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# FLUORESCENCE OF PAINT AND VARNISH LAYERS (PART II)

E. René de la Rie

**Abstract**—The fluorescence under ultraviolet light of linseed oil films and films of some natural resins has been studied with a fluorescence spectrometer. Both materials fluoresce only after some degradation has taken place. The fluorescence appears to be closely related to the processes causing yellowing.

## 1 Introduction

This article is a continuation of the report on the results of measurements of fluorescence of painting materials under ultraviolet light, the first part of which was published in this journal [1]. The subject of this publication will be the fluorescence of linseed oil and some natural resins.

The best approach to an understanding of the role of linseed oil in fluorescence of paints and of resins in varnishes seemed to be the study of thin films of both materials. Some mention has been made of fluorescence of linseed oil in the liquid phase [2–4]. However, to the knowledge of the author there are no reports on the behaviour of dried linseed oil films under ultraviolet light. Also, fluorescence of resin lumps has been described in some early publications [3, 5] but, although fluorescence of old varnish layers on pictures is well known, no study of the fluorescent behaviour of thin resin films could be found.

At an early stage during this study it was evident that fresh films of linseed oil and natural resins did not fluoresce. Because yellowed films did fluoresce and because it is known that yellowing of linseed oil films is accelerated, either by storage in the dark or by exposure to ammonia vapour [6], the films were exposed to such conditions during this study.

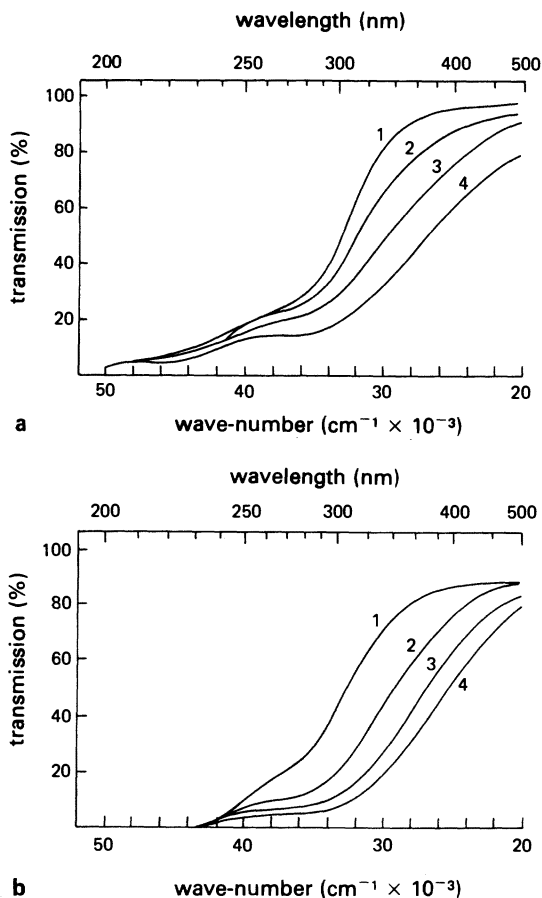
## 2 Results of measurements

The fluorescence\* intensity of a wet or freshly dried linseed oil film appeared to be negligible†. When the

\* Tests for phosphorescence on linseed oil and natural resin films gave negative results [1].

† Also films of dirty, boiled or stand oil—oils that may show considerable fluorescence when present in a pot or cuvette—do not show any fluorescence when applied as thin films. This is, of course, because in thin films a much higher concentration of the chromophores is needed to make the fluorescence visible.

film is stored in daylight‡ for three to four weeks a very weak fluorescence is observed. Subsequent storage in the dark or exposure to ammonia vapour results in strong fluorescence. At the same time, transmission of the film in the ultraviolet and visible



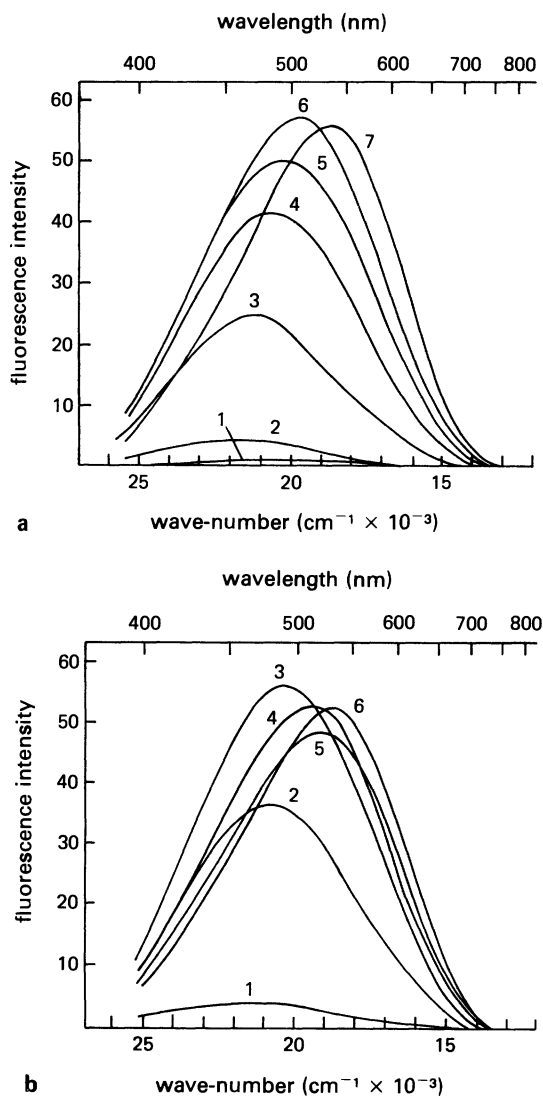
**Figure 1** Transmission spectra of linseed oil films (thickness  $\pm 25\mu\text{m}$ ): (a) three weeks daylight (1), three weeks daylight + nine days dark (2), three weeks daylight + one month dark (3), three weeks daylight + three months dark (4); (b) four weeks daylight (1), four weeks daylight + 10 minutes  $\text{NH}_3$  (2), four weeks daylight + 10 minutes  $\text{NH}_3$  + one day dark (3), four weeks daylight + 10 minutes  $\text{NH}_3$  + 11 days dark (4).

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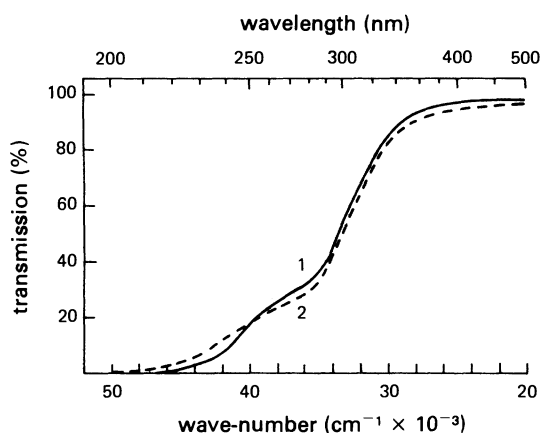
‡ By 'storage in daylight' is always meant storage in a horizontal position near a window facing north.

region decreases strongly, a phenomenon observed visually as yellowing (Figure 1). The fluorescence spectrum consists of a broad, structureless band covering the entire visible spectrum (Figure 2) and



**Figure 2** Fluorescence spectra of linseed oil films (thickness 25–50  $\mu\text{m}$ ): (a) wet film (1), dry film, five weeks daylight (2), five weeks daylight + 10 days dark (3), five weeks daylight + five weeks dark (4), five weeks daylight + eight weeks dark (5), five weeks daylight + four months dark (6), five weeks daylight + seven months dark (7); (b) one month daylight (1), one month daylight + 10 minutes  $\text{NH}_3$  (2), one month daylight + 10 minutes  $\text{NH}_3$  + one day dark (3), one month daylight + 10 minutes  $\text{NH}_3$  + four days dark (4), one month daylight + 10 minutes  $\text{NH}_3$  + 11 days dark (5), one month daylight + 10 minutes  $\text{NH}_3$  + one month dark (6). Wavelength of excitation 365nm.

showing a slight sensitivity to variation of the excitation wavelength between 313 and 436nm. On continued storage in the dark, yellowing as well as fluorescence increases. The fluorescence maximum shifts to longer wavelengths at the same time (i.e. the fluorescence colour changes from bluish to yellowish). Storage in the dark after ammonia treatment produces the same effect as storage in the dark alone, but in a shorter period of time. Prolonged storage in daylight only results in a relatively weak short wavelength fluorescence, and does not produce yellowing (Figure 3). It is possible to bleach yellowed films by exposure to sunlight\*. This bleaching not only makes the yellow colour disappear but also results in the fluorescence shifting back to shorter wavelengths and subsequently decreasing in intensity.



**Figure 3** Transmission spectra of a linseed oil film in daylight after two weeks (1) and after five months (2).

Thin resin films basically show the same phenomena as linseed oil films, that is, fluorescence intensifies and occurs at longer wavelengths as yellowing proceeds (Figure 4). It is also possible to induce yellowing and fluorescence in a mastic and dammar film by treatment with ammonia vapour; however, a longer preliminary period of several months in daylight is required (Figure 5). Yellowing in the dark takes place very slowly.

### 3 Discussion

It appears that the fluorescence of linseed oil is somehow related to the yellowing process. The yellowing

\* This was done by placing the sample in a vertical position in front of a window facing south.

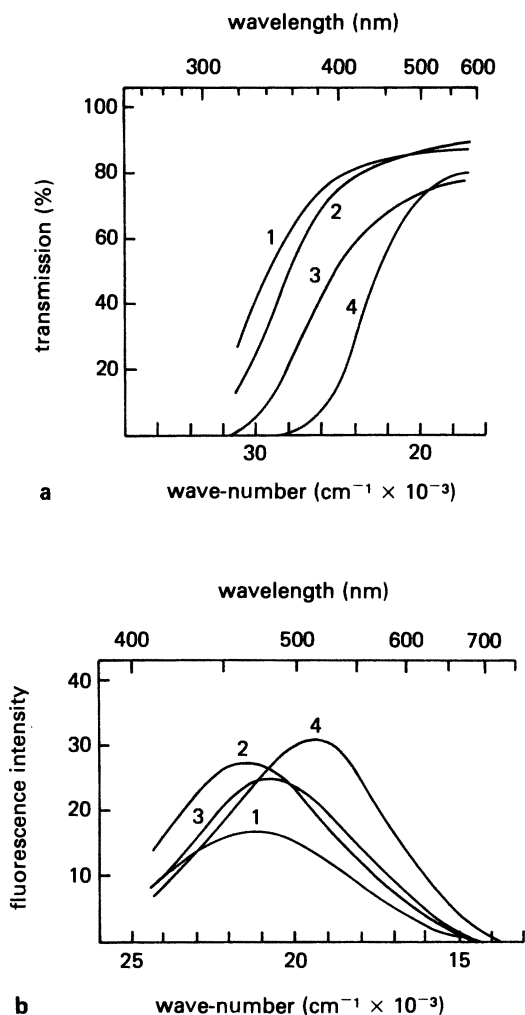


Figure 4 (a) Transmission and (b) fluorescence spectra of old resin films: sandarac (thickness  $\pm 25\mu\text{m}$ ) (1), dammar (thickness  $20\text{--}25\mu\text{m}$ ) (2), mastic (thickness  $30\text{--}45\mu\text{m}$ ) (3), Venetian turpentine (thickness  $\pm 55\mu\text{m}$ ) (4). These films date from 1932–33 (the films are on glass plates and were lent by the National Gallery in London). Wavelength of excitation 365nm.

lowing\* of drying oils is a process about which little is known with any certainty. During the autoxidation process, which does not stop after the drying of the film but continues slowly and is stimulated by light, a great number of low molecular weight compounds are formed as byproducts. Among these are saturated and unsaturated acids, ketones and aldehydes [7]. The most probable explanation for

\* The word 'yellowing' is used for the increase in absorption in the short wavelength visible as well as the long wavelength ultraviolet part of the electromagnetic spectrum.

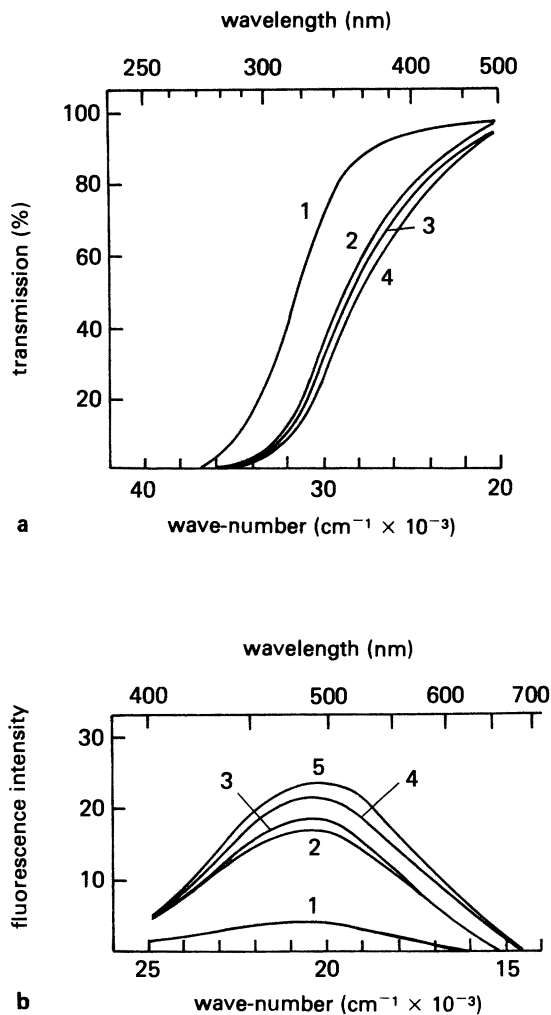


Figure 5 (a) Transmission spectra of a mastic film (thickness  $\pm 10\mu\text{m}$ ): three months daylight (1), three months daylight + 10 minutes  $\text{NH}_3$  (2), three months daylight + 10 minutes  $\text{NH}_3$  + one day dark (3), three months daylight + 10 minutes  $\text{NH}_3$  + one month dark (4). (b) Fluorescence spectra of a mastic film (thickness  $\pm 10\mu\text{m}$ ): three months daylight (1), three months daylight + 10 minutes  $\text{NH}_3$  (2), three months daylight + 10 minutes  $\text{NH}_3$  + four hours dark (3), three months daylight + 10 minutes  $\text{NH}_3$  + one day dark (4), three months daylight + 10 minutes  $\text{NH}_3$  + three weeks dark (5). Wavelength of excitation 365nm.

the formation of coloured compounds is polymerization through aldol-condensation of unsaturated carbonyl compounds [8, 9], a process that is catalyzed by, among others, volatile nitrogen containing bases such as ammonia [10]. It is not unlikely that nitrogen plays a role in the yellowing of linseed oil, since linseed oil is able to absorb nitrogen from the atmosphere [11], and yellowed films appear to have

an increased nitrogen content [6]. Nitrogen is very likely to be involved also in the fluorescence of the oil because malonic aldehyde, a major breakdown product of the model compound methyl linolenate [12], forms fluorescent compounds with amino group containing substances [13]. These fluorescent compounds all contain the chromophore 1-amino-3-iminopropene,  $\sim\sim\text{NH}-\text{CH}=\text{CH}-\text{CH}=\text{N}\sim\sim$ . Probably more than one fluorescent compound as well as fluorescent polymeric structures are formed during the yellowing of linseed oil, since the fluorescence spectrum shifts to longer wavelengths during yellowing. Much more work must be done to reveal the exact nature of the fluorescent compounds.

Yellow and fluorescent compounds contain unsaturated structures, which apparently are easily destroyed by light. Light, therefore, plays a complicated role; on the one hand it stimulates formation of breakdown products, and on the other hand it destroys coloured and fluorescent structures formed from these breakdown products. Of course, it must be remembered that both are degradation processes; the original structure is not restored during the bleaching process!

Autoxidation reactions do take place in natural resins, especially when they are applied as thin films [14], yet it is a process which does not proceed as obviously as in drying oils. Therefore, a longer exposure to light is required to produce breakdown products that can transform into coloured and fluorescent structures. A remarkable similarity between the results of degradation of linseed oil and natural resins appears from this study.

Fluorescence of these organic materials, linseed oil and natural resins, is obviously the result of a degradation process; therefore, it is expected that the fluorescence intensity of these materials, when present in paint and varnish layers, will increase as they become older.

#### 4 Experimental

Fluorescence spectra were determined with the equipment described in the previous paper [1]. For the measurement of transmission spectra a Zeiss PMQ3 spectrometer was employed.

Linseed oil and natural resin films were prepared on quartz plates. They measure  $12.5 \times 45\text{mm}$  and are normally used for the construction of cuvettes. They are very practical, since they fit into every spectrometer cuvette holder. The quartz plates were held against the sample holder of the fluorescence spectrometer by means of small magnets.

Linseed oil from various manufacturers gave the same results. Mastic and dammar films were prepared from solutions in turpentine oil. Exposure to ammonia vapour was done simply by putting con-

centrated ammonia next to the object in a closed vessel.

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**Résumé**—On a étudié à l'aide d'un spectromètre de fluorescence la fluorescence sous ultraviolet de films d'huile de lin et de films de quelques résines naturelles. Ces matériaux ne fluorescent qu'après une certaine dégradation et le phénomène de fluorescence semble étroitement lié au processus de jaunissement.

**Zusammenfassung**—Die Fluoreszenz unter ultraviolettem Licht von Leinölfilmen und Filmen gewisser natürlicher Harze ist mit einem Fluoreszenzspektrometer untersucht worden. Beide Materialien fluoreszieren nur, nachdem ein gewisser Abbau stattgefunden hat. Die Fluoreszenz scheint eng mit den Vergilbung verursachenden Vorgängen verbunden zu sein.