



Fluorescence of Paint and Varnish Layers (Part III)

Author(s): E. Rene de la Rie

Source: *Studies in Conservation*, Vol. 27, No. 3 (Aug., 1982), pp. 102-108

Published by: International Institute for Conservation of Historic and Artistic Works

Stable URL: <http://www.jstor.org/stable/1506145>

Accessed: 13/11/2009 07:44

Your use of the JSTOR archive indicates your acceptance of JSTOR's Terms and Conditions of Use, available at <http://www.jstor.org/page/info/about/policies/terms.jsp>. JSTOR's Terms and Conditions of Use provides, in part, that unless you have obtained prior permission, you may not download an entire issue of a journal or multiple copies of articles, and you may use content in the JSTOR archive only for your personal, non-commercial use.

Please contact the publisher regarding any further use of this work. Publisher contact information may be obtained at <http://www.jstor.org/action/showPublisher?publisherCode=iich>.

Each copy of any part of a JSTOR transmission must contain the same copyright notice that appears on the screen or printed page of such transmission.

JSTOR is a not-for-profit service that helps scholars, researchers, and students discover, use, and build upon a wide range of content in a trusted digital archive. We use information technology and tools to increase productivity and facilitate new forms of scholarship. For more information about JSTOR, please contact support@jstor.org.



International Institute for Conservation of Historic and Artistic Works is collaborating with JSTOR to digitize, preserve and extend access to *Studies in Conservation*.

<http://www.jstor.org>

FLUORESCENCE OF PAINT AND VARNISH LAYERS (PART III)

E. René de la Rie

Abstract—The fluorescence under ultraviolet light of oil-paints and some picture surfaces has been studied with a fluorescence spectrometer. The development of fluorescence and the yellowing of linseed oil appear to be greatly influenced by the presence of pigments. Some pigments have an inhibiting, some an enhancing effect, and some are indifferent. In the light of these results and the material published before, the fluorescence of some picture surfaces is discussed.

1 Introduction

In this, the final contribution to the report on fluorescence of painting materials [1, 2], the fluorescence of oil-paints and picture surfaces will be discussed. Several pigments were ground with linseed oil without further additions and subsequently applied in thin layers on microscope slides. They were allowed to dry in daylight* and were cured by long exposure to daylight, storage in the dark and, finally, exposure to ammonia vapour. Linseed oil films were tested in a similar manner [2]. In addition, the fluorescence of a few picture surfaces was examined.

2 Results of measurements on oil-paints

Pigments appear to have a great influence on the fluorescence and the yellowing of dried linseed oil. Many pigments have an inhibiting effect on the development of fluorescence and yellowing. Storage in the dark or treatment with ammonia vapour have far less effect on such paints than on linseed oil without added pigments. The fluorescence intensity remains at a low level. Among these inhibiting pigments are ochres, siennas, umbers, verdigris, copper resinate, minium, bone black, viridian, malachite, azurite, Prussian blue and green earth. Therefore, little fluorescence is observed in those parts of oil-paintings which contain these pigments (Figure 5—curve 3b).

Other pigments, however, seem to stimulate the development of fluorescence in linseed oil. In paints prepared with these pigments fluorescence is observed immediately after drying. This effect has

*Exposure to daylight was done in a horizontal position near a window facing north.

Received 10 February 1978

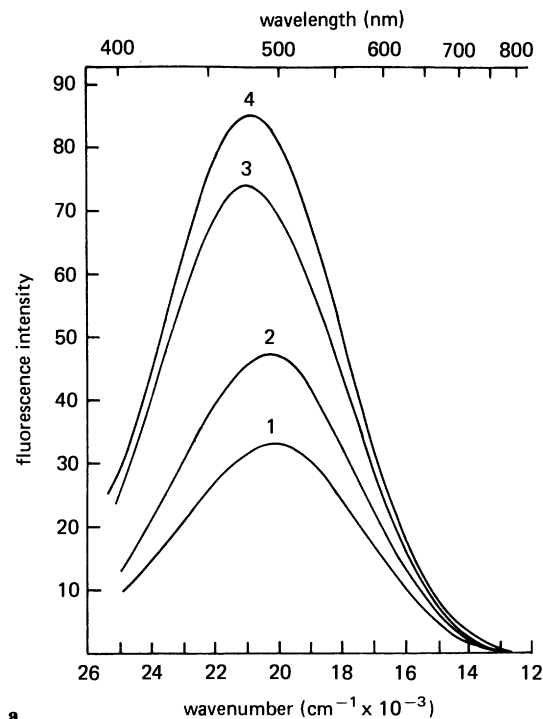
Received in revised form 11 March 1981

been observed in white lead and the following blue pigments: cobalt blue and violet, manganese blue, cerulean blue and ultramarine blue. Freshly dried white lead oil-paint fluoresces as a bluish white with a fluorescence band that covers the entire visible spectrum. The other pigments generate a blue fluorescence in the oil (Figure 1). The fluorescence intensity of a white lead oil-paint increases upon storage in daylight, while the maximum shifts slightly to shorter wavelengths (Figure 1a). Upon storage in the dark or after ammonia treatment, however, the intensity increases even more while the fluorescence maximum shifts to a longer wavelength (the fluorescence colour changes from bluish white to yellowish white) (Figure 2). With this treatment the paint yellows considerably. Yellowed oil-paint can be bleached by sunlight with the result that the fluorescence decreases and shifts to shorter wavelengths.

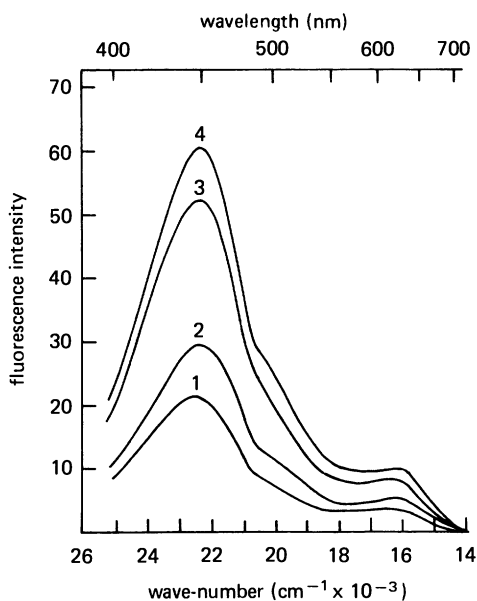
Another group of pigments does not generate fluorescence in the paint directly after drying; however, neither does it inhibit the yellowing and the development of fluorescence in the paint. Examples are titanium white and vermilion. Vermilion oil-paint shows little or no fluorescence after drying. The fluorescence intensity also stays at a low level when the paint is kept in daylight. After storage in the dark or exposure to ammonia vapour, however, a red fluorescence occurs (Figure 3). The fluorescence disappears upon bleaching. If vermilion is mixed at low concentrations with white lead oil-paint, as is often done for flesh colours, a small 'shoulder' is observed on the white lead spectrum directly after the drying of the paint (Figure 4, Figure 5—curves 2a, b).

3 Discussion

The fluorescence of dried white lead oil-paint has been known for a long time. In early publications this fluorescence was connected with the formation of soaps between lead ions and fatty acids [3, 4]. Although these soaps do exist, they are not likely to fluoresce. Since the fluorescence of paints and of plain linseed oil reacts similarly to light and ammonia there is much more reason to believe that fluorescent products with structures such as those in unpigmented linseed oil films [2] are also formed in paints. Deformations in fluorescence spectra as observed, for instance, in cobalt violet and vermilion



a



b

Figure 1 Fluorescence spectra of oil-paints in daylight: (a) white lead and (b) cobalt violet oil-paint, after two and a half weeks (1), after seven weeks (2), after three months (3), after five months (4). Wavelength of excitation 365nm.

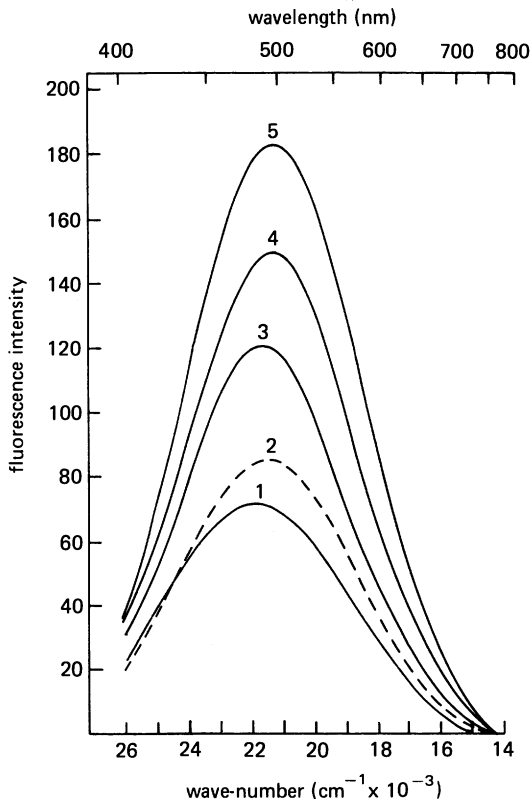


Figure 2 Fluorescence spectra of white lead oil-paint, after three and a half months daylight (1), three and a half months daylight + one week dark (2), three and a half months daylight + three weeks dark (3), three and a half months daylight + 10 weeks dark (4), three and a half months daylight + five months dark (5). Wavelength of excitation 365nm.

paints are probably caused by a partial reabsorption of fluorescence by the pigment. This is suggested by the shape of reflection spectra of these pigments (not published here) which correspond with the deformations in the fluorescence spectra.

Unfortunately, little is known about the chemical interactions between pigments and linseed oil. However, if we look at the pigments that generate fluorescence in paint it is striking that they nearly all contain metal ions such as cobalt, lead or manganese ions. These metal ions are known for their accelerating effect on the drying process of oils. When added to a paint in very high concentration, they accelerate degradation and yellowing of the paint layer [5]. Possibly, therefore, under the influence of these pigments, even at an early stage, degradation products are formed which have the ability to fluoresce.

Also, metal ions can have considerable influence on fluorescence of organic molecules by chelate formation, either enhancing it or completely quenching it [6]. Formation of such metal chelates between fluorescent degradation products and metal ions in oil-paints seems very likely and can explain the very different effects of pigments on the fluorescence of these degradation products.

4 Some picture surfaces

The optical density of most paint layers is very high

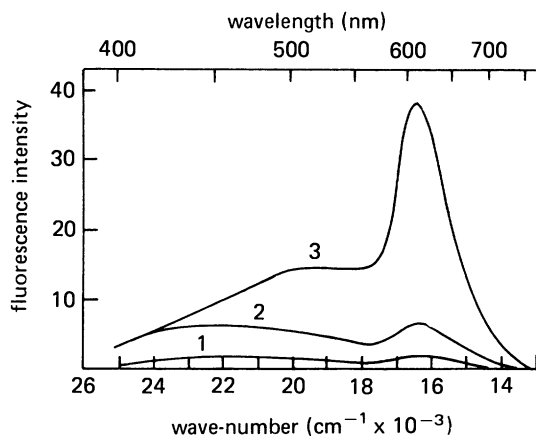


Figure 3 Fluorescence spectra of vermilion oil-paint, after two and a half weeks daylight (1), 15 months daylight (2), 13½ months daylight + seven weeks dark (3). Wavelength of excitation 365nm.

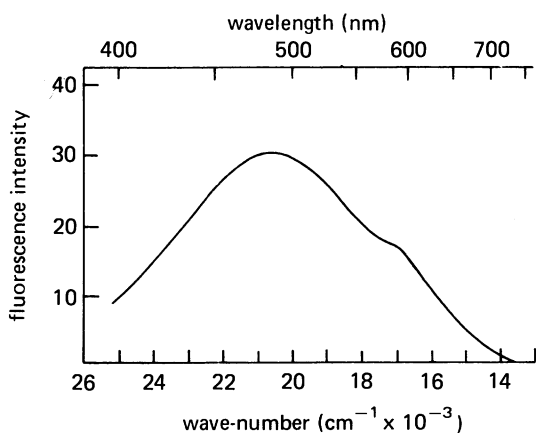


Figure 4 Fluorescence spectrum of a white lead oil-paint containing little vermilion (two and a half weeks daylight). Wavelength of excitation 365nm.

in the ultraviolet as in the visible part of the spectrum. Therefore, as a rule, absorption of ultraviolet light and fluorescence take place only in the outermost surface of the paint layer which was applied last. Varnish layers, on the contrary, are at least in part transparent to ultraviolet and visible light. Films of natural resins show an increasing absorption with decreasing wavelength. The older the film, the higher the absorption. Furthermore, absorption appears at increasingly longer wavelengths.

When ultraviolet light strikes a paint layer with an old varnish layer on top, fluorescence of both layers may be observed. The higher the absorption of the varnish layer, the less the fluorescence of the underlying paint layer, due to absorption both of the ultraviolet light and of the fluorescence (Figures 5, 6). In older pictures the parts containing white lead always appear bright in ultraviolet light (Figures 5, 6). In studying the fluorescence of a picture surface it can be helpful first to clean the surface from dirt, since the latter can severely obstruct the penetration of the ultraviolet radiation (Figure 6).

Great care should be taken in drawing conclusions from observations in ultraviolet light alone. The technique must be applied together with others. This is illustrated by the following examples.

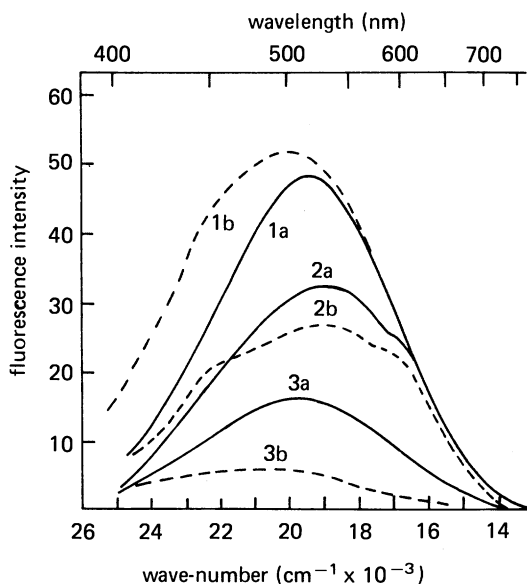


Figure 5 Fluorescence spectra of a nineteenth century oil-painting, before and after removal of the varnish layer; spot in white collar before (1a) and after (1b) cleaning, spot in flesh colour before (2a) and after (2b) cleaning, spot in black robe before (3a) and after (3b) cleaning. Microchemical analysis showed white lead in the collar and white lead and vermilion in the flesh colours. The robe contained mainly carbon pigments. Wavelength of excitation 365nm.

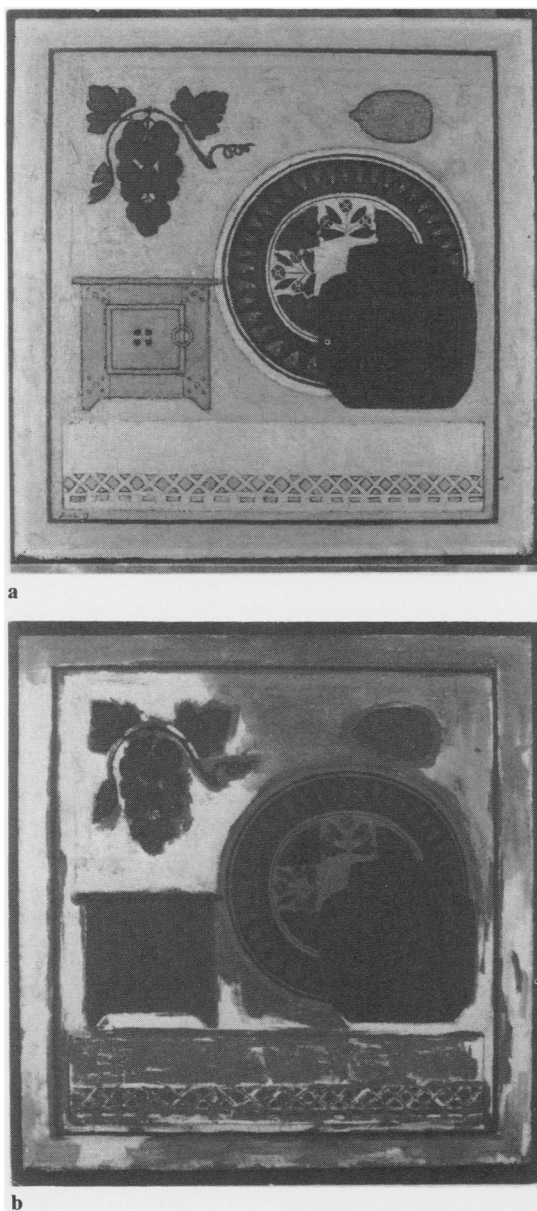


Figure 7 Oil-painting in normal light (a) and ultraviolet light (fluorescence) (b). Still life by Bart van der Leck, 1913. Oil-paint on canvas, unvarnished. Published by courtesy of the Rijksmuseum Kröller-Müller, Otterlo, Holland. Photography by J. J. Susijn, Rijksmuseum H. W. Mesdag, The Hague, Holland.

In a picture, some parts were strongly fluorescent but other parts that appeared the same in normal light were not (Figure 7). The differences in fluorescence intensity gave the impression of a picture that

was highly overpainted. However, careful examination of the surface with a microscope revealed that in some areas the strongly fluorescent paint overlays the weakly fluorescent, and in other places the reverse is the case. The artist has obviously used two kinds of paint. After pigment analysis the origin of the fluorescence differences was explained; the strongly fluorescent paint layers contained mainly zinc white, while in the weakly fluorescent ones zinc white and white lead were shown to be present in comparable amounts. It is important to notice that the 'dark' parts have a fluorescence intensity that can be called reasonably strong (Figure 8). The parts only appear dark in comparison to the other, still stronger, fluorescent parts.

In another picture a strong, light green, fluorescence and a red fluorescence were found (Figure 9). The composition of the paint layers was checked by X-ray fluorescence analysis directly on the picture surface. The light green fluorescence appeared at the white parts of the painting, which contained much zinc. Red fluorescence was found in yellow and various other areas. The yellow parts contained much zinc and much cadmium. The non-yellow parts that fluoresced red contained much zinc and various other elements. Although the maximum of the fluorescence spectra of the red fluorescence is at a somewhat shorter wavelength than has been found on cadmium pigments (Figure 10; see also Part I [1] Figure 3), one's first thought is that cadmium yellow is responsible for this fluorescence. However, in the non-yellow parts that fluoresced red no cadmium was found. A possible explanation for the red fluorescence is a zinc white fluorescence that is partly absorbed by other pigments.

5 Conclusion

The fluorescence of picture surfaces under ultraviolet light is a complicated matter which merits more attention from conservation scientists. This study shows that fluorescence of oil-paint layers is produced by the oil, since only a few pigments fluoresce. Natural resins in varnishes may also cause fluorescence. Fluorescence of these materials becomes stronger as degradation advances. Pigments have a strong influence on the fluorescence of linseed oil in paint layers, and may cause complicated fluorescence phenomena. Therefore, observations under ultraviolet light should be interpreted with care, preferably with additional information obtained through other examination techniques. Future research in this field should concentrate on discovering the exact nature of the fluorescent compounds in linseed oil and natural resins, and on the fluorescence of other painting materials, such as binding media other than oil.

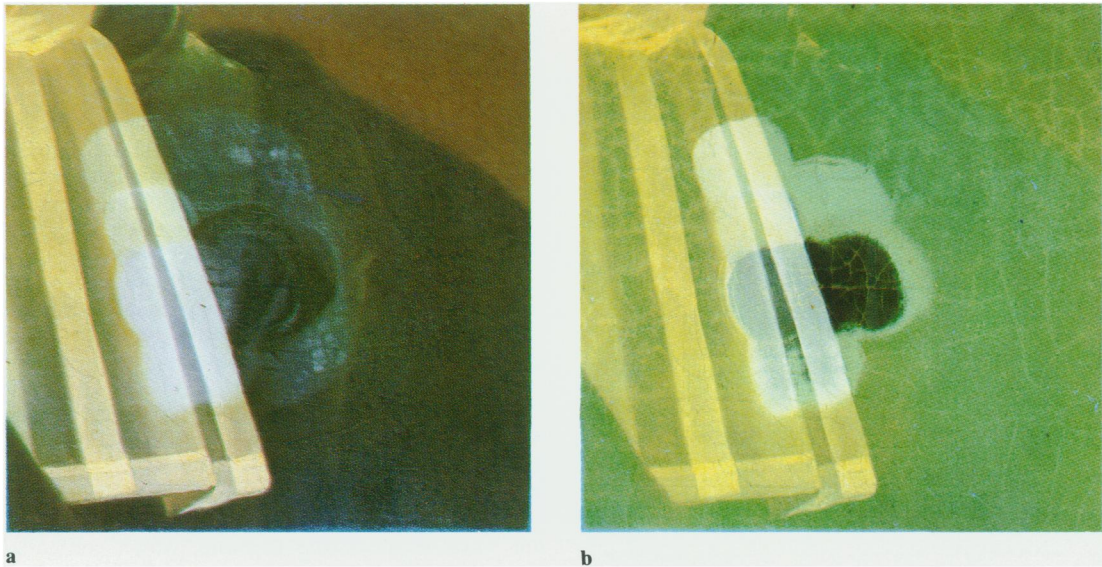


Figure 6 Detail of an oil-painting in normal light (a) and ultraviolet light (fluorescence) (b). Part of the surface was cleaned with a 'picture cleaner' and also the varnish layer was partly removed with an organic solvent. Photography by E. Klusman, Central Laboratory.

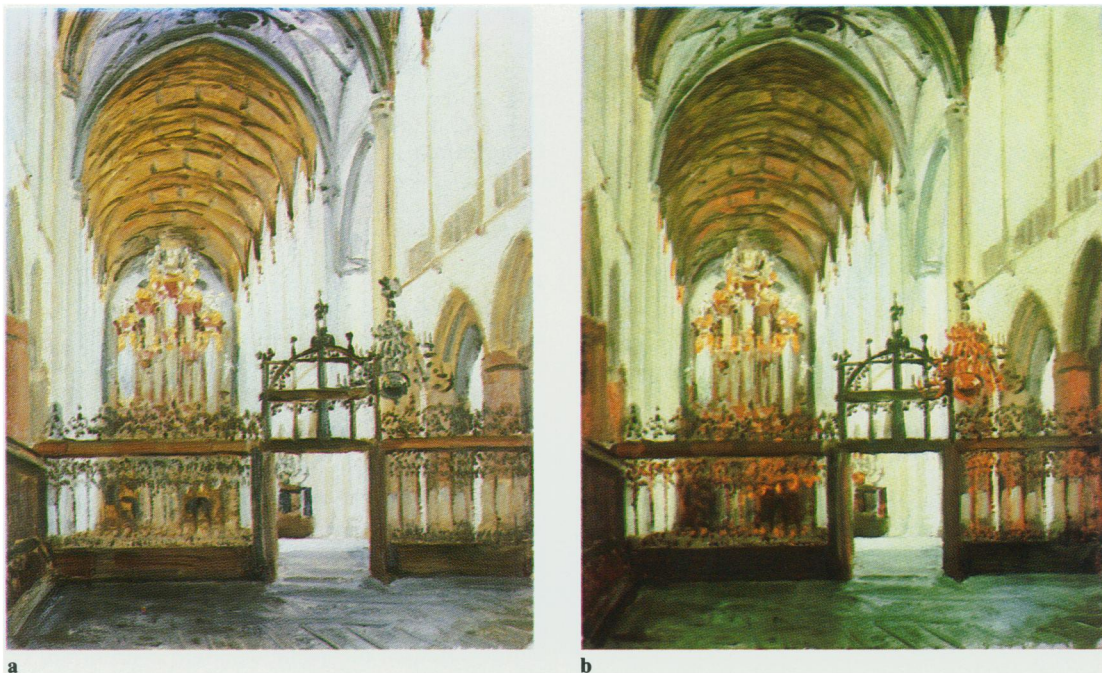


Figure 9 Oil-painting in normal light (a) and ultraviolet light (fluorescence) (b). Church interior by M. J. Richters, undated. Oil-paint on canvas, unvarnished. Published by courtesy of the Dienst voor Verspreide Rijkscollecties, The Hague, Holland. Photography by E. Klusman, Central Laboratory.

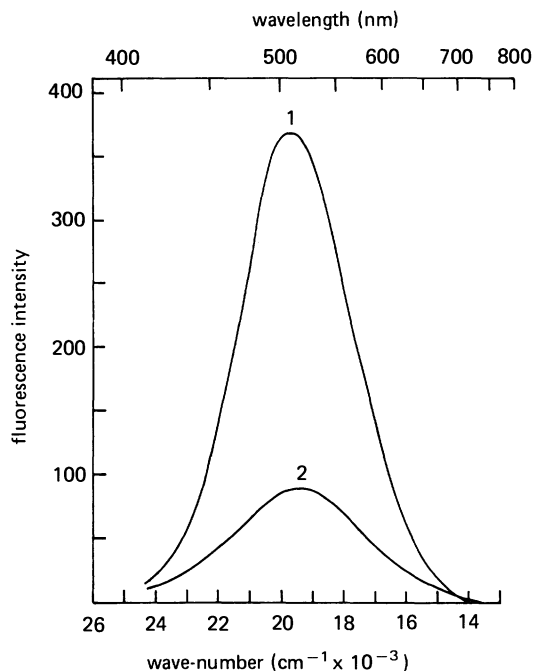


Figure 8 Fluorescence spectra of the picture of Figure 7: strongly fluorescent part in the background (1), 'weakly' fluorescent part in the background (2). Wavelength of excitation 365nm.

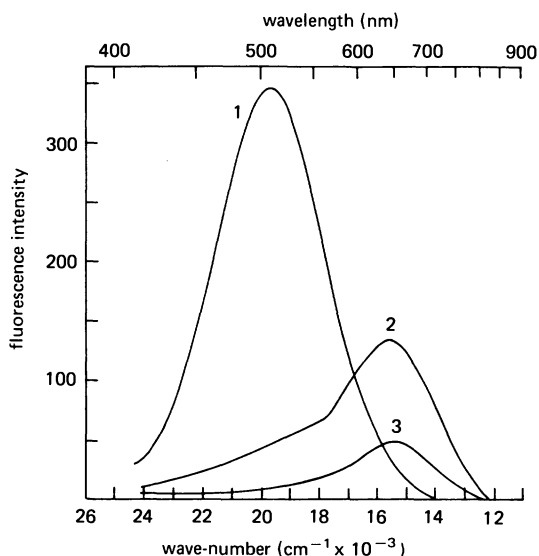


Figure 10 Fluorescence spectra of the picture of Figure 9: fluorescence of a white spot (1), red fluorescence of a yellow spot (2), red fluorescence of a grey spot (3). Wavelength of excitation 365nm.

6 Experimental

Fluorescence spectra and X-ray fluorescence spectra were determined with the equipment described in a previous paper [1]. Oil-paint was made by grinding pigment(s) with linseed oil until a stiff paste was obtained. For this a glass plate and a glass muller were used. Also, a small machine consisting of two glass plates, one grinding on top of the other, was used for this purpose.

Acknowledgements

This work was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). The author is grateful to Mrs Karin Groen for doing microchemical analysis of pigments, to Mr Peter Hallebeek for doing the X-ray fluorescence analysis, to Dr J. R. J. van Asperen de Boer for helpful discussions, to Dr M. Kirby Talley for his stimulating help during the preparation of this publication, and to Professor Dr G. Dijkstra and Ir J. Lodewijks for making this study possible and for their support throughout the work. Publication of colour photographs was made possible by a subsidy from the Prins Bernhard Fonds.

References

- 1 DE LA RIE, E. R., 'Fluorescence of paint and varnish layers (Part I)', *Studies in Conservation* **27** (1982) 1-7.
- 2 DE LA RIE, E. R., 'Fluorescence of paint and varnish layers (Part II)', *Studies in Conservation* **27** (1982) 65-69.
- 3 EIBNER, A., 'Lichtwirkungen auf Malerfarben VII, Die Lumineszenzforschung im Dienst der Bilderkunde und Anstrichtechnik', *Chemiker Zeitung* (1931) 593-604, 614-615, 635-637, 655-656.
- 4 EIBNER, A., 'Les rayons ultraviolets appliqués à l'examen des couleurs et des agglutinants', *Museion* **21-22** (1933) 32-68.
- 5 DOERNER, M., *The Materials of the Artist*, Hart-Davis MacGibbon Ltd, London (1973) 107-108.
- 6 GUILBAULT, G. G., *Practical Fluorescence*, Marcel Dekker Inc., New York (1973) 120-122, 221-264.

E. RENÉ DE LA RIE studied physical chemistry at the University of Amsterdam; joined the Central Laboratory in Amsterdam to work on a subsidized research project; worked during the last few years for a newly established training programme for conservators in Amsterdam; and recently joined the Paintings Conservation Department of the Metropolitan Museum of Art in New York as research chemist. Author's address: Metropolitan Museum of Art, Paintings Conservation Department, Fifth Avenue at 82nd Street, New York, NY 10028, USA.

Résumé—On a étudié à l'aide d'un spectromètre de fluorescence, la fluorescence sous ultraviolet de peintures à l'huile et de quelques surfaces picturales. L'apparition de la fluorescence et le jaunissement de l'huile de lin se sont révélés être grandement influencés par la nature des pigments. Certains ont un effet inhibiteur, d'autres un effet promoteur, et d'autres n'ont aucun effet. A la lumière de ces résultats et de ceux déjà publiés, on discute le phénomène de fluorescence de quelques surfaces picturales.

Zusammenfassung—Die Fluoreszenz unter ultraviolettem Licht von Ölfarben und einigen Bildoberflächen sind mit einem Fluoreszenzspektrometer untersucht worden. Die Entwicklung von Fluoreszenz und die Vergilbung von Leinöl scheinen weitgehend durch das Vorhandensein von Pigmenten beeinflusst zu werden. Manche Pigmente haben eine unterdrückende, andere eine verstärkende Wirkung und andere wieder sind neutral. Angesichts dieser Ergebnisse und des zuvor veröffentlichten Materials wird die Fluoreszenz einiger Bildoberflächen besprochen.