants and light.

Organic acids cause degradation of natural resins, although the degradation effect is better observed when the resin is still quite new. In general an oxidizing power of both acetic and formic acid is observed in almost all cases. In particular oxidation is observed also when the support is glass, and not only steel, indicating that the oxidative power of the organic acids is not metal related. In addition to oxidation, data probably indicate that the acids favour also cross-linking. By estimating the oxidation state of dammar in the model systems containing a layer of dammar and a layer of Regalrez, it was observed that the use of the synthetic resin on top of a natural varnish has a protective effect as it slowed down the oxidation of the natural resin when exposed both to artificial and natural ageing. Synthetic resins are definitely much more resistant to degradation from organic acids.

Notwithstanding this, the investigation of the physical surface properties of the synthetic varnishes revealed an effect of exposure to organic acids: in particular, Regalrez 1094 was more stable than Laropal A81.

5. References

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