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Fluorescence from Pigments in Fresh and Stored Oil Colours under N_2 Laser Excitation

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The identification of pigments in paintings is important in conservation studies.[1] The author has previously reported that the pigments in fresh oil colours can be identified non-destructively by measuring the spectra and decay time of their fluorescence under pulsed laser excitation.[2] However, the fluorescence from oil colours changes with the passage of time, and an additional fluorescence band appears in stored oil colours.[3] This additional band has been ascribed to the polymerization of the oils.[4] In addition to this change, the fluorescence from the pigments also changes.

In the present work, the author studied the fluorescence from pigments in oil colours stored for a few years. The spectra and decay times of fluorescence from stored samples are compared with those from fresh samples in order to examine whether the pigments in stored samples can be identified. The measurement was performed on samples stored in the dark, because the pigments may be affected by light. Although oil paintings are usually exposed to light, the effect of light was avoided here for simplicity, and will be reported elsewhere. The conventional fluorescence was also measured using an Hg lamp in order to examine the effect of the excitation source on the fluorescence spectra.

Samples were prepared on thin Al plates and stored in a steel locker. The laser-induced fluorescence was measured with the apparatus described in the previous paper.[2] The excitation source consisted of a pulsed N_2 laser (λ = 337.1 nm, pulse duration = 5 ns, repetition rate = 4 Hz), and the peak intensity of laser light on a sample was about 100 kW/cm^2. The time-integrated fluorescence spectra were measured with a 50 cm monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator, and a recorder, the transient characteristics of the fluorescence being measured using a storage oscilloscope. The conventional fluorescence was measured under high-pressure Hg-lamp excitation (λ = 365 nm) with a glass filter, UV-D2. The fluorescence spectra were measured with the monochromator, the photomultiplier and the recorder.

Figure 1 shows the fluorescence spectra of fresh cadmium yellow and cadmium yellow stored in the dark (in the locker). The fluorescence band of the stored sample has a tail extending into the long-wavelength region, and the half-width of the fluorescence band is greater than that of the fresh sample. The peak intensity of the fluorescence from the stored sample is almost the same as that from the fresh sample. The tail in the short-wavelength region is attributed to fluorescence from poppy oil in the oil colour.

The effect of oils on the fluorescence has been reported elsewhere.[3] Other oil colours stored in the dark show similar results.

Figure 2 shows the transient characteristics of the fluorescence at the peak wavelength for cadmium yellow. The solid curves represent the experimental results and the open circles represent the theoretical values assuming a single exponential decay of 1 ns. Since fresh samples show rapid decay, the value of the decay time was not measured using the N_2 laser. Other oil colours show similar results. The values of the decay time at the peak wavelength are listed in Table I. The transient characteristics of the fluorescence for red oil colours have previously been examined using an Ar laser (λ = 514.5 nm) and a picosecond photon-counting method.[2] The decay time is calculated from the experimental results as shown in parentheses in Table I. The pigments in the stored oil colours show almost the same decay times, while those in the fresh samples show different decay times. Thus, the decay time is not suitable for identifying pigments in stored oil colours. The decay time of the fluorescence from poppy oil in oil colours was measured, and was found to be 2 ns for both fresh and stored samples. Linseed oil showed a similar result.

The 520 nm ($h\nu$ = 2.4 eV) fluorescence from cadmium yellow is attributable to the band-to-band transition, i.e. the intrinsic transition, because the band gap of CdS (the pigment of cadmium yellow) is 2.4 eV.[5] On the other hand, the tail in the long-wavelength region is thought to be associated with the extrinsic transition. The experimental results on the decay time can be explained by assuming that the band-to-band transition causes rapid decay and the extrinsic transition causes gradual decay. To determine whether this assumption is correct or not, the decay time of the fluorescence was measured as a function of the wavelength, and was found to increase as the observed wavelength became longer, as shown in Fig. 3. This suggests that the assumption is reasonable. Other oil colours show similar results. The extrinsic transition is probably caused by defects in the pigments.[6] However, further investigation of the origin of the extrinsic transition is necessary.

Rie[6,7] measured the fluorescence spectra of oil colours under Hg-lamp excitation, and observed that the fluorescence from vermilion increases with time.[7] The author obtained similar results in other oil colours. Figure 4 shows the fluorescence from oil

colours under Hg-lamp excitation. The fluorescence from pigments in stored samples is stronger than from those in fresh samples, suggesting that the fluorescence under the Hg-lamp excitation is associated with the extrinsic transition. The fluorescence band under the Hg-lamp excitation may correspond to the tail in the long-wavelength region of fluorescence under the N_2-laser excitation. The N_2 laser is more suitable than the Hg lamp for identifying pigments, because the fluorescence associated with the extrinsic transition is dominated by the band-to-band transition (intrinsic transition) under the N_2-laser excitation.

In summary, the fluorescence band from pigments in stored oil colours has a tail in the long-wavelength region. This tail is attributable to the extrinsic transition, which changes the decay time of the fluorescence, so that the decay time is not suitable for identifying pigments in stored oil colours. The fluorescence spectra, however, can be used to identify pigments even in stored oil colours, and the N_2 laser is more suitable than the Hg lamp for identifying pigments.

References

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3) T. Miyoshi: Jpn. J. Appl. Phys. **24** (1985) 371.
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7) E. R. de la Rie: Stud. Conserv. **27** (1982) 102.

Figure captions

Fig. 1. Fluorescence spectra of cadmium yellow under N_2-laser excitation.

Fig. 2. Transient characteristics of fluorescence from cadmium yellow under N_2-laser excitation. The solid curves show the experimental results and the open circles show the theoretical values.

Fig. 3. Wavelength dependence of decay time of fluorescence from cadmium yellow stored for 3.5 years.

Fig. 4. Fluorescence spectra of oil colours under Hg-lamp excitation. The solid curves show fresh samples and the dashed curves show samples stored for 3.5 years.

Table I. Decay time of the fluorescence from oil colours fresh and stored for 0.9 and 3.5 years.

Oil colours	Fresh	Stored	
		0.9 a	3.5 a
Cadmium yellow	< 0.5 ns	0.5 ns	1 ns
Cadmium red	< 0.5 (0.2)	< 0.5	1
Vermilion	< 0.5 (0.05)	2	2
Scarlet lake	< 0.5 (0.1)	1	2
Carmine lake	< 0.5 (0.1)	1	2

Fig. 1

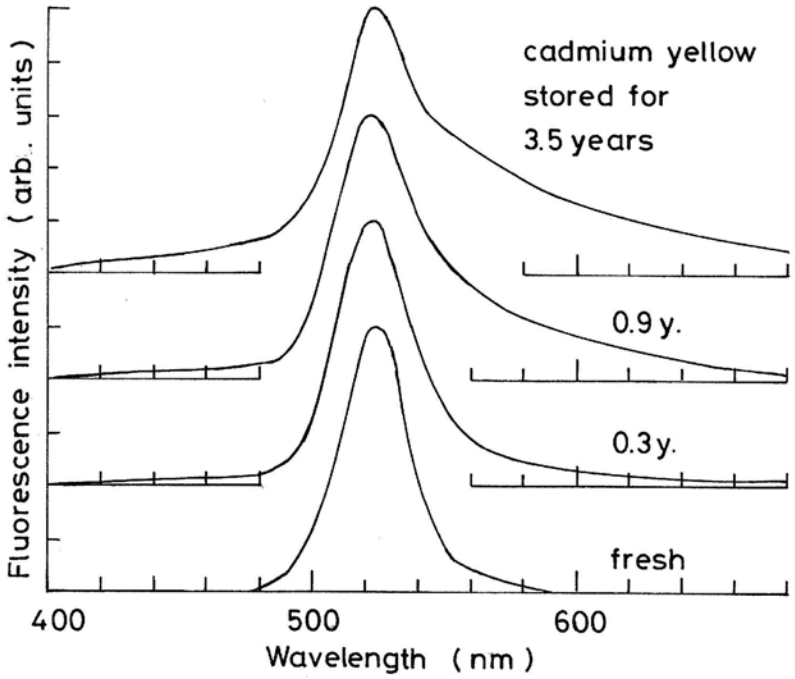

cadmium yellow
stored for
3.5 years
0.9 y.
0.3 y.
fresh
Fluorescence intensity (arb. units)
400
500
600
Wavelength (nm)

Fig. 2

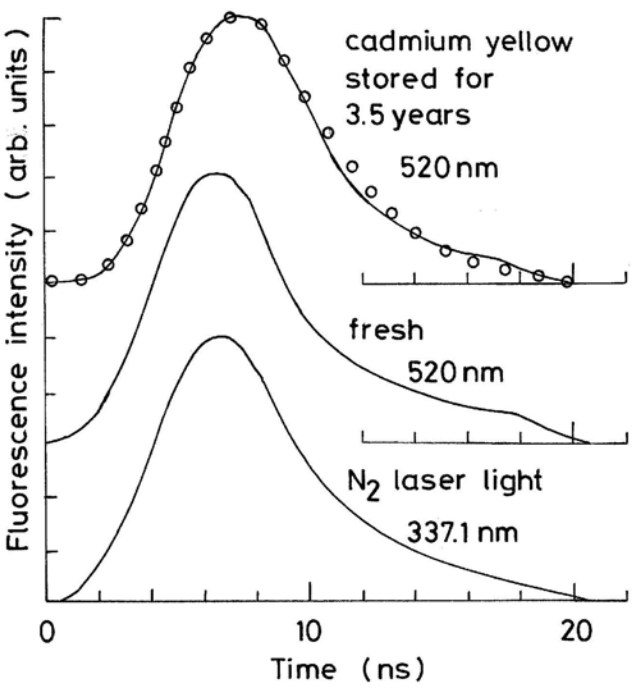

cadmium yellow
stored for
3.5 years
520 nm
fresh
520 nm
N2 laser light
337.1 nm
Fluorescence intensity (arb. units)
0
10
20
Time (ns)

Fig. 3

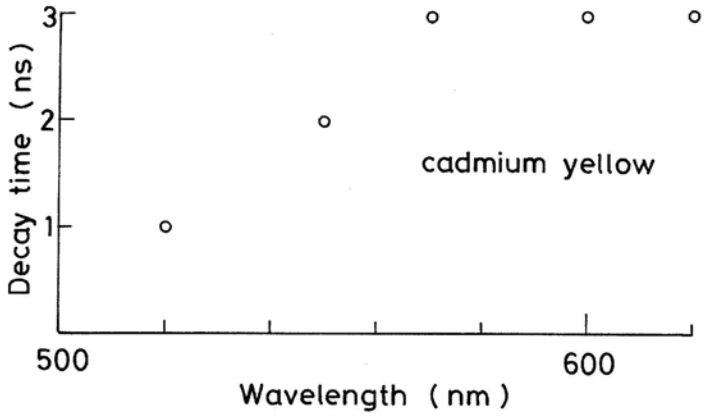
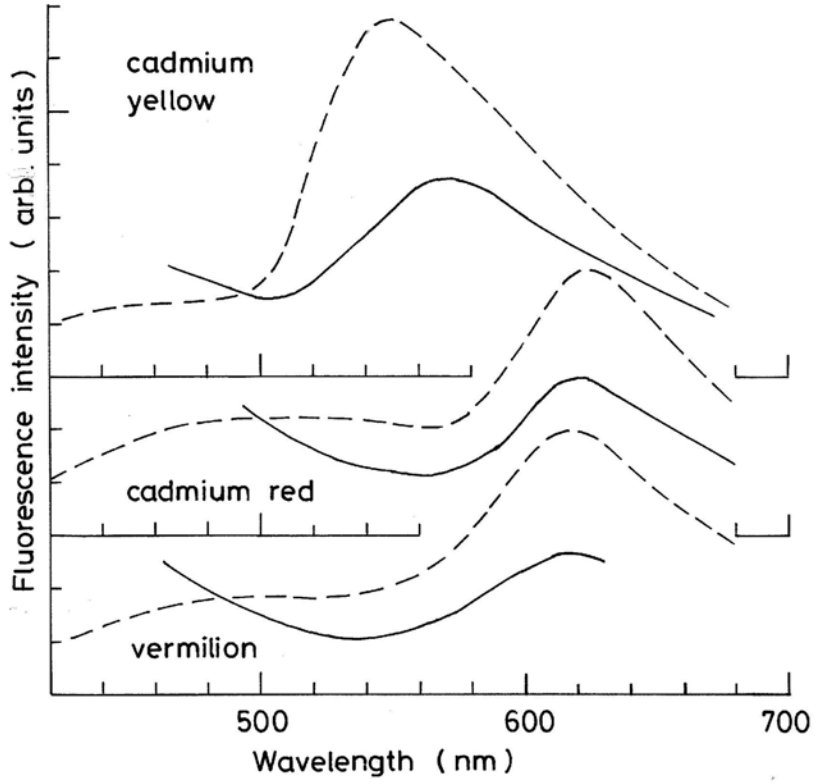

Decay time (ns)
3
2
1
cadmium yellow
500
600
Wavelength (nm)

Fig. 4


Fluorescence intensity (arb. units)
cadmium yellow
cadmium red
vermilion
500
600
700
Wavelength (nm)