Technical Papers

Dammar and Mastic Infrared Analysis

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Recent interest in the identification of natural resins used in the fine arts chiefly concerns the application of paper chromatography (*1*). The use of infrared spectroscopy for this purpose has not been extensively treated. Hanson (*2*) recently reported spectra for dammar and East India Pale, in conjunction with the analysis of mediums once used by J. M. W. Turner. Elizabeth Jones (*3*) at the Fogg Museum, Harvard University, used infrared analysis to study the softening of aged films under the action of solvents, although spectra were not reported. This paper discusses the identification, by infrared spectroscopy, of dammar and mastic, resins of considerable interest in the study of paintings in oil.

Absorption of dammar and mastic was measured in films cast from resins dissolved in chloroform (Fig. 1). The curve for dammar is similar to that reported by Hanson. The curve for mastic is practically identical, except for lack of absorption at 890 cm^{-1}. This band, apparently the same as that reported at 897 cm^{-1} by Hanson, is perhaps the most significant difference between the absorption of these two resins, which are the most commonly used for the final picture varnish. The absorption at 760 and 1220 cm^{-1} is attributed to chloroform. The presence of residual solvent is not expected to alter the spectra. Samples dried overnight under high vacuum were compared with samples dried at room conditions for 10 min. No alteration in the spectra of the resins was noticed, although the adsorption of chloroform at 760 cm^{-1} decreased from 100 to 65 percent.

The curves of good and poor grades of mastic and dammar, the poor grades being more intensely colored, were practically identical. Samples of recently purchased Batavia and Singapore dammar were practically the same, as was a sample of Batavia dammar that had been in stock for about 35 yr. These similarities are not entirely unexpected since the two resins contain mixtures of several components representing much the same class, that is, resinols, resin acids, essential oils. This situation makes it much more difficult to obtain a "characteristic" spectrogram. Their remarkable similarity is emphasized by the fact that the spectrum of sandarac and that reported for East India Pale are readily distinguishable. The resins are also more similar in physical properties than is generally assumed (*4*). Mills and Werner have likewise reported similarities in the chromatograms.

The work of Jones demonstrated that the decreased ease of solubility of dammar and mastic, noticed upon aging, is in part due to a physical change rather than, for example, to the formation of crosslinked bonds. However, some oxidation probably does take place with age, accompanying the well-known discoloration of these resins. In experiments in this laboratory a gain in weight was indeed detected. To determine to what extent these changes are detected by infrared analysis, spectra were taken of samples exposed for 200 hr in a Fade-O-Meter (National Accelerated Fading Unit, Type XV). Samples on window glass were air-dried several weeks. Several were baked for 3 days at 70°C to drive off most of the solvent before exposure. No essential difference in the behavior of the two types of samples was noticed. The samples attained a temperature of about 55°C in the Fade-O-Meter. Comparative tests at this temperature indicated that serious deterioration was largely dependent on the ultraviolet radiation rather than upon temperature alone.

Scrapings of the badly cracked and discolored resins were cast from chloroform solution as before. Despite severe physical deterioration, the spectra of the exposed samples were quite similar to the unexposed. For both resins, however, there occurred loss in detail between 800 and 1200 cm^{-1}. This would tend to indi-

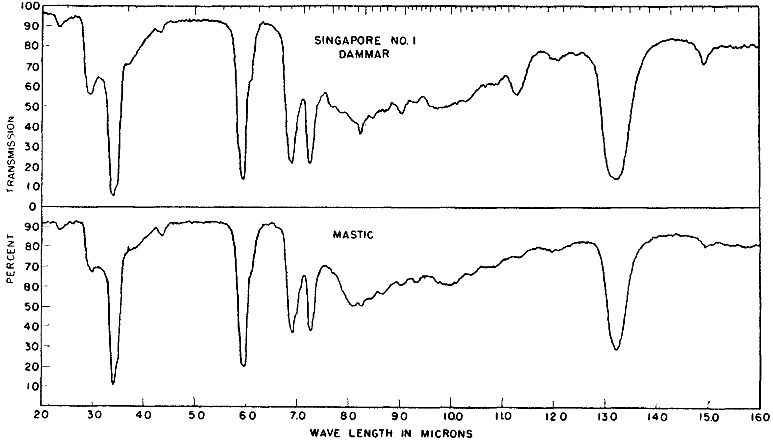

Fig. 1. Transmission as a function of wave number or wavelength.

cate a greater mixture of absorbing components in the aged material. In mastic, the methyl band at 1375 cm^{-1} is less intense than the methylene band at 1450; in the aged resin the intensities were reversed. This finding may be explained in two ways. If the intensity of absorption per methyl or methylene group remained constant, then there may have been an increase in the relative number of methyl groups (as by chain termination) or a decrease in the relative number of methylene groups (as by oxidation). Alternatively, the intensity per group might alter, implying a change in molecular environment in the immediate vicinity. No matter which effect may be at work, a chemical change is reflected. However, because carbonyl and carboxyl groups are present in relatively large amounts in the initial resins, marked change and ready analysis are not immediately forthcoming. Considering the relatively slight change in spectra after severe deterioration, the consistency in the spectra of very old samples and "poor" grades is not surprising.

Infrared analysis is known not to be sensitive in the analysis of trace materials and is not particularly adapted to the study of extensive mixtures. In the examination of materials used in the fine arts, these factors will limit the effectiveness of the method. The great similarity of the spectra of dammar and mastic, an important pair, draws special attention to the problem.

References and Notes

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1. J. S. Mills and A. E. A. Werner, *Nature* **169**, 1064 (1952); *J. Oil & Colour Chemists' Assoc.* **37**, 131 (1954); K. Macek and M. Hamsík, *Umĕni* (*Prague*) **2**, 58 (1954) and *Chem. Abstr.* **48**, 7315 (1954).
2. N. W. Hanson, *Off. Dig. Federation of Paint & Varnish Production Clubs*, No. 338 (1953), p. 163.
3. Anon., *Better Analysis*, No. 2 (Baird Associates Inc., Cambridge, Mass., 1950), p. 9.
4. R. L. Feller, *Museum News* **29**, No. 20, 7 (1952).

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Antiperoxidative Action of the Cobaltous Ion and Its Consequences for Plant Growth

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The cobaltous ion is known to cause dramatic increases in the rate of growth of several plant tissues that have in common a marked sensitivity to red light (*1, 2*). Co^{++} is also known to protect brain tissue against damage caused by high levels of oxygen (*3*) and mice against x-irradiation damage (*4*). The two injurious effects on animals are believed to involve the formation of free radicals and peroxides (*5*), Co^{++} apparently affording protection by negating the effects of these substances. We believe that the action of Co^{++} on plant growth is explicable in similar terms.

We have previously shown (*6*) that Mn^{++} increases the apparent rate of peroxide genesis in etiolated pea tissues, leading to increased peroxidative destruction of the plant growth hormone indoleacetic acid (IAA) by the IAA-oxidase system (*7*), and thus to a decreased growth rate. The Co^{++} ion, however, works in the reverse direction, decreasing peroxigenesis, thus sparing IAA and increasing growth.

The root systems of 3-day-old Alaska pea seedlings were utilized in these experiments (*8*), and peroxide genesis was measured by two independent methods. The former is based on the peroxidative conversion of pyrogallol to purpurogallin (*6*), and the latter is based on the peroxidative destruction of IAA (*7*). Since both tests are performed in the absence of exogenous H_2O_2, the amount of endogenously produced peroxide can be deduced from the amount of peroxidation accomplished.

The data of Fig. 1 show that $10^{-4}M$ Co^{++} (supplied as $CoCl_2 \cdot 6H_2O$) decreases the rate of IAA destruction by about 20 percent, while $3 \times 10^{-5}M$ Mn^{++} (also supplied as the chloride) increases IAA destruction by about the same percentage. Similar data may be obtained with pyrogallol as the substrate and have been interpreted as meaning that Mn^{++} raises and Co^{++} depresses the effective peroxide level of the cell.

The toxic effect of 100-percent oxygen and its negation by Co^{++} may also be shown with pea roots. Excised roots were incubated either in $2 \times 10^{-4}M$ IAA buffered at *p*H 6.1 or in $0.005M$ pyrogallol buffered at *p*H 4.5. With each substrate, various Co^{++} and Mn^{++} concentrations were introduced. The vessels were shaken at 30°C in a stream of pure oxygen. The data, shown in Table 1, demonstrate clearly that Mn^{++} enhances and Co^{++} depresses peroxigenesis, as measured by the oxidation of either substrate.

Control roots that had been exposed to pure oxygen for 5 hr were greatly injured, as was shown by their failure to float on the medium, their yellow color, their extreme transparency, their jellylike consistency (Fig. 2), and the extreme turbidity of the medium. The development of these symptoms of injury was almost completely prevented by the inclusion in the medium

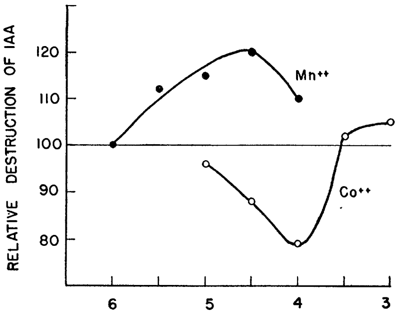

Fig. 1. Effect of the Mn^{++} and Co^{++} ions on peroxide genesis in pea tissues, as measured by the rate of oxidation of indoleacetic acid.