
Appendix to chapter 2

Abstract

A dammar precipitate is usually formed when preparing a solution of dammar varnish. GCMS, DTMS and SEC analysis demonstrated that this precipitate consists of relatively polar, acidic material together with a fraction of dimerised or highly oxidised triterpenoid material.

1. Analysis of the precipitated fraction in fresh dammar varnish

Dammar varnishes are usually prepared by dissolving dammar in turpentine or white spirit. It is well known among painting conservators that dammar solutions can get cloudy and that precipitates can occur. The reason for this phenomenon is not exactly known. The water content of the resin or the presence of the dammar polymer ('dammar wax') is sometimes believed to be responsible [1]. There are a number of approaches in which painting conservators deal with these precipitates. Their measures range from a rejection of the whole varnish to filtering or dissolving the precipitates or shaking them up.

Wenders has studied these dammar precipitates [2]. She found that dammar films, which contain the precipitate, show more yellowing and cracking after artificial ageing compared to dammar films in which the precipitate was filtered out. It was also observed, that older dammar resins produced more precipitate. For this reason, it is recommended in conservation practice to use fresh dammar resin and to filter out the precipitate.

In collaboration with Wenders, various dammar precipitates were analysed and compared to fresh dammar resin in order to determine the chemical

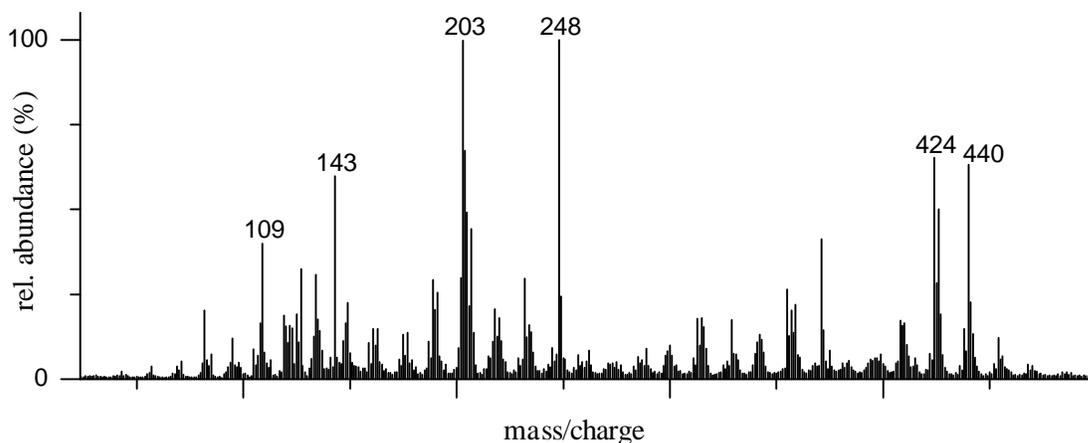


Figure 1 *EI(16 eV)-DTMS summation spectrum of the dammar precipitate formed after dissolution in white spirit.*

composition. The analytical results of the various dammar precipitates were found to be very similar. This thesis discusses the analytical results of one dammar precipitate. We refer to the thesis of Wenders for a discussion of the analytical results of precipitates from a variety of sources of dammar resin using a number of different solvents [2]. Both DTMS (16 eV) and GCMS show that there were only some small differences between the dammar resin and the dammar precipitate. As shown by DTMS (Figure 1), the precipitate contains a relatively large fraction of constituents with acidic groups, compared to the fresh resins (Chapter 2, Figure 11). The base peak at m/z 248 indicates the presence of a relatively large amount of ursonic/oleanonic acid. A relatively large amount of ocotillone type molecules is also present, as indicated by the peak at m/z 143.

Molecular weight information was obtained with Size Exclusion Chromatography (SEC). The particles of the SEC column packing have different size pores and pore networks, so that the analyte molecules are retained or excluded on the basis of their hydrodynamic molecular volume, which is a combination of their size and shape [3]. The precipitate was found to be soluble in tetrahydrofuran (THF). Figure 2 shows the SEC traces of fresh dammar resin (a) and of the dammar precipitate (b), using a UV detector at 240 nm and THF as the mobile phase. Fresh dammar resin mainly contains triterpenoid molecules with masses of approximately 400 to 500 dalton. The peak around 200 dalton is likely to be due to sesquiterpenoids. A broad hump at approximately 10,000 dalton points to the presence of the dammar polymer, polycadinene. In addition, a small peak is present at approximately 900 dalton, which may be caused by the presence of dimerised triterpenoids. However, the presence of dimerised triterpenoids could not be confirmed when studied by a number of mass spectrometric techniques (see

page 71 of section 3.5.). It is possible that the peak at 900 Da represents strongly oxidised triterpenoids, which are relatively polar compounds with a lower molecular weight than 900 Da. These compounds will have more affinity for the polar eluent THF than the less polar triterpenoids, represented by a peak at 400/500 Da. This will result in a peak at a relatively shorter retention time, i.e. a peak at higher molecular weight. Compared to fresh resin, the precipitates contain a higher proportion of dimeric or highly oxidised and possibly trimeric triterpenoids, in addition to a triterpenoid fraction. Furthermore, the SEC results also indicate that the precipitate does not consist of polycadinene.

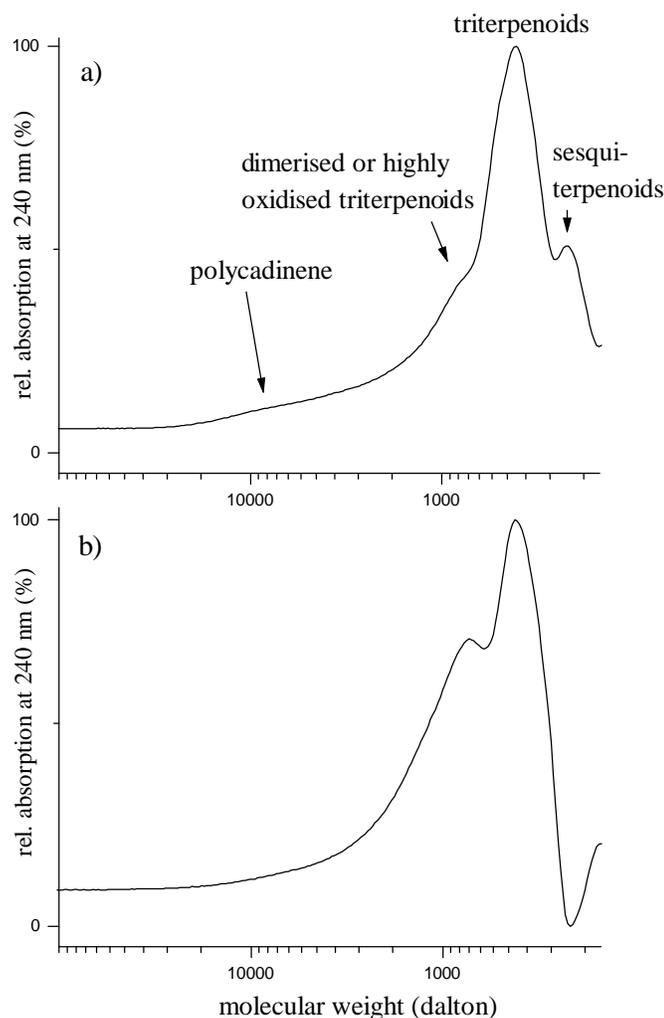


Figure 2 SEC traces at 240 nm of fresh dammar resin (a) and of the dammar precipitate formed after dissolution in white spirit (b).

2. *Conclusions*

According to the resin sampled it is likely that the precipitate that is often encountered by painting restorers when preparing a solution of dammar varnish consist of relatively polar, acidic material together with a fraction of dimeric or highly oxidised triterpenoid material. Contrary to what was believed, in our samples at least, the precipitate does not contain polycadinene.

3. *Experimental*

For the preparation of the dammar precipitate, one part dammar was put inside a filter in five parts of white spirit (Siedegrenzbenzin, Sb 140-200 °C, Kremer Pigmente). After 24 hours a nearly clear, yellowish solution was formed. The filter was taken out, because there were no residues present. The following days, precipitates started to be formed, which were filtered after 8 weeks [2]. GCMS, DTMS and SEC experiments were carried out as described in Chapter 3.

References

- 1 Gettens, R. J., and Stout, G. L., *Painting materials: a short encyclopaedia*, Dover Publications, Inc., New York (1966).
- 2 Wenders, E., *Dammar als Gemäldefirnis - Untersuchungen zu Löslichkeit, Glanz und Oberflächenrauhei.*, Diplomarbeit, Staatliche Akademie der Bildenden Künste Stuttgart (1998).
- 3 Willard, H. H., Merritt, L. L., Dean, J. A., and Settle, F. A., *Instrumental methods of analysis*, Wadworth Publishing Company, Belmont, Ca (1988).