
Annex B. Monitoring the effects of traditional 19th-century additives on the chemical drying of oil paint by Mass Spectrometry

Introduction

Many 19th-century paintings are showing physical evidence for failure of the painting materials. Oil paints in that period were prepared by independent colormen and artists would modify these paint formulations according to their own ideas. This implied the addition of terpenoids as balsams, resins or turpentine, plant or animal derived waxes, various geo-materials such as asphalt, bitumen or coal tar, and prepolymerised plant oils. As these materials tended to retard drying of the paint, copious amounts of drying agent were introduced as well.

Results and Discussion

Apart from developing analytical strategies to trace these various materials in the paintings, we have developed a test system based on the oxidation and cross-linking of linseed oil, a common ingredient of oil paint. The oil is dissolved in dichloromethane and exposed to moderate light conditions for an extended period of time. The dichloromethane act as solvent and free radical producing agent. Additives such as Copaiba balsam, mastic and dammar resin, and asphalt are dissolved in the DCM-oil solutions to investigate how they interfere with the oxidation and cross-linking processes of the oil. Changes in the molecular weight distribution are analysed with Size Exclusion Chromatography (RI and UV detection). Direct Temperature resolved Mass Spectrometry (DTMS) is applied to determine the chemical changes in the triglycerides of the oil due to oxygenation and to trace the formation of condensates. More detailed HRMS and HRMSMS research of the triglycerides, oxygenated triglycerides, their dimers and trimers in the exposed oils is performed with ESI-FTMS using a modified 7T Bruker Apex system.

Light exposure of the native oil in the test system leads to formation of oxidised triglycerides and high molecular weight cross-linked fractions enriched in saturated and monounsaturated fatty acids. The latter not unlike what is observed in prepolymerised oils such as stand oil (cross-linked under limitation of oxygen). Introduction of the additives changes the rate of chemical change in the oil. 12 weeks of light exposure show the following. Asphalt is a very potent inhibitor of oxidation and cross-linking in the oil. No chemical change in the oil nor the asphalt is evident after 8 weeks. ESI-FTMS shows incorporation of oxygen in oil triglycerides after 8 weeks. DTMS of the oils after 12 weeks points to formation of cross-linked triglycerides. However the data after 8 weeks point out that the oxidised terpenoids

are acting as accelerators of oil oxidation. Copaiba balsam being the strongest accelerator leads to almost complete consumption of the unsaturated C18 fatty acid moieties.

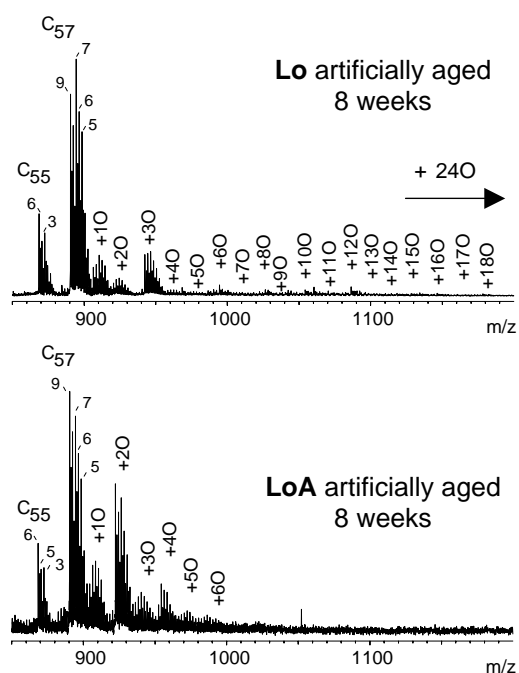


Fig. 1. Partial ESI-FTMS showing autoxidation (i.e. photo-oxidation) of linseed oil artificially aged for 8 weeks as such (incorporation of up to 24 atoms of O) and in the presence of asphalt (only 6 fold oxygenation).