Japanese Journal of Applied Physics, **24** (3) (1985) 371-372

Fluorescence from Oil Colours, Linseed Oil and Poppy Oil under N_2 Laser Excitation

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(Received November 24, 1984; accepted January 26, 1985)

Identification of pigments in paintings is important in the study of conservation and restoration.[1] In a previous paper,[2] the author reported that fluorescence spectra are observed in oil colours immediately after painting and the identification of pigments is possible using a laser-induced fluorescence technique. However, linseed oil or poppy oil in oil colours shows fluorescence. The fluorescence intensity of oils increases after solidification.

In this report, the author has studied the effect of oils on oil colours. Fluorescence spectra of oil colours stored for three years are compared with those of fresh oil colours. Then, the fluorescence from oils is examined as a function of stored time in order to investigate the effect of oils on the fluorescence from pigments in oil colours.

Rie[3] has independently investigated fluorescence from linseed oil films under a 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 temperature and stored time on the fluorescence intensity nor did he investigate poppy oil, in spite of the fact that poppy oil is usually used in oil colours.

In this paper we examine the fluorescence from linseed and poppy oil films stored in the dark and in daylight as a function of stored time. Influence of temperature on the fluorescence is also examined for oil films stored in the dark. Weak fluorescence from oil films immediately after solidification is easily measured using the laser-induced fluorescence, because of its greater sensitivity as compared with ordinary fluorescence which uses an Hg lamp such as that described in ref. 2.

Fluorescence spectra are measured with the apparatus described in the previous paper.[2] The excitation source is 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 is about 100 kW/cm^2. The fluorescence spectra are measured with a 50 cm monochromator, a photomultiplier (Hamamatsu R955), a boxcar integrator and a recorder.

Samples are prepared on thin Al plates. Since oils were affected by light,[3] samples are stored in a steel locker in the laboratory, which has a yearly mean temperature of about 20^{o}C. In order to examine the effect of temperature and light, some samples are stored in a pyrostat, in a refrigerator (in the dark) or in a shady position near a window (in daylight).

Figure 1 shows the fluorescence spectra of some oil colours fresh (curve 1) and stored (curve 2) in the dark (in the locker) for three years. While the peak wavelength of the fluorescence from pigments in stored samples is almost the same as that in fresh samples, the spectral shape is slightly changed. An additional fluorescence band is observed at about 500 nm in stored samples. The additional band can be ascribed to the fluorescence from linseed oil or poppy oil in oil colours. Since the additional band affects the spectral shape of the fluorescence from pigments, in this work the fluorescence from linseed and poppy oil films as a function of stored time is examined.

Figure 2 shows fluorescence spectra of linseed oil films stored in the dark for 3 to 190 weeks. New oil film shows a fluorescence band at about 430 nm, and old oil film at about 550 nm. Poppy oil films exhibit similar behavior.

Figure 3 shows peak wavelength and peak intensity of the fluorescence from linseed and poppy oil films as a function of stored time. The fluorescence intensity increases for several months, reaches a maximum and then falls gradually. The peak wavelength shifts to longer wavelengths up to about one year. The peak shift is very gradual after one year. Yellowing is observed in both linseed and poppy oil films whose fluorescence peak is longer than about 450 nm, while new oil film is colourless. The fluorescence spectra of yellowed oil films are similar to those under an Hg lamp excitation.[3)]

Dependence of the fluorescence on stored time is due to polymerization of oils resulting from autoxidation reactions.[3)] The reaction depends on temperature and light. In order to examine the effects of temperature and light, the fluorescence is measured for oil films stored in the dark at 5, 30 and 50^{o}C and in daylight at 30^{o}C. Figure 4 shows peak wavelength and peak intensity of the fluorescence from linseed oil films stored at 5, 30 and 50^{o}C. Change in the fluorescence is rapid at higher temperatures. Linseed oil film stored in daylight shows rapid increase in peak intensity and gradual change in peak wavelength.

Fluorescence spectra are measured for oil films stored in the dark at 5^{o}C and in daylight at room temperature for about 70 weeks. Linseed oil film stored at 5^{o}C for about 70 weeks exhibits a fluorescence band at 480 nm. The peak intensity of the band is slightly weaker than that stored at room temperature in the dark. Since change in the fluorescence is very slow, the peak wavelength and the peak intensity will be close to

those stored at room temperature after several years. Linseed oil film stored in daylight for about 70 weeks shows almost the same fluorescence band as that stored for 7 weeks. Yellowed film of linseed oil is bleached by exposure to light.[3] Linseed oil film stored in the dark for 150 weeks and then stored in daylight for 40 weeks shows fluorescence band at 490 nm. Thus, linseed oil films stored for several years will show fluorescence band at about 480 nm for samples stored in daylight and at about 550 nm for samples stored in the dark.

Similar results are obtained for poppy oil films. Poppy oil films stored for several years will show fluorescence band at about 440 nm for samples stored in daylight and at about 500 nm for samples stored in the dark. This result suggests that oil colours in Fig. 1 include poppy oil. Difference in fluorescence characteristics of the linseed oil from poppy oil is due to the difference in composition of oils. Fatty acids in linseed oil are mainly composed of oleic acid and linolenic acid, while main composition of poppy oil is linoleic acid.

In summary, an additional fluorescence band is observed in old oil colours. The additional band is due to the fluorescence from poppy oil. Fluorescence from oil films shows change in peak wavelength and peak intensity as the time goes on. The rate of the change depends on temperature and light. Yellowing and optical bleaching are observed in poppy oil films as well as linseed oil films. The influence of oils on the fluorecence from pigments in oil colours will be small tens of years after solidification, because the fluorescence intensity of oils decreases after about one year following solidification.

References

1) A. Petrakiev, A. Samov and G. Dimitrov: Jena Rev. **16** (1971) 250
2) T. Miyoshi, M. Ikeya, S. Kinoshita and T. Kushida: Jpn. J. Appl. Phys. **21** (1982) 1032.
3) E. R. de la Rie: Stud. Conserv. **27** (1982) 65.

Figure captions

Fig. 1. Fluorescence spectra of red colours. Curves 1 show fresh oil colours and curves 2 show oil colours stored for three years in the dark at room temperature. Peak intensities are normalized.

Fig. 2. Fluorescence spectra of linseed oil films stored in the dark at room temperature. Figures are stored time in weeks.

Fig. 3. Peak wavelength and peak intensity of fluorescence from linseed and poppy oil films stored in the dark at room temperature as a function of stored time. (a) peak wavelength, (b) peak intensity.

Fig. 4. Peak wavelength and peak intensity of fluorescence from linseed oil films stored at 5, 30 and 50^{o}C as a function of stored time. Solid curves correspond to oil films stored in the dark and dashed curves stored in daylight, (a) peak wavelength, (b) peak intensity.

Fig. 1

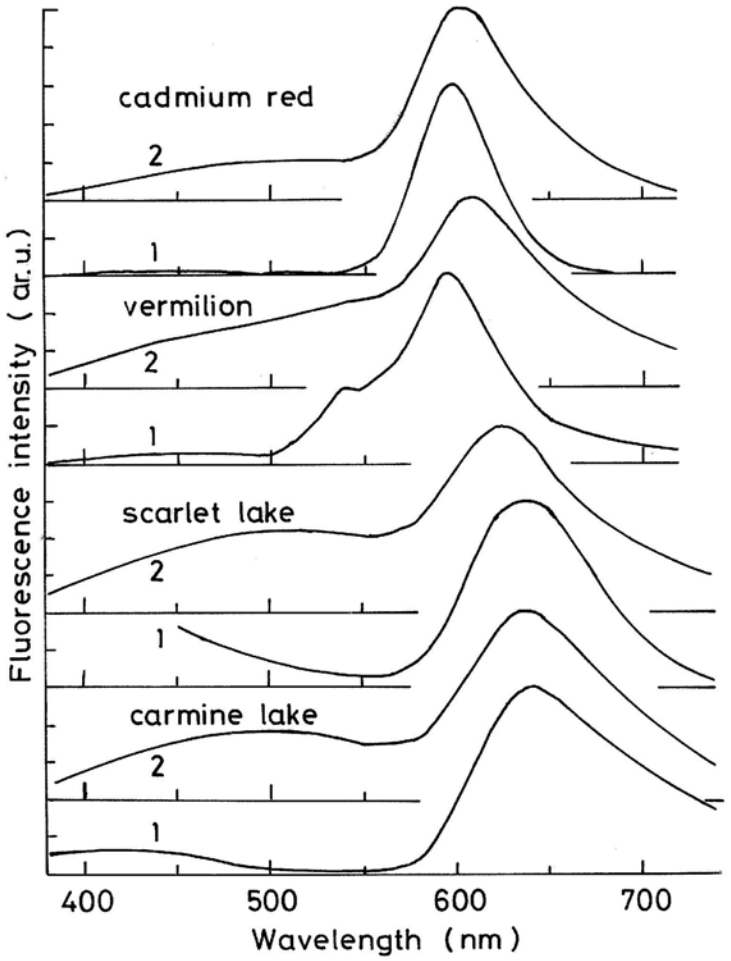

cadmium red
2
1
vermilion
2
1
scarlet lake
2
1
carmine lake
2
1
Fluorescence intensity (ar.u.)
400
500
600
700
Wavelength (nm)

Fig. 2

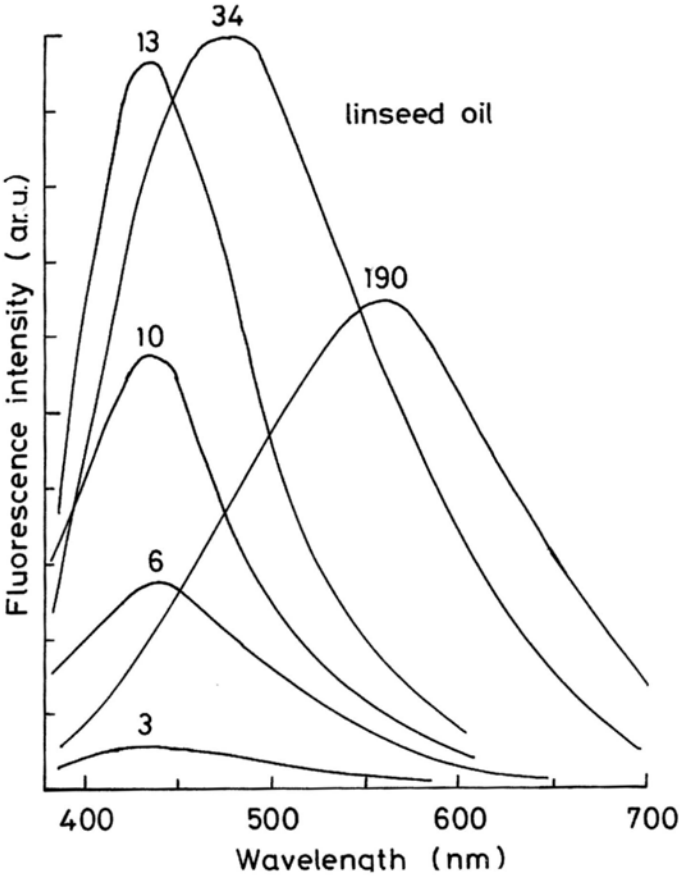

34
13
linseed oil
190
10
6
3
Fluorescence intensity (ar.u.)
400
500
600
700
Wavelength (nm)

Fig. 3

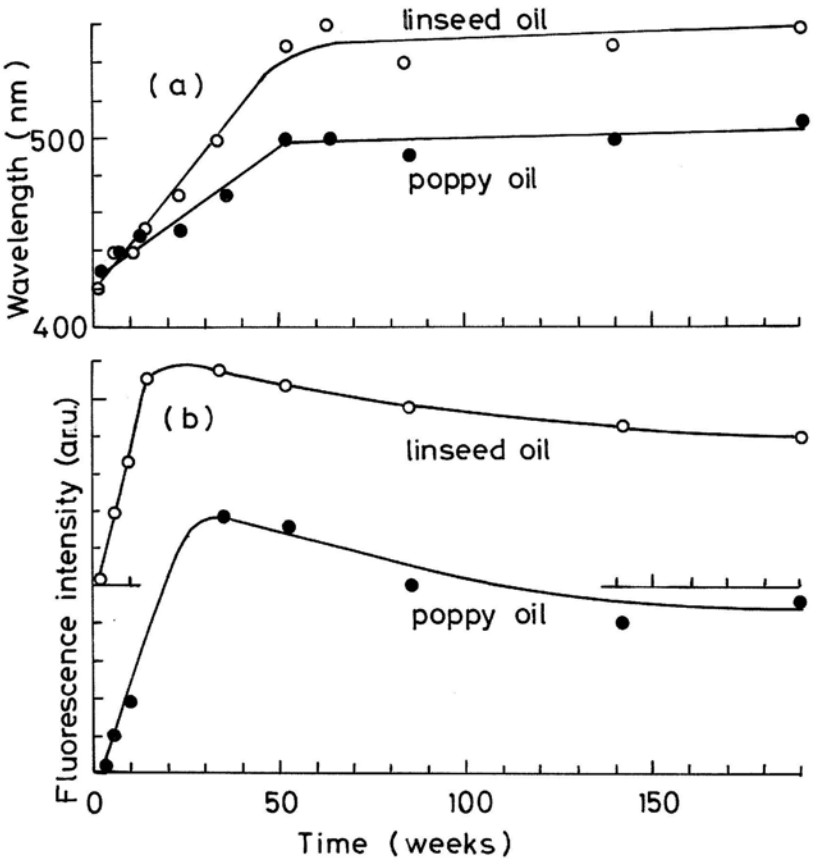
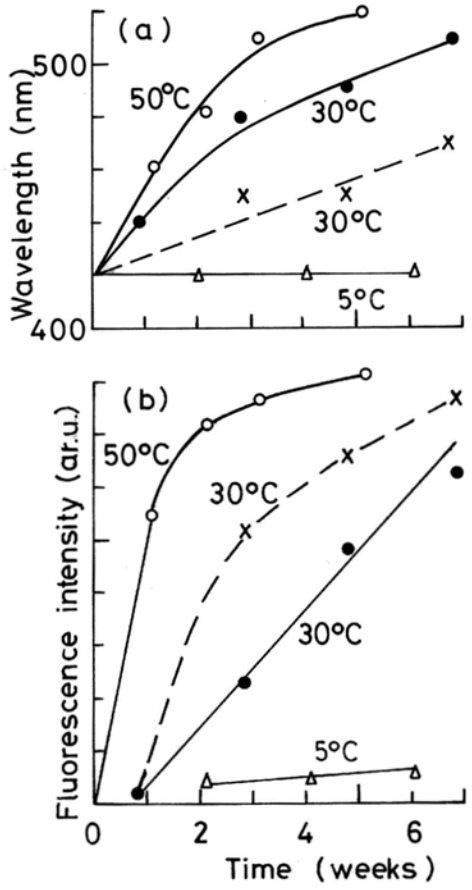

linseed oil
(a)
Wavelength (nm)
500
400
poppy oil
(b)
linseed oil
Fluorescence intensity (ar.u.)
poppy oil
0
50
100
150
Time (weeks)

Fig. 4


(a)
Wavelength (nm)
500
400
50°C
30°C
30°C
5°C
(b)
Fluorescence intensity (ar.u.)
50°C
30°C
30°C
5°C
0
2
4
6
Time (weeks)