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Fluorescence from Varnishes for Oil Paintings under N_2 Laser Excitation

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The fluorescence spectra of varnish films have been measured as a function of the storage time. The varnishes used were made from natural resins (copal, mastic and dammar), synthetic resin and beeswax. Peak wavelengths of the fluorescence shifted to longer wavelengths with long-time storage. The effect of light on the fluorescence spectrum was found to be small.

In the field of conservation and restoration, the identification of pigments in paintings is important. In previous papers,[1-3] the author reported that fluorescence spectra can be observed in oil colours and that an identification of pigments is possible using a laser-induced fluorescence method. The effect of oils in oil colours has also been examined.[2] However, varnishes used in oil paintings show fluorescence; thus, they can affect the spectral shape of the fluorescence from pigments in oil colours.

Rie[3] has investigated the fluorescence from varnish films under medium-pressure Hg-lamp excitation, and has examined the effect of light and ammonia vapour on the fluorescence spectra. However, he did not examine the dependence of the storage time on the fluorescence spectrum. In this study, the author investigated the effect of the storage time on the fluorescence spectra of varnish films.

The fluorescence spectra were measured with the apparatus described in ref. 1. The excitation source was a pulsed N_2 laser (λ = 337.1 nm pulse duration = 5 ns, repetition rate = 4 Hz). The peak intensity of laser light on a sample was about 50 kW/cm^2. The fluorescence spectra were measured with a 50 cm monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator and a recorder.

The varnishes used were obtained from Holbein Works, Ltd. Resins in the varnishes are listed in Table I. Copal, mastic and dammar are natural resins. These natural resins are mainly composed of resin acids and resenes. Varnishes made from synthetic resin and beeswax were also examined in order to compare these with natural resins. Beeswax is composed of alcohols, acids, esters and other carbohydrates. Samples were prepared on thin Al plates and stored in a steel locker in the laboratory, which had a yearly mean temperature of about 20^{o}C. In order to examine the effect of light, some samples were stored in a shady position near a window.

Figure 1 shows the fluorescence spectra of varnish films on the Al plates. Peak wavelengths of fluorescence from stored varnish films (dashed curves) are longer than those from fresh varnish films. Varnish films prepared on glass plates also show similar results to those on Al plates. Figure 2 shows the peak wavelengths of the fluorescence from varnish films as a function of the storage time. The shift in the peak may be due to the oxidation of resins. The peak wavelength is shorter than 390 nm for tableaux, which is made from synthetic resin; thus it was impossible to determine whether the peak wavelength shifts or not.

Varnishes also contain other ingredients (listed in Table I); thus the effect of the ingredients on fluorescence spectrum were examined. No fluorescence was observed for turpentine and petrol. On the other hand, fluorescence was observed for silica and stand linseed oil, a polymerized linseed oil at high temperature without air. The fluorescence spectrum of silica was measured; the peak wavelength for silica is shorter than 390 nm. Thus, silica may affect the spectrum of blanc mat in the shorter-wavelength region. The peak shift in stored blanc mat is considered to be due to the oxidation of beeswax. The fluorescence spectrum of linseed oil was also measured. Figure 3 shows the fluorescence spectra of stand linseed oil and picture copal varnish films (fresh and stored in the dark for a few days). The fluorescence of picture copal shows two peaks; the 410 nm peak is similar to that for linseed. Thus, the 410 nm peak is considered to be attributable to stand linseed oil and the 510 nm peak to copal. While the fluorescence intensity of the 410 nm peak of stand linseed oil decreases with time, that of picture copal varnish decreases more rapidly. This may be caused by the fact that picture copal includes siccatif (drier), which contains metallic salts and accelerates the oxidation of oils.

Fluorescence from oil films is affected with light,[2)] so that the effect of light on the fluorescence spectrum was also examined for varnish films. However, a significant effect was not observed for the varnishes listed in Table I.

The fluorescence intensity is almost independent of the storage time, except for the new picture copal film shown in Fig. 3. Fluorescence intensities for varnishes were compared with that for cadmium red, which is a standard oil colour for fluorescence intensity in oil colours.[1)] The peak intensity for picture copal, except for new film of this varnish, is almost the same as that for cadmium red and is about two-times that of other varnish films.

In summary, the fluorescence spectra of varnish films were measured under N_2 laser excitation. The peak wavelengths of the fluorescence shift to longer wavelengths with the storage time. The effects of the storage time and light on the fluorescence spectra for varnishes were less than those for oils.[2)]

References

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Figure captions

Fig. 1. Fluorescence spectra of varnish films. Solid curves show fresh varnish films and dashed curves show varnish films stored for 143 weeks in the dark at room temperature. Peak intensities are normalized.

Fig. 2. Peak wavelengths of fluorescence from varnish films stored in the dark at room temperature as a function of the storage time.

Fig. 3. Fluorescence spectra of picture copal varnish and stand linseed oil films fresh and stored in the dark at room temperature. Numbers indicate the number of days stored.

Table I. Varnishes used in this experiment.

Name	Resin[1)]	Other ingredients[1)]
Picture Copal	Copal	Stand linseed oil, Turpentine
Mastic	Mastic	Turpentine
Retoucher	Dammar	Petrol
Tableaux	Synthetic resin	Petrol
Blanc mat	Beeswax[2)]	Silica, Petrol

[1)] Ingredients are quoted from a catalogue by Holbein Works, Ltd.

[2)] Beeswax is not resin but main ingredient.

Fig. 1

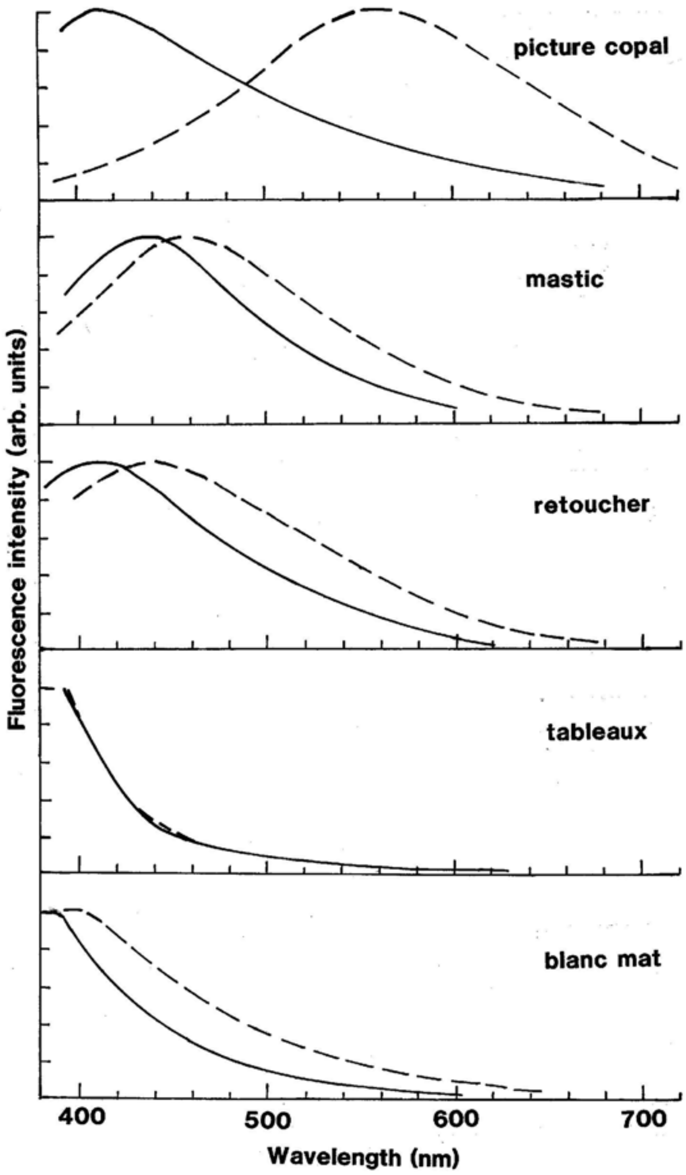

picture copal
mastic
retoucher
tableaux
blanc mat
Fluorescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 2

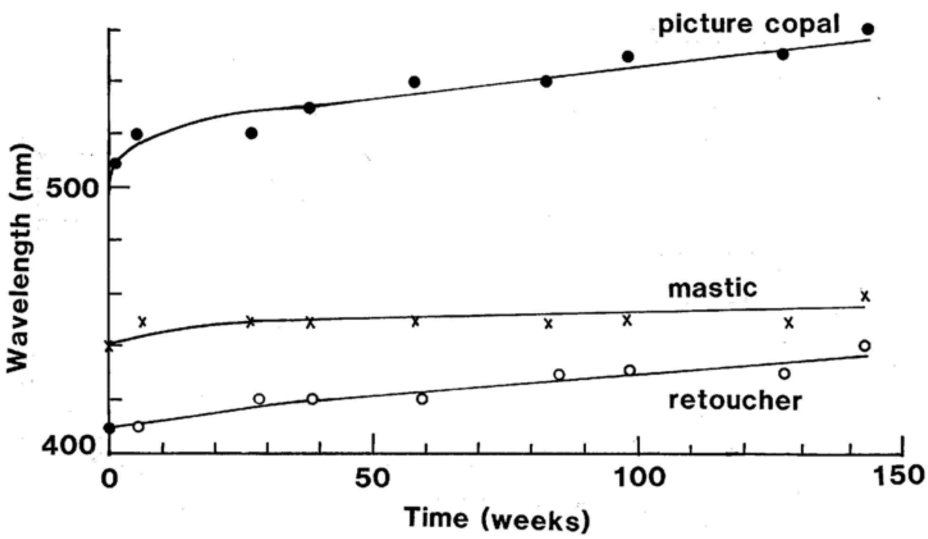
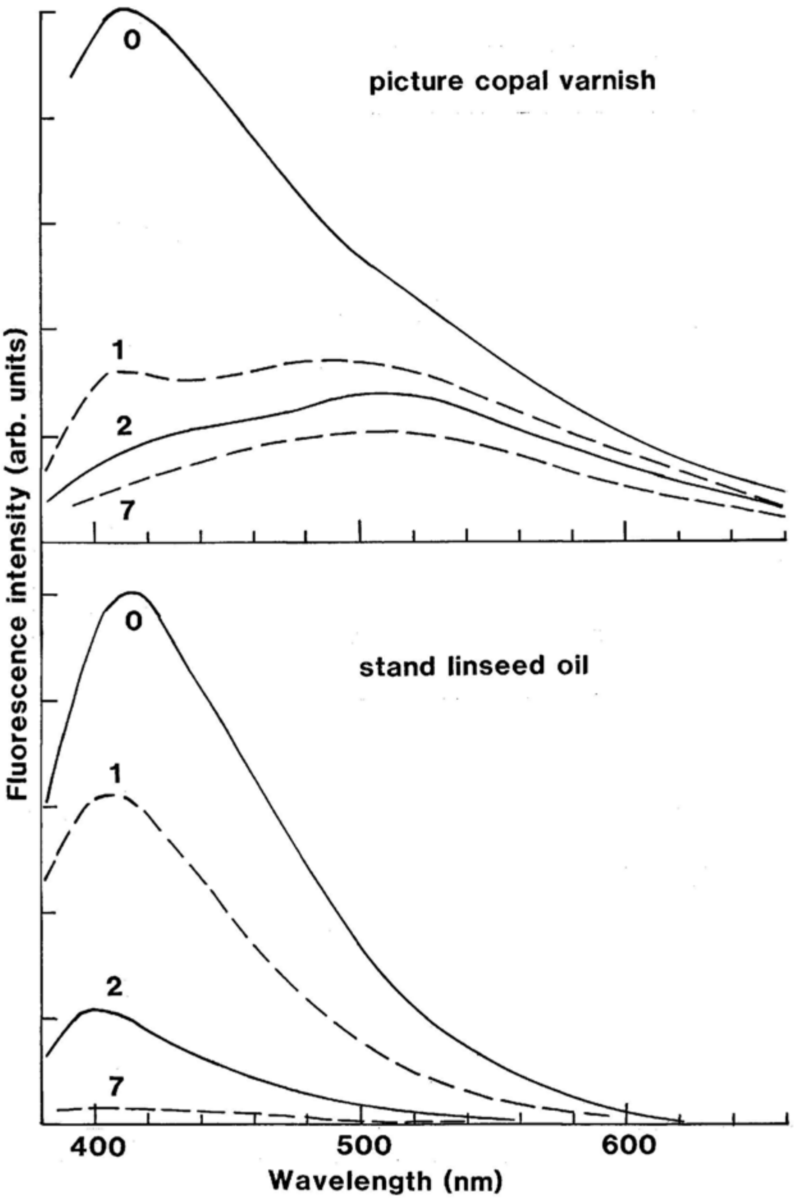

picture copal
mastic
retoucher
Wavelength (nm)
500
400
0
50
100
150
Time (weeks)

Fig. 3



0
picture copal varnish
1
2
7
0
stand linseed oil
1
2
7
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)