147. *Fading and Tendering Activity in Anthraquinonoid Vat Dyes. Part II.*[1] *Fluorescence, Absorption Spectra, and Stability to Light of Dyed Films.*

By J. J. Moran and H. I. Stonehill.

A modification of the Beer–Lambert law is derived, which allows for the effect of fluorescence. The modified law is verified by absorption measurements on dyed cellulose films. A simple method, involving comparison of absorption spectra obtained with dispersion respectively before and after absorption, is employed to detect the fluorescence of dyed cellulose acetate films, and to locate approximately the wavelength regions of fluorescence excitation and emission. This method is also used in investigations of fading and tendering (oxidative degradation) of these films, for which purpose it is more sensitive than conventional spectrophotometric or visual examination. There is no simple correlation of fluorescence with molecular structure for the dyes examined, or of either fluorescence or absorption spectra with fading and tendering activity.

In Part I [1] it was shown that fluorescence of vat dye solutions caused deviations from Beer's and Lambert's laws on use of the usual type of photoelectric absorption spectrophotometer with no dispersion (" monochromatisation ") after absorption, *e.g.*, the Hilger Uvispek instrument. Fluorescence excited by monochromatic absorbed light reaches the non-selective photocell in this type of instrument and affects it as if it were unabsorbed incident light, causing spuriously low optical density readings. This effect, which has been discussed by Braude, Fawcett, and Timmons [2] and by Ovenston,[3] could be virtually eliminated by monochromatisation both before and after absorption, or by balancing out the fluorescence-induced fraction of the photocell current by the output of a second photocell excited by light collected at 90° to the direction of the incident light.

In this paper, (i) the Beer–Lambert law is modified to allow for fluorescence, and the modified law is verified by absorption measurements on dyed cellulose films, (ii) a method involving comparison of absorption spectra obtained with dispersion respectively before and after absorption is employed to detect the fluorescence of dyed cellulose acetate films, and to locate approximately the wavelength regions of fluorescence excitation and emission, and (iii) this method is used to study fading and tendering (oxidative degradation) of the dyed films.

Experimental

The purification of the dyes has been described.[1] To prepare dyed films, 50 × 20 cm. sheets of glycerol-plasticised regenerated cellulose, 0·0025—0·0625 mm. thick (British Sidac Ltd.) and somewhat smaller sheets of unplasticised commercial cellulose acetate, *ca.* 1 mm. thick, were dyed for 1—2 hr. in 50 ml. of 0·05N-sodium hydroxide containing 3—4 g. of sodium dithionite and *ca.* 0·5 g. of dye at 50—70°, depending on the dye.[4] The films were then washed in running water and steamed for 15 min. The thick acetate films dried satisfactorily in the air, but the thinner cellulose films tended to wrinkle. They were therefore stretched over a flat glass plate while wet, smoothed with a glass rod, folded in half four times, smoothing after each fold, stretched over a 10 × 4 cm. flat glass plate, secured by rubber bands, and allowed to dry in the air; the resulting homogeneous laminated films could be progressively decreased in thickness by peeling off layers. Unlike the acetate, the cellulose film absorbed ultraviolet light strongly because of the plasticiser present.

[1] Part I, Moran and Stonehill, preceding paper.
[2] Braude, Fawcett, and Timmons, *J.*, 1950, 1019; Braude and Timmons, *Photoelectric Spectrometry Group Bull.*, 1953, No. 6, 139.
[3] Ovenston, *Photoelectric Spectrometry Group Bull.*, 1953, No. 6, 132.
[4] Fox, " Vat Dyestuffs and Vat Dyeing," Chapman and Hall, London, 1946.

For determining spectra with the films in the normal or " *a* " position of the Hilger Uvispek instrument (between prism and photocell), dyed and reference undyed films, held flat in suitable sheet-metal frames which exposed rectangular areas similar to those of absorption cells, were placed in the holder normally occupied by absorption cells. Spectra were also determined with the films in the " *b* " position (between light source and prism), the metal frames being held in a vertical plane perpendicular to the light beam and arranged so that either the dyed or the undyed film could be interposed in the beam. The frames were painted with matt optical-black paint to minimise reflection. Errors in the " *b* " position due to defocusing of the lamp-filament image, diffraction, etc., were minimised by varying the position of the lamp to obtain maximum photocell response; matching of the apertures of the two frames was checked by photocell response. A cell containing sodium nitrate solution was interposed between the lamp housing and the films in the " *b* " position to filter out any ultraviolet light and to absorb heat, thus preventing undue rise in vibrational energy levels. A didymium test filter was used to check the equivalence of spectra in the " *a* " and the " *b* " position for a non-fluorescent system.

Fading tests were carried out on long strips of dyed cellulose acetate films, which were cut into four equal parts. The absorption spectrum of one part was determined immediately after dyeing, and that of a second part at intervals over a period of 2 months during which the sample

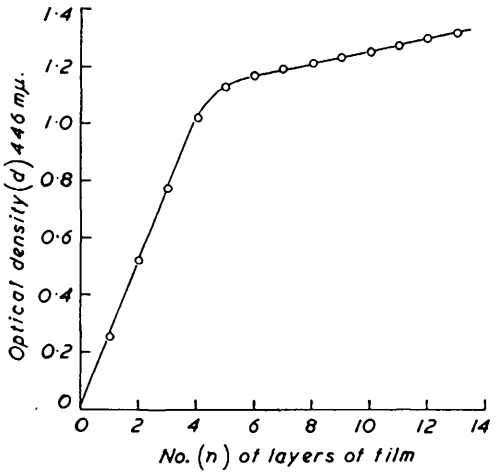


FIG. 1. *Effect of fluorescence on optical density of various thicknesses of cellulose film dyed with Cibanone Golden Yellow GK.*

was irradiated by a Point-o-Lite arc. The arc was placed at the focus of a parabolic reflector, vertically above the film, which rested on a glazed white porcelain slab. To control humidity, a large flat dish of water was held beneath the porcelain slab, and a slow stream of air was directed by a fan partly on the films and partly on the water surface. The fading-test apparatus was housed in a wooden box; an enclosed thermometer showed no signficant departure from 24° during tests. A third portion of dyed film was exposed in the fading-test apparatus while shielded from light, in order to test the effect of atmospheric weathering. The first and the fourth portion of the film were used to examine semiquantitatively the effects of soaping and soaking in dilute hydrogen peroxide before irradiation.

RESULTS AND DISCUSSION

(i) *Deviation from Beer's and Lambert's Laws due to Fluorescence.*—Fig. 1 is a typical plot of optical density d against thickness l (expressed as the number n of equal layers in the laminate) for cellulose film dyed with Cibanone Golden Yellow GK, held in the normal (" *a* ") position, the monochromator of the Uvispek being set at 446 mμ, an absorption maximum for the system. It consists of two essentially linear sections of different slope, joined by a smooth curve. Similar graphs were obtained when d was plotted against l for various constant concentrations c for chlorobenzene solutions of the same dye at absorption peak wavelengths 411, 438, and 466 mμ, the deviations from linearity (Lambert's law) being most pronounced at 456 mμ and least at 411 mμ. The data of

these plots also revealed a similar deviation from the linear Beer's law relation between d and c at constant l. Similar results were obtained with d–l plots for chlorobenzene solutions of several other vat dyes listed in Table 1 of Part I, and for p-benzoquinone in n-hexane, at visible absorption-peak wavelengths. It may be shown as follows that this type of plot, deviating from Beer's and Lambert's laws, is to be expected whenever fluorescence emission reaches the photocell of the spectrophotometer. Let I_x be the intensity of a beam of monochromic fluorescence-exciting light, of molar extinction coefficient $\varepsilon = k/2{\cdot}303$, after it has traversed a path-length x in an absorption cell of length l containing solution of molarity c. Then

$$dI_x = -kcI_0e^{-kcx}dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Suppose that a fraction α of the absorbed light $-dI_x$ is emitted as fluorescence in the direction of the exciting beam. Then the change in the intensity of the fluorescence due to passage through path-element dx is the sum of a term similar to dI_x for absorption and another equal to $-\alpha dI_x$ for emission. Thus, using primes to refer to the fluorescent light, we have

$$dI'_x = -k'cI'_xdx + \alpha kcI_0e^{-kcx}dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the approximation has been made of using an average value of $k' = 2{\cdot}303\varepsilon'$ over the wavelength range of the fluorescence. Since $I'_0 = 0$, this gives, upon integration between $x = 0$ and $x = l$,

$$I'_l = I_0\,(e^{-kcl} - e^{-k'cl})\alpha k/(k' - k) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Lauer [5] obtained an expression for dI'_x for a somewhat different geometrical arrangement; if it is modified so as to apply to the present system, it leads on integration to expression (3).

With the reasonable simplifying assumption that the photocell response is the same for exciting and fluorescent light, the observed optical density is:

$$d = \log I_0(I_l - I'_l) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Using (3) and noting that $I_l = I_0e^{-kcl}$, we have

$$d = -\log e^{-kcl} - \log[1 - (e^{(k-k')cl} - 1)\alpha k/(k - k')] \quad . \quad . \quad . \quad (5)$$

The first term on the right-hand side of eqn. (5) is equal to $d_{\text{true}} = -\log (I_l/I_0) = kcl/2{\cdot}303 = \varepsilon cl$, the true optical density for the exciting light, which would be observed in the absence of fluorescence. Since $k > k'$ in view of the relative probabilities of the two optical transitions concerned, it follows from eqn. (5) that $d < d_{\text{true}}$ always.

We now consider two limiting special cases. First, for small values of cl, eqn. (5) approximates to:

$$d = (1 - \alpha)\varepsilon cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus the graph of d against cl is linear near the origin, with a slope $s_1 = (1 - \alpha)\varepsilon$ which is smaller than the Beer–Lambert value by a factor which is a function of the fluorescence efficiency. The observed agreement with the Beer–Lambert law for dilute solutions or short absorption paths is only apparent.

Secondly, for large values of cl, eqn. (5) approximates to:

$$d = \varepsilon' cl + \log[(\varepsilon - \varepsilon')/\alpha\varepsilon] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Again the graph of d against cl is linear, with a slope $s_2 = \varepsilon'$ and an intercept $\log i$, where $i = (\varepsilon - \varepsilon')/\alpha\varepsilon$. From the above values of s_1, s_2, and i, it follows that

$$\varepsilon = (is_1 - s_2)/(i - 1),\ \varepsilon' = s_2, \text{ and } \alpha = (s_1 - s_2)/(is_1 - s_2) \quad . \quad . \quad (8)$$

Equations (8) were applied to laminated cellulose films dyed with various vat dyes, rather than to dye solutions, in order to minimise complications due to association,

[5] Lauer, *J. Opt. Soc. Amer.*, 1951, **41**, 482.

TABLE 1. *Corrected extinction coefficients for dyes on cellulose.*

Dye	Monochromator setting (mμ)	ε	ε′	α
Cibanone Golden Yellow GK	440	12,700	363	0·0745
Cibanone Yellow GK	480	11,850	425	0·002
Caledon Red 5G	510	8,950	105	0·034
Caledon Yellow 5GK	430	12,400	445	0·058
Caledon Yellow 4G	440	24,500	710	0·032
Indanthren Yellow FFRK	420	15,100	1240	0·094
Cibanone Brilliant Orange RK	530	20,600	625	0·078
Caledon Jade Green XN	605	28,800	210	0·028

FIG. 2.

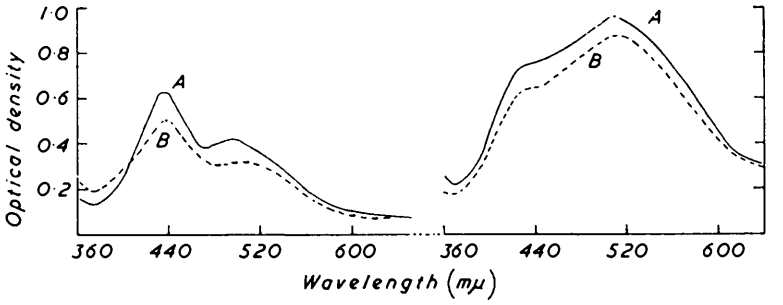


FIG. 3.

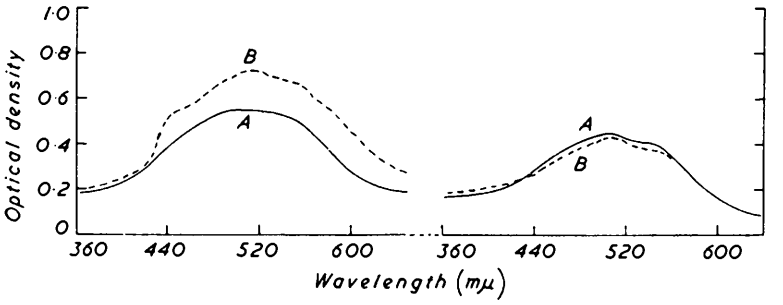
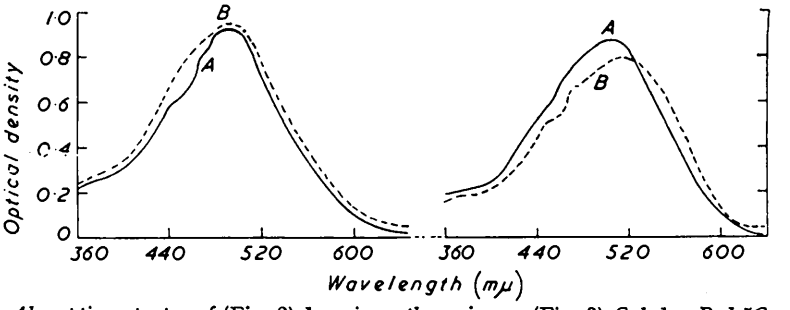


FIG. 4.



FIGS. 2—4. *Absorption spectra of* (Fig. 2) *1-aminoanthraquinone,* (Fig. 3) *Caledon Red 5G, and* (*Fig.* 4) *Cibanone Yellow 2GR, dyed on cellulose acetate. Left-hand plots before and right-hand plots after exposure. Continuous lines are "a" curves, broken lines "b" curves.*

quenching, etc. The value of cl was varied by peeling off successive equally thick layers from the laminate. The results obtained are listed in Table 1. Since the value of i is the same whether d is plotted against cl or against n, the number of layers in the laminate, it follows that α may be calculated from eqn. (8) by using the slopes of the d–n graphs, which are equal to as_1 and as_2, where a is the value of cl for a single layer. However, to

TABLE 2. *Spectra of dyed cellulose acetate films (wavelengths in* mμ).

Dye or compound	$\lambda_{max.}$ in EtOH	Film before exposure: $\lambda_{max.}$ "a"	Film before exposure: $\lambda_{max.}$ "b"	Film before exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film before exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Film after exposure: $\lambda_{max.}$ "a"	Film after exposure: $\lambda_{max.}$ "b"	Film after exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film after exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Light fastness [11]	Tendering activity [11]	Light-exposure behaviour
(Acyl)aminoanthraquinones												
1-Aminoanthraquinone	497	435	438	<407	407—630	436	436	—	360—640	—	none	Film darkened and became very brittle, owing to film degradation and formation of probably a polymerised aniline black.
		497	510			510	514					
Algol Yellow WG	430·5	460	458	360—640	—	463	460	360—640	—	low	none	Marked fading (both ε_a and ε_b decrease, ε_b more than ε_a). Benzoylation renders attack less severe than in previous case.
Caledon Red 5GS	538	~500	512	422—640	<422	505	508	360—430	430—570	v. good	high	Behaves like preceding dye. "a" and "b" curves become almost coincident (loss of fluorescence)
Cibanone Yellow GK	425	480	473	410—437	<410	472	468	>485	360—485	v. good	high	Both ε_a and ε_b increase, minimally at absorption peaks, and film becomes opalescent (not observed with a dark control), showing fading swamped by light scattered by degraded film.
	465			505—640	437—505							
Caledon Red X5BS	538	546	545	410—640	<410	548	552	360—640	—	v. good	—	Slight fading, but "a" and "b" curves remain separated, showing that fluorescence is unaffected by exposure.
Caledon Yellow 5GK	426	432	434	414—490	—	438	435	400—444	>444	good	high	Similar to Cibanone Yellow GK.
Caledon Yellow 4G	490	452	454	360—640	—	438	437	360—620	—	good	mild	Similar to Cibanone Yellow GK.
Carbazoles												
Indanthren Yellow FFRK	438	420	420	<412	412—640	422	424	360—410	410—440	v. good	high	ε_a remains greater than ε_b in the peak region, but decreases owing to fading, while ε_b increases, indicating diminished fluorescence due to film degradation, which outweighs fading.
Caledon Olive 1R	505	430	436	—	360—640	433	436	—	360—640	v. good	prob. low	Similar to Indanthren Yellow FFRK.
Caledon Gold Orange 3G	464	464	463	—	360—510	464	466	490—600	360—490	v. good	low	Similar to Indanthren Yellow FFRK.
Cibanone Yellow 3R	421	460	460	360—640	—	456	458	—	360—640	v. good	none	Exposure reverses the relative positions of "a" and "b" curves to those characteristic of Indanthren Yellow FFRK, suggesting degradation of the dye towards the structure of the latter.
		608	608			600	604					
Triazines												
Cibanone Yellow 2GR	427·5	491	492	360—640	—	506	512	528—640	360—528	moderate	high	ε_a and ε_b decrease (fading) and reverse relative magnitudes near wavelengths of main bands, which are emitted as fluorescence after exposure.
Cibanone Red G	473	512	513	—	360—640	512	513	—	360—640	good	prob. none	Both ε_a and ε_b increase and tend towards equality, indicating film degradation which diminishes fluorescence.
		526	521			527	523					
Cibanone Red 4B	485	513	514	360—640	—	518	521	360—640	—	good	prob. none	Despite structural similarity to preceding two dyes, there is no film degradation or loss of fluorescence, only slight fading.
	514 [b]											

TABLE 2. (*Continued*)

Dye or compound	$\lambda_{max.}$ in EtOH	Film before exposure: $\lambda_{max.}$ "a"	Film before exposure: $\lambda_{max.}$ "b"	Film before exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film before exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Film after exposure: $\lambda_{max.}$ "a"	Film after exposure: $\lambda_{max.}$ "b"	Film after exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film after exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Light fastness [11]	Tendering activity [11]	Light-exposure behaviour
Anthanthrones												
Cibanone Brilliant Orange GK	515	507	510	405—640	—	510	508	360—538	—	v. good	moderate	ε_a increases more than, and nearly overtakes, ε_b, indicating film degradation which reduces fluorescence emission.
	528	526	530			530	529					
Cibanone Brilliant Orange RK	520	507	503	360—640	—	470	466	360—610	—	v. good	moderate	Does not behave like preceding structurally similar dye. Exposure completely destroys dye, producing a new absorbing species.
	533	530	531			488	487					
Dibenzopyrenequinones												
Cibanone Golden Yellow GK	415	438	442	—	360—510	438	442	—	360—505	good	high	Slight fading. Note difference in fluorescence characteristics (relative positions of "a" and "b" curves) between this and the following dye despite structural similarity.
	435											
	465											
Cibanone Golden Yellow RK	415	438	448	428—640	<428	428	427	432—580	360—432	v. good	low	Slight fading. Cf. preceding dye.
	435											
	464											
Pyranthrones												
Caledon Gold Orange G	432	475	473	518—640	360—518	468	471	518—640	360—518	moderate	high	Film becomes dull and brittle. Some fading, swamped by reduced fluorescence due to film degradation, as with Indanthren Yellow FFRK.
	482											
Caledon Orange 2RTS	479	478	479	>535	560—535	475	479	477—640	360—477	good	low	Similar to preceding dye.
Caledon Brilliant Orange 4RN	476	495	490	360—640	—	477	488	481—524	360—481	v. good	low	Despite structural similarity to preceding two dyes, no film degradation, but considerable dye disintegration and loss of fluorescence (ε_a and ε_b decrease greatly and become equal).
(iso)*Dibenzanthrones*												
Caledon Jade Green XN	416	436	436	<409	409—640	440	430	360—425	>425	v. good	prob. none	Slight fading. Dichromatism in solution [1] probably due to long-wavelength fluorescence excited by absorption at the 600 mμ band.
	~610	600	597			600	602					
Caledon Brilliant Purple 4RN	422	422	434	360—640	—	420	418	360—640	—	moderate	prob. none	Slight fading.
	570	528	530			526	526					
Cibanone Brilliant Green 2B [a]	—	426	438	—	360—640	424	434	—	360—640	—	—	Slight fading.
		591	597			591	599					
Cibanone Navy Blue RA [a]	402	424	430	540—640	360—424	422	435	545—640	360—438	v. good	prob. none	Slight fading.
	550	557	562			556	557					
Caledon Brilliant Green 4G [a]	—	434	438	360—565	>565	436	440	360—415	415—431	—	—	Slight fading.
		592	592			592	586	431—568	568—640			

TABLE 2. (*Continued*)

Dye or compound	$\lambda_{max.}$ in EtOH	Film before exposure: $\lambda_{max.}$ "a"	Film before exposure: $\lambda_{max.}$ "b"	Film before exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film before exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Film after exposure: $\lambda_{max.}$ "a"	Film after exposure: $\lambda_{max.}$ "b"	Film after exposure: λλ for which $\varepsilon_b > \varepsilon_a$	Film after exposure: λλ for which $\varepsilon_b < \varepsilon_a$	Light fastness [11]	Tendering activity [11]	Light-exposure behaviour
Indanthrones												
Cibanone Blue RSN	442	420	425	424—512	<424	418	426	406—640	—	v. good	prob. none	Slight fading. Longer-wavelength band excites fluorescence after exposure.
	598	558	556		512—628	560	561					
Caledon Blue RC	609	612	618	360—640	—	600	601	378—640	—	v. good	prob. none	Little effect except some loss of fluorescence ("a" and "b" spectra approach coincidence after exposure).
	668											
Flavanthrones												
Caledon Yellow GN	440	428	428	—	360—468	446	450	360—415	415—470	good	none	Exposure destroys dye, producing a new absorbing species.
Caledon Yellow 2R [a]	430	422	422	—	360—640	424	445	—	360—640	—	—	Some fading.
Caledon Yellow 3RF [a]	—	427	426	—	360—640	447	447	540—640	360—540	—	—	Some fading and loss of fluorescence (difference between ε_a and ε_b decreases).
			447									
Miscellaneous S-*containing dyes*												
Caledon Yellow 5G	400	435	436	444—580	<444	430	433	444—550	360—444	moderate	v. high	ε_a and ε_b increase, as with Cibanone Yellow GK, indicating film degradation.
Cibanone Orange R	422	422	424	>453	360—453	—	—	—	—	moderate	high	Film became brittle, powdering readily, and milky with dark patches. No spectra measurable with degraded film.
Miscellaneous N-*containing dyes*												
Cibanone Red 2B	448	514	512	>522	360—522	508	518	360—640	—	good	prob. none	Similar to Indanthren Yellow FFRK.
	532 [b]											
Cibanone Red RK	451·5	439	438	407—640	<407	436	441	399—640	<399	v. good	low	Both ε_a and ε_b increase, indicating tendering of substrate, which partly quenches fluorescence emission.
	520 [b]	512	514			514	516					
Cibanone Red FBB	429	412	415	—	360—608	416	422	—	360—610	good	moderate	Slight fading.
	~450	506	506			508	504					
Indanthren Brilliant Orange GR	486	496	498	452—640	<452	500	501	438—640	<438	good	low	Similar to Cibanone Red RK.
	544	526	524			520	520					

[a] Structure unknown, but spectra suggest assigned class. [b] In chlorobenzene.

determine ε and ε' from eqn. (8), the value of a was required. It was evaluated by measuring d for a dilute ethanolic solution of the dye concerned at a known concentration, calculating ε from eqn. (6) with the value of α obtained for the film by eqn. (8), and then using this value of ε to calculate cl by applying eqn. (6) to the value of d observed for a single layer of dyed film.

The fluorescence efficiency could be calculated from the value of α and the geometry of the system, but this was not attempted.

(ii) *Wavelength Regions of Fluorescence Excitation and Emission.*—Although the measurements described above demonstrate the existence of fluorescence, they are tedious, and moreover give no information about the wavelength region of the fluorescence. A technique was therefore used of comparing the visible spectra (360—640 mμ) of dyed films of cellulose acetate (chosen for rigidity) with the films in alternative positions. These were (*a*) between monochromator and photocell, the normal arrangement, which gives a low apparent optical density at wavelengths which excite fluorescence, and (*b*) between polychromatic light source and monochromator, which leads to low optical-density readings when the monochromator is set at a wavelength at which fluorescence is emitted. Thus, if the "*a*" and "*b*" spectra are superimposed, the "*a*" will lie above the "*b*" curve at fluorescence emission wavelengths, and below it at excitation wavelengths. If, therefore, the main visible absorption band excites fluorescence of much longer wavelengths, the "*a*" curve will lie below the "*b*" over most of the visible spectrum. If, however, the fluorescence is excited by the near-ultraviolet and lies within or near the main visible absorption band, the reverse will be true. Lastly, if exciting and excited wavelengths are similar, a combination of the two previous effects may occur, and the "*a*" and the "*b*" curve will cross; their relative positions will still indicate, as described above, the spectral regions of excitation and emission.

The results obtained are exemplified by Figs. 2—4 and summarised in Table 2 (cols. 5 and 6). Apart from a general slight bathochromic shift, the film spectra are similar to those of ethanolic solutions of the dyes (cf. Table 2, cols. 3 and 4), with the exception of Caledon Red 5G, Gold Orange G, and Brilliant Purple 4R. Since reabsorption of fluorescence occurs preferentially on the short-wavelength side of the emission band, altering the position of maximum fluorescence and the apparent fluorescence band shape,[6] the present technique gives only limited and approximate information about emission and exciting wavelengths. In the few cases where the "*b*" lies above the "*a*" curve at one absorption peak, and below it at a longer-wavelength peak, it may be assumed that absorption at the shorter wavelength is followed, after some energy degradation, by re-emission in the region of the longer wavelength. In all other cases, the precise exciting- and excited-wavelength regions are unknown, so that correlation of fluorescence properties with fading or tendering activity is impossible; it is necessary for this purpose to use a technique [7,8] which minimises reabsorption of fluorescence. The present method does, however, provide a sensitive indication of fading and tendering of dyed films, as shown in the next section. It also leads to an explanation of the well-known effect of soaping and steaming in increasing the optical absorption of dyed films. Waters, Sumner, and Vickerstaff [9] explained this as due to dye aggregation, resulting in perturbed dye energy levels and transitions of lower energy and greater probability. We have found that soaping decreases the extent of fluorescence but does not cause the bathochromic shift expected from this theory. This suggests that dye aggregation decreases fluorescence emission by self-quenching,[10] thus increasing the apparent optical density.

[6] Bowen and Wokes, "Fluorescence of Solutions," Longmans Green, London, 1953, pp. 55—56.
[7] Lauer and Rosenbaum, *J. Opt. Soc. Amer.*, 1951, **41**, 451.
[8] Bowen, *Photoelectric Spectrometry Group Bull.*, 1953, No. 6, 124.
[9] Waters, Sumner, and Vickerstaff, *J. Soc. Dyers and Colourists*, 1953, **69**, 181.
[10] Bowen, "Chemical Aspects of Light," Oxford Univ. Press, 2nd. Ed., 1946, p. 168.

(iii) *Weathering and Light-exposure Tests on Dyed Films.*—Atmospheric weathering in the dark had little or no effect on the spectra; on the other hand, only for Cibanone Red 4B was simultaneous weathering and light exposure without appreciable effect. Pretreatment by soaping and with hydrogen peroxide decreased and increased, respectively, the exposure effects, as is to be expected.

The effects of light exposure on the spectra of the dye–substrate complex may be diverse. Either the "*a*" or the "*b*" spectrum intensities can independently increase or decrease. A decrease may be due to actual fading or to decreased self-quenching of fluorescence, the latter arising from either decreased dye-particle size,[10] or from weakened binding of dye to substrate after tendering. Light-scattering by degraded film may also decrease apparent optical density. An increased intensity may be caused if film degradation strengthens the binding of dye. All of these possibilities were realised, as shown in the film exposure results given in Table 2, which refer to the state where further exposure had little effect. Generally a long induction period was followed by a steady change to the final state. In all cases the initially lower of the two absorption curves was the more sensitive to exposure, responding more rapidly at first, but also falling off in further response more rapidly. The interim effect was thus a differential movement of the relative positions of the "*a*" and the "*b*" curves. Some of the films darkened visibly and became brittle during exposure. In the most severe example, with Cibanone Orange R, this rendered determination of the final spectrum impossible. The interim spectra for this dye were anomalous in that the optical density first decreased, and then increased to values far greater than the initial. This behaviour was shown to a smaller extent by all the active yellow and orange dyes, and is due to tendering, the films becoming duller and, in some cases, opalescent.

As expected, exposure produced most marked effects with the active yellow and orange dyes, the most severe cases being Cibanone Orange R and Cibanone Brilliant Orange RK. With the latter, a spectral change was observed after only 3 days' exposure; after 1 month, the original spectrum had disappeared completely, leaving a spectrum of similar form to the original but displaced hypsochromically by some 40 mμ. However, no differential shift of the "*a*" and the "*b*" curve occurred, so the fluorescence emission–excitation properties were unchanged. This behaviour is the more anomalous in that Cibanone Brilliant Orange GK, which differs structurally from the RK dye merely in the replacement of bromine by chlorine and is initially almost indistinguishable from it spectrally, is scarcely affected by exposure. Only 1-aminoanthraquinone and Caledon Yellow GN exhibited similar large spectral shifts on exposure.

Beyond the expected greater sensitivity of the acknowledged active dyes to light, there is little regularity in the results of the exposure tests. Even within the class of active dyes there is little consistency. A slight alteration in molecular structure leads to great variations in exposure effects. The difference in behaviour between Algol Yellow WG and Cibanone Yellow GK (1-benzamido- and 1 : 5-dibenzamido-anthraquinone) is as marked as that between chloro- and bromo-anthanthrones noted in the previous paragraph. The anomalous light-stability of the 4-acylamino-anthraquinones is of interest since the solution spectra of these dyes do not fall into line with those of other acylamino-anthraquinones.[11] Within the triazine group of dyes there is again considerable diversity in behaviour on exposure. The carbazole group behaves fairly uniformly, except for Cibanone Yellow 3R which apparently changes spectrally on exposure towards the parent unsubstituted dye of this group.

In conclusion, the absorption–emission characteristics of these dyes on cellulose acetate substrate are not simply correlated with either molecular structure or fading-tendering activity. It is noteworthy, however, that observation of changes in fluorescence-emission properties on exposure is far more sensitive as a criterion of fading or tendering than either a visual or a simple spectrophotometric examination.

[11] Fox, *J. Soc. Dyers and Colourists*, 1949, **65**, 508; Landolt, *ibid.*, p. 659.

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