Chapter V

Ultraviolet radiation fluorescence of paint and varnish layers

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1. INTRODUCTION*

The ultraviolet lamp is a common tool for the examination of painted surfaces of art objects such as easel paintings and wall paintings[1-13]. Ultraviolet light excites fluorescence of certain materials on the surface. Different materials may exhibit different colours and intensities of fluorescence, which can provide information on the condition of the paint surface. Later additions may be observed in this way, because new retouchings and overpaints often appear dark under ultraviolet light, whereas old paint layers may show considerable fluorescence. Old varnish layers generally fluoresce strongly ; thus, the use of an ultraviolet lamp during their removal can be helpful (Fig. 1). For documentary purposes, fluorescence is often recorded photographically[12-15].

The ultraviolet lamp has been applied to the examination of old pictures ever since it became commercially available around 1925. Oddly enough, no studies of interest on the fluorescence of painting materials have been published since the pioneer works of Eibner and others appeared around 1930[2-4, 16-20].

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Fig. 1. Oil painting in normal light (a) and in ultraviolet light (b). The strong fluorescence of the varnish layer is clearly visible. At the lower part of the inner oval the portrait was presumably partly cleaned, resulting in a less strong varnish fluorescence. The strong fluorescence of white lead containing oil paint (collar, hair and flesh colours) appears through the varnish layer. The dark spots in the collar are retouchings. Portrait of Casper Barlaeus, probably a seventeenth century copy of a miniature by Gerard ter Borch. Oil paint on panel, 17 x 12 cm. Published by courtesy of the University of Amsterdam. Photography by E. Klusman, Central Laboratory.

2. The phenomenon of fluorescence

When electromagnetic radiation, such as ultraviolet light, impinges upon matter, part of it can be absorbed, causing electronic transitions in some of the molecules of the material. Such *excited* molecules rapidly lose their excess electronic energy by conversion into other forms of energy, such as vibrational energy, or it may be partly emitted as radiation. Simplified, this process can be described as follows (see also the diagram in Fig. 2). Most molecules have a singlet ground state (S_0), that is, a ground state with paired electron spins, and absorption takes place from this ground state to a singlet excited state (S_1, S_2, etc.). Superimposed on these electronic states are the vibrational states. Normally, an excited molecule returns immediatly and without emission of radiation to the lowest vibrational state of the first excited singlet state S_1 (within about 10^{-12}sec.). Transition from S_1 to S_0 may take place through the

emission of radiation, the process being called *fluorescence* (occurring within about 10^{-8}sec.).

Because of this, fluorescence is always of longer wavelength than the absorbed radiation (Stokes rule). Moreover, fluorescence in one compound takes place at a fixed wavelength, independent of the wavelength of the radiation that is absorbed.

It should be pointed out that most substances do not fluoresce, which implies that the transition S_1—S_0 can also occur without the emission of radiation. A third possibility occurs when so-called 'intersystem crossing' from S_1 to T_1, the first excited triplet state (a state with parallel electron spins), takes place. This state is between S_1 and S_0. From this triplet state, too, the molecule returns to the ground state S_0, without or with the emission of radiation, which is then called *phosphorescence*. The process of phosphorescence is much slower than that of fluorescence and can last up to several seconds or even longer, resulting in a visible afterglow.

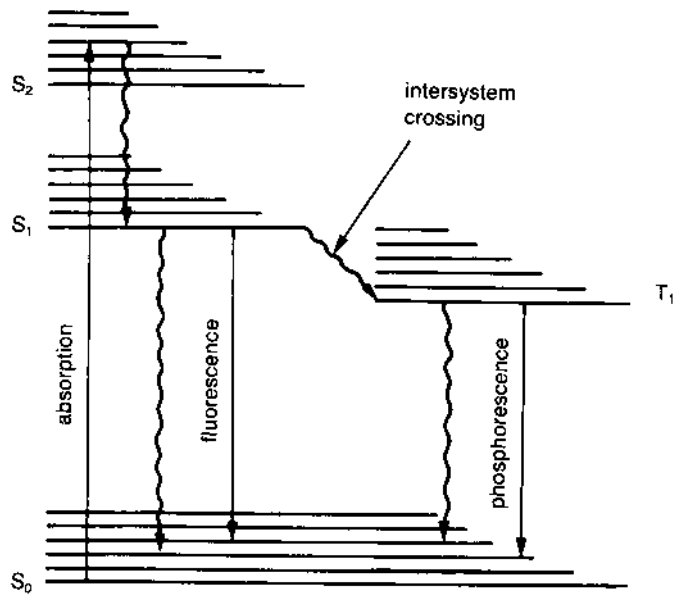

Fig. 2. Scheme showing absorption and emission processes. ⟿ = radiationless transition. This diagram is highly simplified. The radiationless transitions do not occur in one step as might be concluded from the picture.

Most fluorescent compounds are organic compounds ; in inorganic compounds fluorescence is a rare phenomenon.

In organic molecules π-electrons and, occasionally, nonbonding (n-) electrons, especially those in conjugated and aromatic systems, are the ones involved in absorption and emission processes in the near ultraviolet (above 200 nm) and visible region.

Inorganic crystalline compounds may show fluorescence or phosphorescence, although this is very often associated with irregularities in the crystal structure such as vacancies and impurities. These act as luminescence centres, and can be created on purpose in the manufacture of phosphors. These phosphors are used, for example, in fluorescent lamps.

Strong fluorescence occurs in a great number of metal chelates, which are inorganic ions combined with organic ligands. The formation of these fluorescence chelates is used in analyzing many inorganic ions.

Fluorescence, if in the visible part of the electromagnetic spectrum, can be observed with the naked eye. It must be clear, however, that for more precise information the fluorescence spectrum should be recorded. Descriptions of fluorescence spectrometers can be found in the literature[21].

Basically, they are composed of a unit which produces monochromatic exciting radiation and a unit which analyses the fluorescent light.

3. Results of measurements on pigments

Although fluorescence colours of a large number of pigments have been described by some authors[20, 22], only a few pigments with a fluorescence of considerable intensity were found during the present study. These pigments are : zinc white, cadmium yellows, oranges and reds and genuine madder. All other pigments that were studied lacked fluorescence or showed a very weak fluorescence. These pigments include : ochres, siennas, umbers, verdigris, copper resinate, minium, bone black, viridian, malachite, azurite, Prussian blue, green earth, white lead and titanium white.

The fluorescence of zinc white is yellow-green. The spectrum consists of a broad, unstructured band (Fig. 3a). Between samples of various origin little difference could be discovered. A sample of reagent grade zinc oxide in practice fluoresces in much the same way as the zinc white samples of various origins. On some picture surfaces, however, a fluorescence originating from zinc white has been found which has a considerably higher intensity than that of the samples.

The fluorescence of cadmium pigments falls in the red and infrared part of the electromagnetic spectrum.** The fluorescence spectra consist of relatively narrow bands (Fig. 3b, c). The bands shift with the colour of the pigments ; those of the cadmium reds lie at longer wavelengths than those of the oranges, which occur at longer wavelengths than those of the yellows. However, in samples of different origin, different fluorescence maxima and

** The wavelength area in which the emissions of the cadmium pigments fall explains the results obtained when photographing this fluorescence with infrared sensitive film.

marked variation in the intensities of the fluorescence were found. Moreover, some cadmium pigments as well as reagent grade cadmium sulphide did not fluoresce.

Genuine madder, prepared from the madder root, fluoresces with a red colour. The spectrum consists of a relatively narrow band (Fig. 3d). Among samples of various origin, small differences in the wavelength of the fluorescence maxima and great differences in the fluorescence intensities were found.

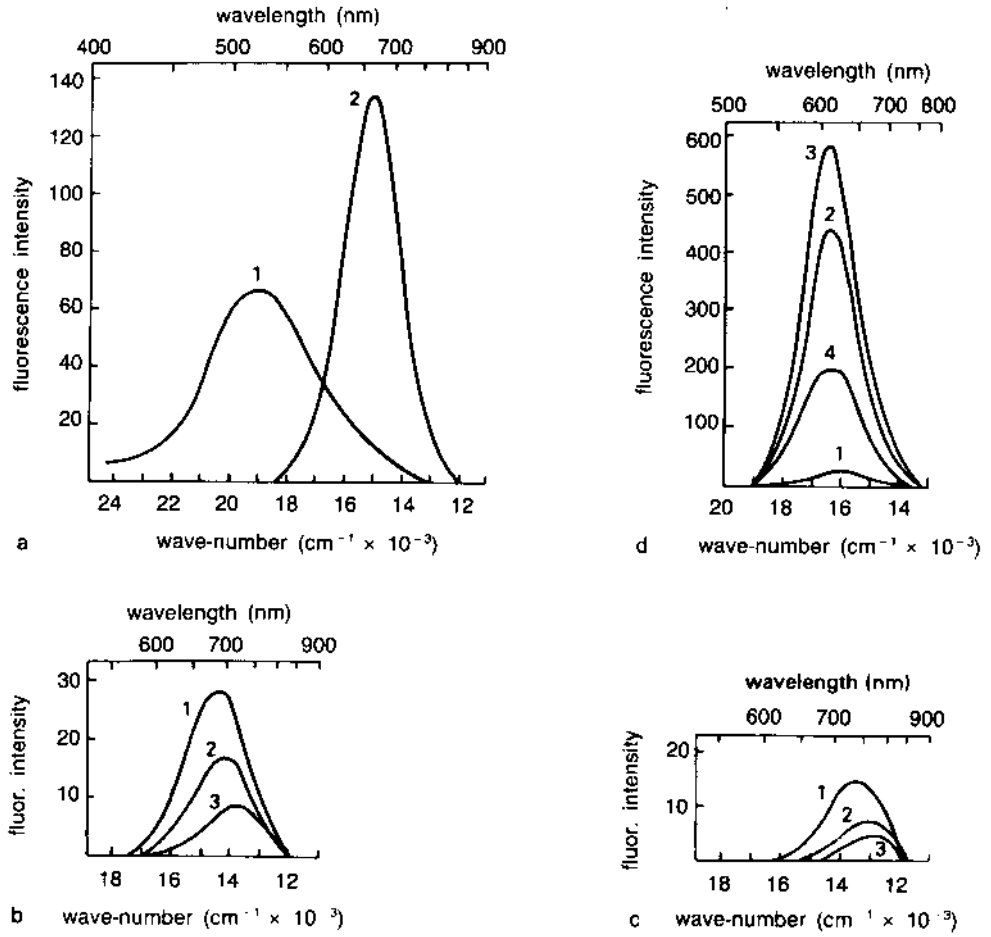

Fig. 3. Fluorescence spectra of pigments : (a) zinc white from van der Linde, Amsterdam (1) and cadmium yellow lemon from the Oudt Hollandse Olieverven Makerij (OHOM), Scheveningen, Holland (2) ; (b) cadmium yellow light (1), middle (2) and dark (3) from OHOM ; (c) cadmium orange (1), cadmium red light (2) and dark (3) from OHOM ; (d) rose madder (1) and pink madder (2) from C. Roberson & Co. Ltd, London, 1935, madder lake prepared by A.P. Laurie (3) and rose madder prepared by M. Cowell (4). (All the madders were kindly supplied by the Courtauld Institute of Art in London). Wavelength of excitation 365 nm.

To date there has been no indication that changes occur in the course of time in the fluorescence characteristics of pigments. The fluorescence spectra of the pigments are independent of the wavelength of excitation, which means that pigments fluorescing at long wavelengths — madder and cadmium pigments — can also be excited by visible light.

It is not surprising that most pigments, being inorganic compounds for the greater part, do not fluoresce. The question arises as to why some of them do show fluorescence.

The main component of zinc white is zinc oxide (ZnO) ; cadmium yellow, orange and red mainly consist of cadmium sulphide (CdS) or cadmium selenium sulphide, a complex compound of cadmium sulphide and cadmium selenide (CdS/CdSe). Zinc oxide and cadmium sulphide belong to a class of compounds that are known to be made easily luminescent[23]. In pure form the crystals do not fluoresce. Very small quantities of impurities make the compounds strongly fluorescent. No regular differences appear in the composition of the fluorescent and the non-fluorescent cadmium pigments. However, impurities at concentrations much below those that can be detected by X-ray fluorescence analysis can make cadmium sulphide fluorescent.

The fluorescence of genuine madder is of a different nature. Its main colouring matter is alizarin, although other compounds, of which purpurin is the most important, are present as well. Alizarin and purpurin are organic dyestuffs of the hydroxy-anthraquinone family.

Lake pigments are prepared by precipitation of the dyestuffs on an inorganic base such as calcium sulphate, barium sulphate or aluminium hydroxide.

Since the end of the last century alizarin has also been prepared synthetically. Because pigments prepared with alizarin do not show fluorescence, it has been stated that the fluorescence in madder originates from purpurin[2].

Purpurin is able to fluoresce when combined with other substances, such as a solvent, a paper substrate or an inorganic base such as $Al(OH)_3$. The fluorescence of genuine madder, therefore, most likely originates from purpurin chelates. Metal chelates of hydroxy-anthraquinones are known for their ability to produce a strong and pH-dependent fluorescence[21b]. The observed differences in the fluorescence spectra of madder samples of different origin might well be caused by the use of different bases and by varying purpurin content.

4. Fluorescence of linseed oil and of some natural resin films

The fluorescence intensity of a wet or freshly dried linseed oil film is negligible. When the film is stored in daylight for three to four weeks a very

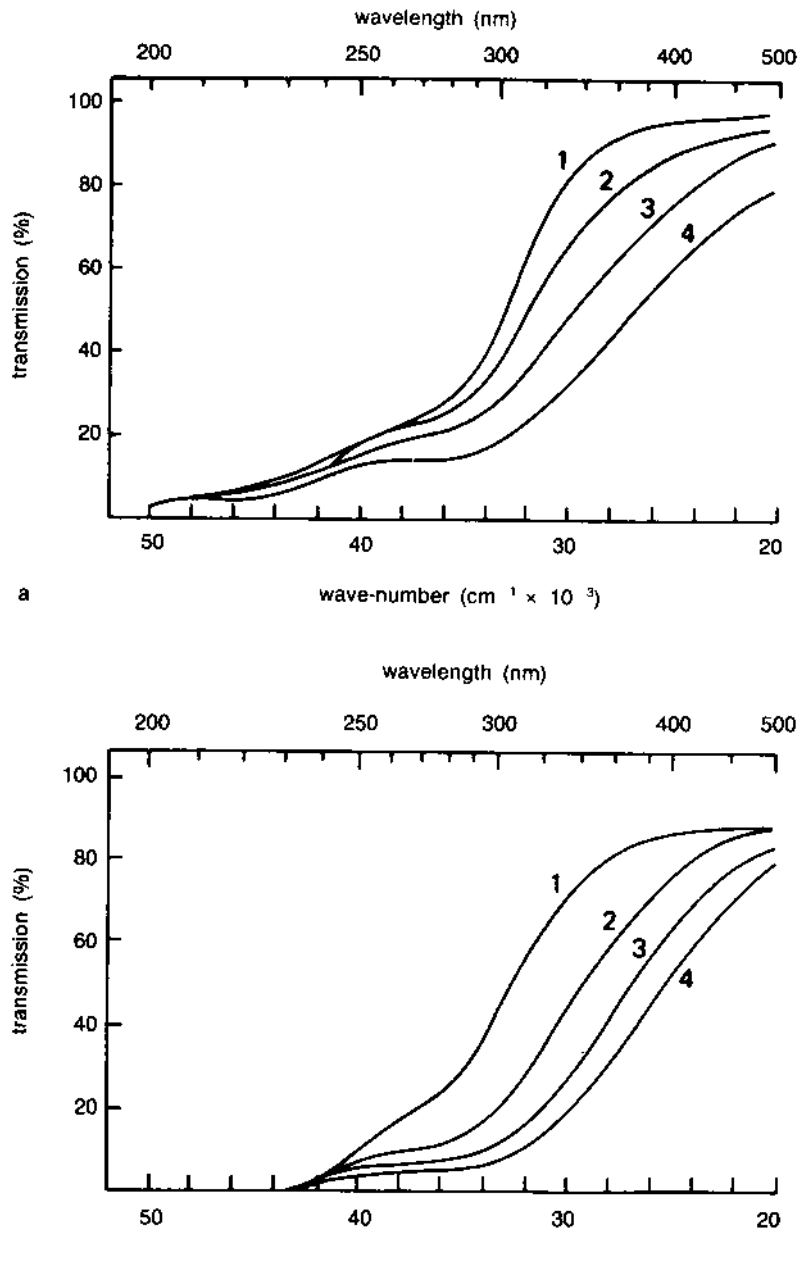

Fig. 4. Transmission spectra of linseed oil films (thickness ± 25 μm) : (a) three weeks daylight (1), three weeks daylight + nine days dark (2), three weeks daylight + one month dark (3), three weeks daylight + three months dark (4) ; (b) four weeks daylight (1), four weeks daylight + 10 minutes NH_3, (2), four weeks daylight + 10 minutes NH_3, + one day dark (3), four weeks daylight + 10 minutes NH_3, + 11 days dark (4).

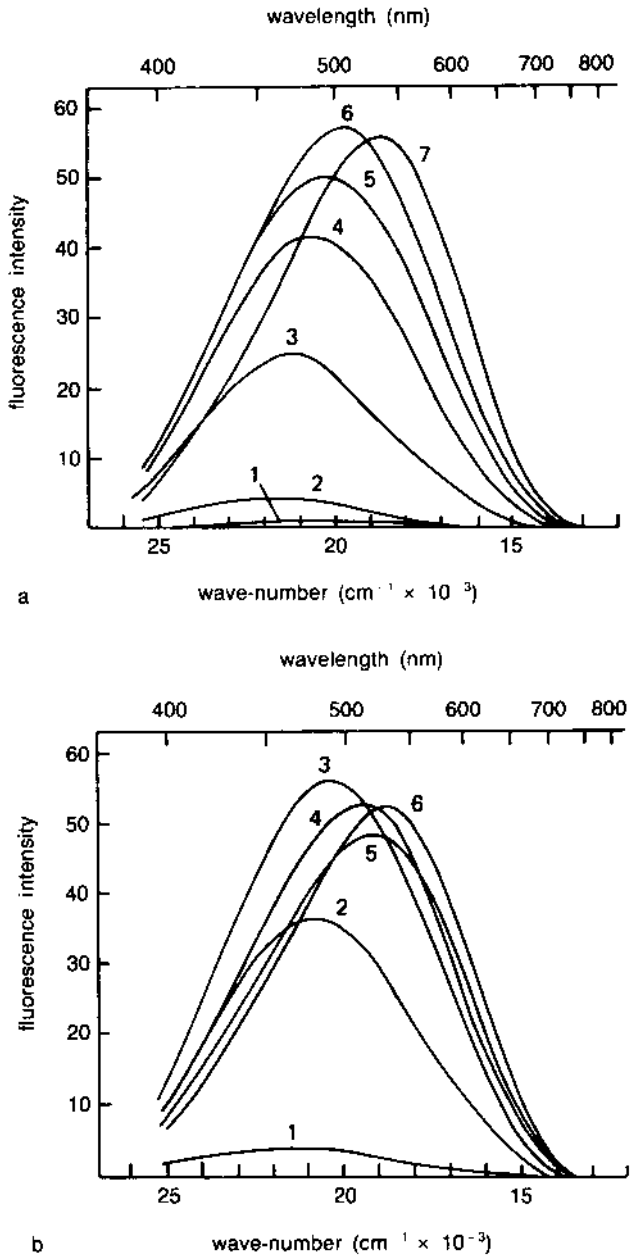

Fig. 5. Fluorescence spectra of linseed oil films (thickness 25-50 μm) : (a) wet film (1), dry film, five weeks daylight (2), five weeks daylight + 10 days dark (3), five weeks daylight + five weeks daylight + four months dark (6), five weeks daylight + seven months dark (7) ; (b) one month daylight (1), one month daylight + 10 minutes NH_3 (2), one month daylight + 10 minutes HN_3 + one day dark (3), one month daylight + 10 minutes HN_3 + four days dark (4), one month daylight + 10 minutes HN_3 + 11 days dark (5), one month daylight + 10 minutes NH_3 + one month dark (6). Wavelength of excitation 365 nm.

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 region decreases strongly, a phenomenon observed visually as yellowing (Fig. 4). The fluorescence spectrum consists of a broad, structureless band covering the entire visible spectrum (Fig. 5) and showing a slight sensitivity to variation of the excitation wavelength between 313 and 436 nm. 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. 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.

Thin resin films basically show the same phenomena as linseed oil films, that is, fluorescence intensifies and occurs at longer wavelenghts as yellowing proceeds. 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. Yellowing in the dark takes place very slowly.

It appears that the fluorescence of linseed oil is somehow related to the yellowing process. The yellowing*** 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[24]. The most probable explanation for the formation of coloured compounds is polymerization through aldol-condensation of unsaturated carbonyl compounds[25-26], process that is catalyzed by, among others, volatile nitrogen containing bases such as ammonia[27]. 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[28], an yellowed films appear to have an increased nitrogen content[29]. 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 methyllinolenate[30], forms fluorescent compounds with amino group containing substances[31]. These fluorescent

*** 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.

compounds all contain the chromophore 1-amino-3-iminopropene (NH — CH = CH — CH = N). 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[32], 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.

5. The fluorescence of 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.

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 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

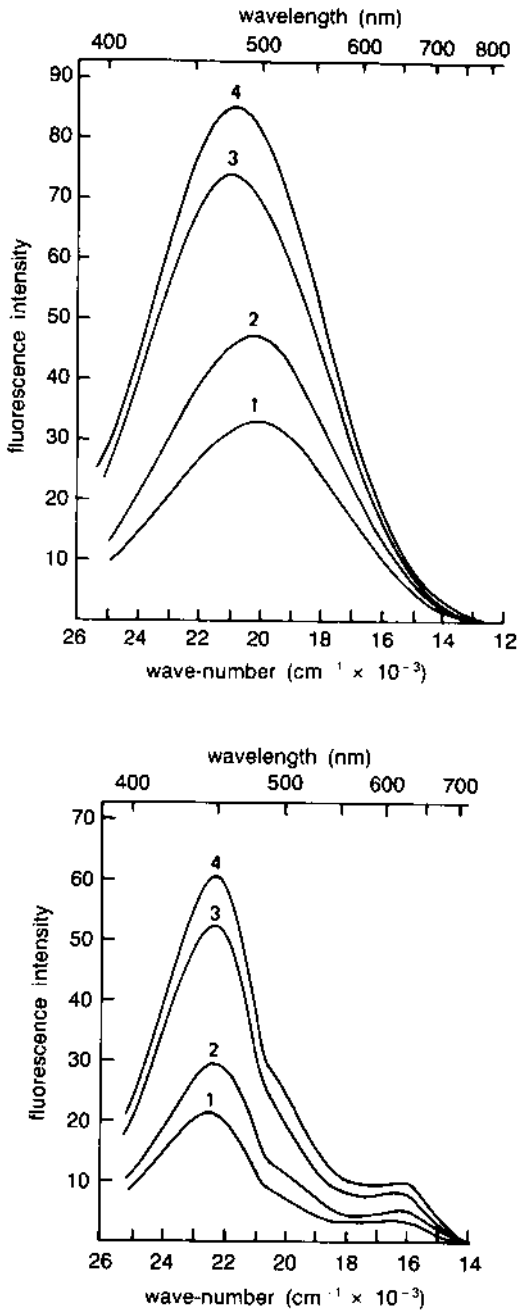

Fig. 6. Fluorescence spectra of oil-paints in daylight : (a) white lead and (b) cobalt violet oil-paint, after two and a half weeks (1), after seven weeks (2), after three months (3), after five months (4). Wavelength of excitation 365 nm.

visible spectrum. The other pigments generate a blue fluorescence in the oil (Fig. 6). The fluorescence intensity of a white lead oil-paint increases upon storage in daylight, while the maximum shifts slightly to shorter wavelengths (Fig. 6a). 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). 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.

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[2-3]. 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 are also formed in paints. Deformations in fluorescence spectra as observed, for instance, in cobalt violet and vermilion 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[33]. 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[21a]. 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.

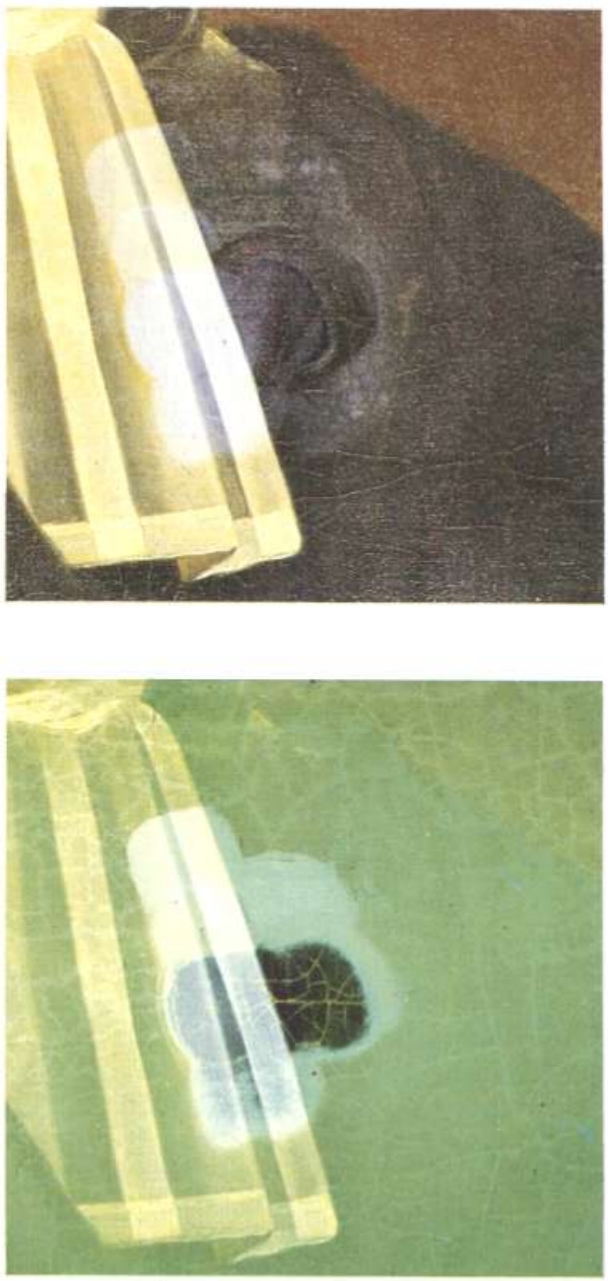

Fig. 7. Detail of an oil-painting in normal light (a) and ultraviolet light (fluorescence) (b). Part of the surface was cleaned with a 'picture cleaner' and also the varnish layer was partly removed with an organic solvent. Photography by E. Klusman, Central Laboratory, Amsterdam.

6. Picture surfaces

The optical density of most paint layers is very high 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 (Fig. 7). In older pictures the parts containing white lead always appear bright in ultraviolet light (Fig. 7). 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 (Fig. 7).

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 example.

In a picture, some parts were strongly fluorescent but other parts that appeared the same in normal light were not (Fig. 8). 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 (Fig. 9). The parts only appear dark in comparison to the other, still stronger, fluorescent parts.

7. 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

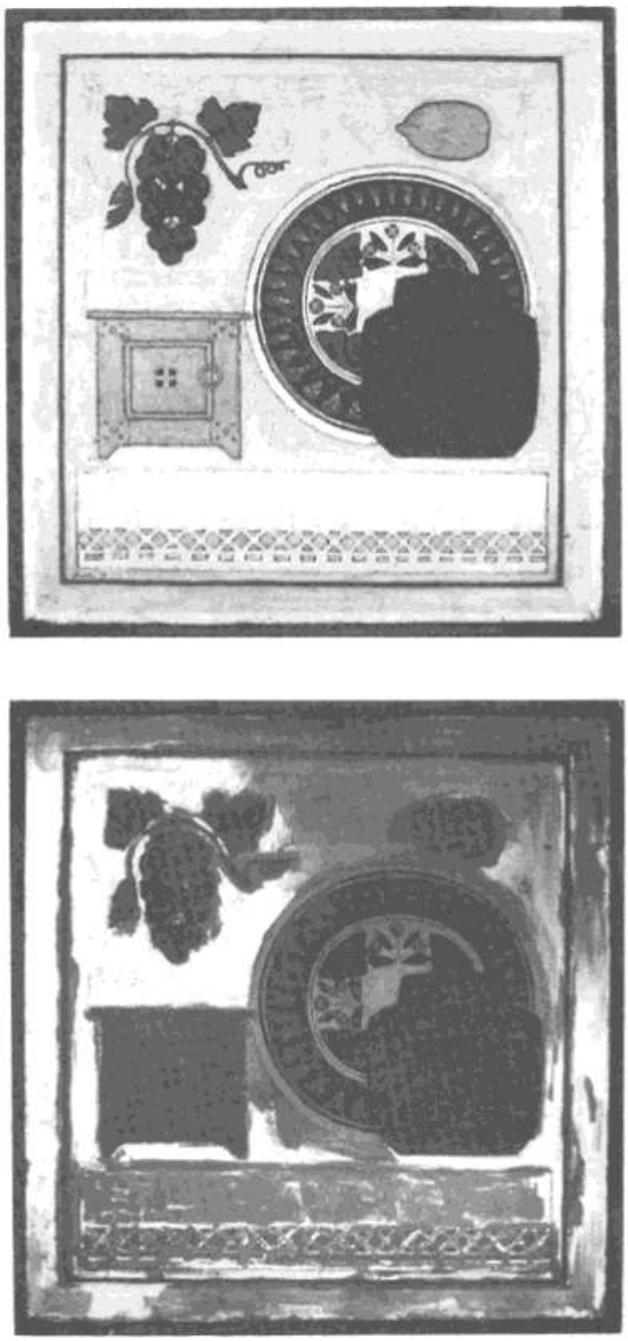

Fig. 8. Oil-painting in normal light (a) and ultraviolet light (fluorescence) (b). Still life by Bart van der Leck, 1913. Oil-paint on canvas, unvarnished, Published by courtesy of the Rijksmuseum Kroller-Müller, Otterlo, Holland. Photography by J.J. Susijn, Rijksmuseum H.W. Mesdag, The Hague, Holland.

advances. Pigments have a strong influence on the fluorescence of linseed oil in paint layers, and may cause complicated fluorescence phenomena. Therefore, observation under ultraviolet light should be interpreted with care, preferably with additional information obtained through other examination techniques.

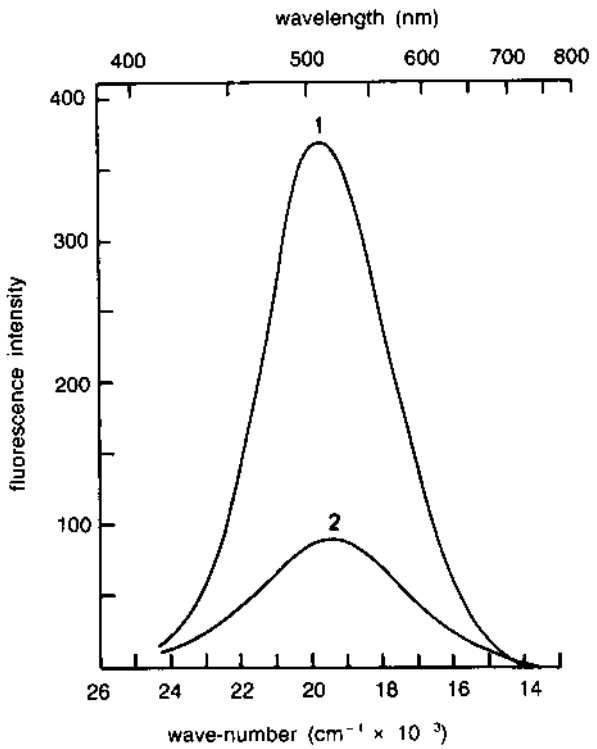

Fig. 9. Fluorescence spectra of the picture of Figure 8 : strongly fluorescent part in the background (1), 'weakly' fluorescent part in the background (2). Wavelength of excitation 365 nm.

8. NOTES

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9. RÉSUMÉ

Dans le cadre d'une étude portant sur la fluorescence des couches de peinture et de vernis sous lumière ultraviolette, on a mesuré la fluorescence d'un certain nombre de pigments à l'aide d'un spectromètre de fluorescence. De l'ensemble des pigments examinés, seuls le blanc de zinc, les pigments au cadmium et la laque de garance ont une fluorescence très importante. On trouvera discutée la physico-chimie de la fluorescence en général et celle des pigments en particulier.

Ensuite 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.

Enfin, à l'aide d'un spectromètre de fluorescence, on a étudié 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, on discute du phénomène de fluorescence de quelques surfaces picturales.