

148. Fading and Tendering Activity in Anthraquinonoid Vat Dyes. Part III.* Free-radical Production and Probable Reaction Mechanisms.

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Most of the tendering-active, and some of the inactive, members of a group of 37 anthraquinonoid vat dyes initiate the polymerisation of methyl methacrylate, by free-radical production, when their oxygen-free ethanolic solutions or aqueous *leuco*-solutions are exposed to visible light. On the probable assumption that dye semiquinone radicals are initially produced, either by transfer of an electron from or to a solvent-sheath water molecule, or by hydrogen-atom transfer from cellulose substrate, mechanisms are proposed for (a) the photo-oxidation-dehalogenation of *leuco*-solutions of halogenated dyes, (b) the production of acetaldehyde, dye peroxy-derivatives, and hydrogen peroxide in light-exposed oxygen-free ethanolic dye solutions, and (c) fading and tendering of dyed cellulose films exposed to light in air. Most dyes active in (c) emit fluorescence wavelengths shorter than about 500 m μ , which could provide sufficient energy for detaching a hydrogen atom from a cellulose hydroxyl group before its transfer to a dye molecule. The protective action of some inactive dyes in mixed dyeings with fading-tendering dyes is probably due to overlap of the fluorescence band of the active dye and the absorption band of the inactive dye in the mixed crystal, in which these bands are essentially unperturbed.

VARIOUS mechanisms have been suggested for the fading and tendering reactions of anthraquinonoid vat dyes. Scholefield and Turner¹ held that active dyes are photo-reduced to the *leuco*-form, which, on reoxidation by air or otherwise, yields a peroxy-compound which attacks the substrate directly or after releasing hydrogen peroxide. The latter is known to result on reoxidation of active and inactive dye *leuco*-solutions² or on illumination of vat-dye suspensions. Waly, Preston, Scholefield, and Turner³ observed that only active dyes underwent on illumination a shift of characteristic redox potential to more negative values. This shift, which Hadfield⁴ could not reproduce, was ascribed to a change in either the chemical nature or the solubility of the dye or its *leuco*-derivative. Later, Turner⁵ suggested that the cause was a very active unidentified species produced during reduction of the dye to quinol *via* semiquinone. Egerton⁶ found that the tendering-active species formed when vat-dyed cotton was exposed to visible light was transferable to near-by unexposed undyed cotton ("action at a distance"), and concluded that it was activated molecular oxygen formed by energy transfer from photo-excited dye, or else its reaction product with moisture, hydrogen peroxide. Of interest in this connection is

* Part II, preceding paper.

¹ Scholefield and Turner, *J. Textile Inst.*, 1933, **24**, p 131.

² Atherton and Turner, *J. Soc. Dyers and Colourists*, 1946, **62**, 108.

³ Waly, Preston, Scholefield, and Turner, *ibid.*, 1945, **61**, 245.

⁴ Hadfield, M.Sc.(Tech.) Thesis, Manchester, 1947.

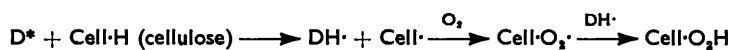
⁵ Turner, *J. Soc. Dyers and Colourists*, 1949, **65**, 637.

⁶ Egerton, *ibid.*, 1947, **63**, 161; 1948, **64**, 336; 1949, **65**, 764; *J. Textile Inst.*, 1948, **39**, r 293,

Ashton and Probert's observation⁷ that for vat dyeings in visible light, extent of fading increases with relative humidity, but tendering is often less severe at 50% than at 0% or 100% relative humidity. Bamford and Dewar⁸ maintained that in the presence of moisture the main tendering agent was hydrogen peroxide, formed by oxidation of hydroxyl ions in the moisture by photoactivated dye (D*):



In the absence of moisture the tendering was assumed to occur *via* an unstable cellulose hydroperoxide, formed by the reactions:



Fading in certain cases was ascribed to the formation of colourless anthrones by the isomerisation of the acid *leuco*-compounds:



Fiala found that only activated oxygen, and neither hydrogen peroxide⁹ nor dye peroxide¹⁰ resulted on illumination of fluorescein dyes with or without attackable substrate, confirming the views of Kautsky and his co-workers.¹¹ Hillson and Rideal¹² concluded, from a study of the Becquerel effect of electrodes coated with azo- or triphenylmethane dyes, that the photo-excited dye *reduces* water or cellulose by abstracting OH, releasing either H or cellulose radicals. This reducing action accords with the marked tendering activity of strongly reducing *leuco*-dyes, and with the frequent colour change of illuminated vat dyes other than towards the colour of the acid *leuco*-form.¹³

Lewis and his co-workers¹⁴ obtained semiquinone radicals by photochemical oxidation of quinols in rigid media at low temperatures, and Linschitz, Kennert, and Korn¹⁵ obtained such radicals both by photo-oxidation of a quinone or diamine and by photo-reduction of a quinol or di-imine, confirming Weiss's views.¹⁶ It is thus clearly desirable to investigate the photo-production of free radicals in vat dyes. As criterion of production of free-radicals we have taken the ability to initiate polymerisation of methyl methacrylate.¹⁷

EXPERIMENTAL

The purification of the dyes was described in Part I.¹⁸ Methyl methacrylate was freed from quinol stabiliser by extraction with sodium hydroxide solution, washed with water, and redistilled immediately before use.

To detect free radicals in illuminated dye solutions in absolute ethanol, 10 ml. portions of saturated solutions of each dye were added to new Pyrex test-tubes (previously boiled out with solvent) containing 2 ml. of methyl methacrylate. Oxygen was removed by boiling the mixtures and bubbling in carbon dioxide. The tubes were then sealed with the dead space filled with

⁷ Ashton and Probert, *J. Textile Inst.*, 1953, **44**, r 1.

⁸ Bamford and Dewar, *J. Soc. Dyers and Colourists*, 1949, **65**, 674.

⁹ Fiala, *Chem. Listy*, 1945, **39**, 14.

¹⁰ Fiala, *Biochem. Z.*, 1949, **320**, 18.

¹¹ Kautsky, de Bruijn, Neuwirth, and Baumeister, *Ber.*, 1933, **66**, 1588; Kautsky, *Trans. Faraday Soc.*, 1939, **35**, 216.

¹² Hillson and Rideal, *Proc. Roy. Soc.*, 1953, **A**, **216**, 458.

¹³ Landolt, *J. Textile Inst.*, 1951, **42**, **A**, 563.

¹⁴ Lewis and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 2801; Lewis and Bigeleisen, *ibid.*, 1943, **65**, 2419, 2424.

¹⁵ Linschitz, Kennert, and Korn, *ibid.*, 1954, **76**, 5839.

¹⁶ Weiss, *Trans. Faraday Soc.*, 1939, **35**, 48; 1946, **42**, 116, 133; *J. Soc. Dyers and Colourists*, 1949, **65**, 719.

¹⁷ Waters, "The Chemistry of Free Radicals," Oxford Univ. Press, 2nd edn., 1948, p. 17.

¹⁸ Moran and Stonehill, *J.*, 1957, 765.

carbon dioxide, and exposed to full May-June sunlight while held at 30° to the vertical, facing south and sheltered from wind and rain. Control mixtures, from which the dye was omitted, and to some of which hydrogen peroxide or Fenton's reagent was added, were similarly treated. Although in many cases visible polymer was precipitated, the non-appearance of a precipitate did not exclude the occurrence of polymerisation since ethanol-soluble short-chain polymers could be present. For non-precipitating mixtures, therefore, the optical density was compared with that of an identical mixture which had been kept in the dark; the Hilger "Uvispek" spectrophotometer was used at a wavelength not appreciably absorbed by any constituent present. Any significant increase in optical density on exposure was assumed to be due to light scattering by polymer particles too small for visual detection.

To detect free radicals in *leuco*-dye solutions, the dyes, dispersed in aqueous sodium hydroxide, were reduced with hydrogen and Raney nickel, and blown over with hydrogen into a 2 cm. optical absorption cell (as used with the "Uvispek" instrument), which contained a layer of methyl methacrylate. The cell was fitted with an air-tight Polythene cap carrying inlet and outlet glass capillaries, the lower ends of which were cut off flush with the lower surface of the cap. The entire apparatus was previously flushed with hydrogen, and the *leuco*-solution stream was blown through the cell until no trace of unreduced dye colour remained therein. The inlet and outlet were then closed by screw clips on the connecting polyvinyl chloride tubing. Care was taken not to disturb the methacrylate layer during the addition of *leuco*-solution. The filled cell was exposed to light from a Point-o-Lite lamp at a distance of about 12 in. and observed visually.

RESULTS

The results of the experiments on methyl methacrylate polymerisation induced by irradiated ethanolic dye solutions are given in Table 1, and of those with aqueous *leuco*-solutions in Table 2.

TABLE 1. *Polymerisation of methyl methacrylate induced by irradiated ethanolic dye solutions.*

Dye	Exposure (hr.)	Extent of polymern.	Light fastness ^{19, 20}	Tendering activity ^{19, 20}
Cibanone Yellow 3R	2	Total solidificn.	V. good	None
Caledon Orange 2RTS	2	"	Good	Low
Cibanone Orange R	3	"	Moderate	High
Indanthren Brilliant Orange GR	3	"	Good	Low
Cibanone Brilliant Orange RK	24	Dense precipitate	V. good	Moderate
Caledon Yellow 3G	24	"	V. good	High
Caledon Yellow GN	24	"	Good	None
Cibanone Golden Yellow GK	24	"	Good	High
Cibanone Golden Yellow RK	24	"	V. good	Moderate
Caledon Gold Orange G	24	Slight precipitate	Moderate	High
Algol Yellow WG	24	"	Low	None
Cibanone Brilliant Orange GK	24	"	V. good	Moderate
Caledon Yellow 5GK	24	"	Good	High
Caledon Brilliant Orange 4RN	24	"	V. good	Low
Caledon Yellow 5G	24	"	Moderate	V. high
Other dyes in Table 3, Part I ¹⁸	500	Negligible or none	—	—

TABLE 2. *Methyl methacrylate polymerisation induced by irradiated leuco-dye solutions in water.*

Dye	Time for polymer layer to form	Light fastness ^{19, 20}	Tendering activity ^{19, 20}
Cibanone Brilliant Orange RK	1 sec.	V. good	Moderate
Indanthren Brilliant Orange GR	1 min.	Good	Low
Caledon Gold Orange G	1 min.	Moderate	High
Cibanone Yellow 3R	2 min.	V. good	None
Cibanone Brilliant Orange GK	15 min.	V. good	Moderate
Cibanone Golden Yellow GK	25 min.	Good	High
Cibanone Golden Yellow RK	25 min.	V. good	Low
Caledon Brilliant Orange 4RN	60 min.	V. good	Low

In the latter experiments, polymerisation-inducing dyes caused rapid formation of a polymer layer at the interface between monomer and *leuco*-solution, which acted as insulation between remaining monomer and precipitated oxidised dye, preventing further polymerisation. For the ethanolic dye solutions, addition of a few per cent of water to the solvent markedly reduced the induction period before polymerisation started; addition of acid or alkali retarded polymerisation, the retardation being less pronounced when a tendering-inactive green or blue dye was mixed with an active yellow or orange dye; addition of alkali also changed the colour of the dye solution towards that of the corresponding *leuco*-solution, suggesting that *leuco*-dye is an intermediate in the reaction of the unreduced dye.

The most active polymerisation-inducing dye of those examined was Cibacron Yellow 3R. The effect of immersing a cellulose acetate film dyed with this dye in an ethanolic solution of methyl methacrylate was therefore investigated. Complete polymerisation required 10 days of sunlight, compared with 2 hr. for the dye in solution, presumably because of the necessity for the film to swell before monomer could reach the dye. Localised surface polymerisation, removable by immersing the film in chloroform, occurred rapidly at first. After some time the film swelled visibly, small excrescences appeared, and small particles became detached, floating in the monomer solution and initiating local polymerisation. Careful dissolution of the final solid product in chloroform showed that the film had completely disintegrated. This did not occur with an undyed film or with one dyed with an inactive dye, and is probably the result of physical stress due to polymer growth, together with free-radical attack.

The visible absorption spectra of active dye-monomer mixtures in ethanol, determined with the Hilger "Uvispek" instrument, exhibit a slight bathochromic shift and a sharp increase in peak intensities, compared with ethanolic solutions of the dyes alone. This indicates some dye-monomer association which causes fluorescence quenching and thus increased apparent optical density. The bathochromic shifts were too small to be due to electron-transfer spectra involving dye and monomer.

The above results confirm the view that most tendering-active dyes (more sensitive detection techniques might extend this to all active dyes) as well as some inactive dyes give rise on illumination to free radicals, in the reduced and the unreduced state in solution, and also in the dyed state. The radicals are assumed to be semiquinonoid, since they may be obtained from either the quinone or the quinol forms of the dyes.

DISCUSSION

In the light of the present results and those of Parts I¹⁸ and II,²¹ we may now suggest mechanisms for some photo-reactions of vat dyes.

(i) *Photo-oxidation and Dehalogenation of Halogenated leuco-Dyes.*—The dehalogenation of *leuco*-solutions of many chloro- or bromo-substituted vat dyes on irradiation has long been known.²² Goldstein and Gardner²³ found that α - were more labile than β -halogen substituents in *leuco*-anthraquinones. Cooper²⁴ prepared *leuco*-dye solutions by mild catalytic reduction (platinum-hydrogen) to avoid the excess of dithionite present in the earlier work, and found that, in addition to dehalogenation, complete precipitation of the *leuco*-solution as reoxidised dehalogenated dye resulted rapidly on irradiation. Moreover, only one halogen atom per dye molecule was removed, appearing finally as halide ion; hence a dibromo-dye could undergo two, and a tribromo-dye (*e.g.*, Caledon Brilliant Orange 4RN) three successive reduction-irradiation-precipitation cycles before becoming inert to irradiation in the *leuco*-form, the absorption spectrum of the precipitated dye approaching that of the unhalogenated analogue as dehalogenation progressed. This precipitation was confirmed during an attempt in the present work to determine the absorption spectra of dithionite-free *leuco*-dye solutions.

¹⁸ Fox, *J. Soc. Dyers and Colourists*, 1949, **65**, 508.

²⁰ Landolt, *ibid.*, p. 659.

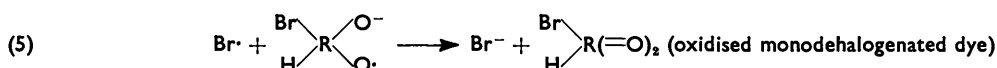
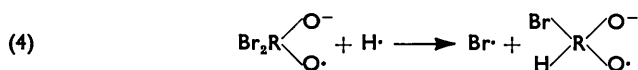
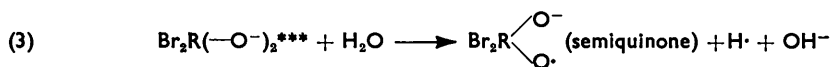
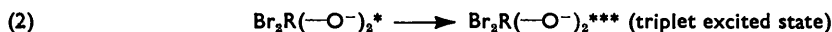
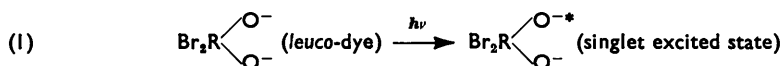
²¹ Moran and Stonehill, preceding paper.

²² Weber, *Amer. Dyestuff Reporter*, 1933, **22**, 157; *Dyestuffs*, 1933, **33**, 1.

²³ Goldstein and Gardner, *J. Amer. Chem. Soc.*, 1934, **56**, 2131.

²⁴ Cooper, unpublished work in this laboratory.

The mechanism we propose for the photo-oxidation-dehalogenation of a dibrominated dye, e.g., Cibanone Brilliant Orange RK, is :



Stage (2), suggested by the fluorescence of the dyes concerned, involves a spin-reversal transition from the excited singlet to the nearest lower-energy triplet-excited state, from which return to the ground state is highly forbidden, and may be facilitated by the presence of the halogen atom in the molecule.²⁵ Some or all of the energy thus released may be transferred to a hydration-shell water molecule, facilitating electron-transfer step (3). The energy (*ca.* 120 kcal./mole²⁶) required to break the H—OH bond is contributed by the absorbed light (*ca.* 60 kcal./mole), the electron affinity of the water molecule, and hydration energy changes in (3), but not significantly by the oxidation of quinol to semiquinone, for which the redox potential is only about -0.4 v on the hydrogen scale.²⁷ The hydrogen atom and semiquinone produced are held together by the solvent-cage effect,²⁸ as in normal fluorescence-quenching reactions,²⁹ permitting step (4) to occur; the latter may also be facilitated by light absorbed by the semiquinone.

When strong reductants (very active Raney nickel and hydrogen) are used to prepare *leuco*-Cibanone Brilliant Orange RK, the precipitated irradiation product is not the dehalogenated analogue of the original dye obtained with mild reductant, but a different substance, resembling spectrally the product of fading tests on dyed film (Part II²¹), the main visible absorption peak shifting some 30 m μ towards the violet instead of about 14 m μ observed on simple dehalogenation. The absorption spectrum and slight solubility in warm alkali suggest that an anthrone-like substance is formed. To account for this, we may suppose that under strong reducing conditions the *leuco*-dye, besides undergoing the reactions of the above scheme, can in its tautomeric oxanthrol form be photochemically reduced to an anthrone.^{30,31,32} However, it is not clear why the analogous chlorinated dye, Cibanone Brilliant Orange GK, does not behave similarly, either in *leuco*-solution or in dyed films. Bamford and Dewar's related view⁸ that fading of certain dyes was due to formation of colourless anthrones has already been mentioned.

(ii) *Irradiation of Oxygen-free Ethanolic Dye Solutions.*—The effect of water in decreasing

²⁵ McClure, *J. Chem. Phys.*, 1949, **17**, 905.

²⁶ Uri, *Chem. Rev.*, 1952, **50**, 375.

²⁷ Gupta, *J.*, 1952, 3473, 3479; Marshall and Peters, *J. Soc. Dyers and Colourists*, 1952, **68**, 289; *Bull. Inst. Textile France*, 1952, **30**, 415.

²⁸ Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.

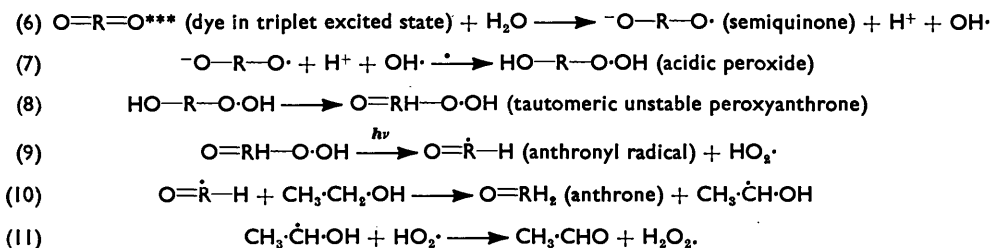
²⁹ Boaz and Rollefson, *J. Amer. Chem. Soc.*, 1950, **72**, 3443.

³⁰ Gill and Stonehill, *J.*, 1952, 1857.

³¹ Coffey, *Chem. and Ind.*, 1953, 1068.

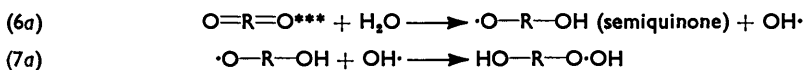
³² Bradley and Maisey, *J.*, 1954, 274.

the induction period and accelerating the polymerisation of methyl methacrylate by irradiated dye solutions suggests the first step of the following scheme :



In contrast with (3), step (6) involves *removal* of an electron from water; the dye accommodates this electron in the "hole" left by the optical electron, and is thus photoreduced to semiquinone. This scheme accounts for the production of acetaldehyde, organic peroxy-compounds, and hydrogen peroxide (detected with starch-iodide) on irradiation of ethanolic solutions of active dyes, as observed in this and earlier work.¹ The intermediate acidic peroxide postulated would be spectroscopically almost indistinguishable from the acid-*leuco*-form of the dye, which would explain why Scholefield and Turner¹ suggested that active dyes become photoreduced to the *leuco*-form. The above scheme applies to any dye having either a readily accessible triplet or a singlet state in which it is easily photoreduced to a semiquinone. The relative inactivity as a polymerisation catalyst of Cibacron Brilliant Orange GK as compared with its brominated analogue may be due to the effect of the bromine atoms in facilitating the spin reversal from excited singlet to triplet state²⁵ which precedes step (6).

Wells³³ has recently suggested that hydrogen-atom transfer rather than electron transfer may occur in dye photo-reactions. If this applies here, steps (6) and (7) would be modified to :



subsequent steps being unchanged.

(iii) *Irradiation of Dyed Cellulose in Presence of Oxygen.*—In the dyed state, the dyes occur as crystalline aggregates, especially after soaping and steaming. Crystals of several of the dyes concerned here, and of related substances, are semiconducting in light.^{34,35} Thus the energy levels of the individual dye molecules become merged into energy bands characteristic of a whole crystal. Upon illumination, electrons occupying the "filled" lowest-energy bands in the ground state are promoted to the relatively empty conduction bands, and may move freely throughout the crystal. The energy gap for conduction is about half the transition energy corresponding to the long-wavelength absorption maximum of an isolated molecule,³⁴ and for these strongly fluorescent dyes probably corresponds approximately to the maximum fluorescence emission wavelength, especially when fluorescence is excited by the main visible absorption band. The absorbed light energy, or part of it, is stored by the whole crystal, and may help to initiate a chemical reaction with the substrate if it is concentrated at a hydrogen-bond point of attachment of the dye crystal to a cellulose hydroxyl group^{36,37} or adsorbed water molecule.

The preceding reaction scheme may now be adapted to the present system. Although oxygen, in its diradical triplet ground state, can effect spin reversal from singlet to triplet excited state of the dye, this is not essential. It is sufficient that the photoexcited dye D*

³³ Wells, *Nature*, 1956, **177**, 483.

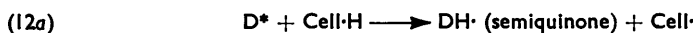
³⁴ Eley, Parfitt, Perry, and Taysum, *Trans. Faraday Soc.*, 1953, **49**, 79.

³⁵ Inokuchi, *Bull. Chem. Soc. Japan*, 1951, **24**, 222; 1952, **25**, 28.

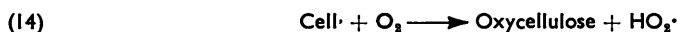
³⁶ Peters and Sumner, *J. Soc. Dyers and Colourists*, 1955, **71**, 130.

³⁷ Waters, *ibid.*, 1950, **66**, 544.

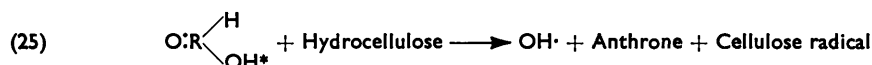
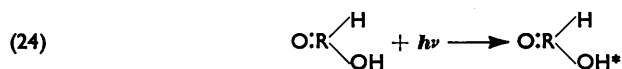
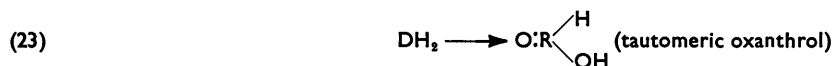
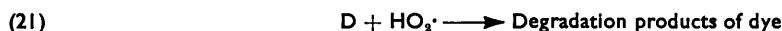
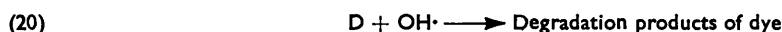
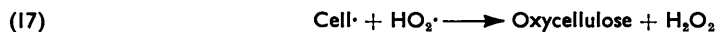
abstracts an electron followed by a proton, or more probably³³ a hydrogen atom in one step, from the cellulosic substrate (Cell·H) or a water molecule adsorbed on it. This is probably a fluorescence-quenching type of process, the products of which are held together by the "cage" effect:²⁸



Further reaction leading to fading and tendering can occur only if some more mobile free radical is produced by an additional process, namely, the reaction of oxygen with either Cell· or DH· radicals; the relative immobility of the latter was demonstrated by the absence of polymerisation of oxygen-free methyl methacrylate in solution by dyed films unless the monomer was strongly absorbed into the films. We then have:



The products OH·, HO₂·, and H₂O₂ undergo further reactions with both dye and substrate, of which the following are only a few possible ones:



The above scheme, some of the reactions in which have been suggested by Bowen,³⁸ explains the production of hydrogen peroxide (detected with starch-iodide) in fading and tendering. Egerton's⁶ "activated oxygen" is probably OH· or HO₂·, and his "action at a distance" is probably due to vapour-phase migration of these mobile radicals. The observed inefficiency of fading-tendering reactions is due to the lability of these radicals and the open-pore structure of textiles, which provides ample opportunities for deactivation or chain termination despite abundant production of radicals. The reducingoxy- and hydro-celluloses involved are probably produced during dyeing, acid "souring," soaping, or steaming. Freshly dyed cellulose films developed a Prussian Blue stain on immersion in dilute potassium ferricyanide, owing to the presence of reducing modifications of cellulose; this stain test was particularly sensitive with lightly coloured yellow and orange dyeings and when the leuco-dye was reoxidised with dilute hydrogen peroxide. By spectrophotometric determination of the methylene-blue uptake of successively detached portions of a cellulose film dyed with Indanthren Brilliant Orange GR and an undyed film, both exposed

³⁸ Bowen, *J. Soc. Dyers and Colourists*, 1949, **65**, 613.

to full June sunlight, it was shown that dyeing enhanced the rate of production of carboxy-cellulose. The difference between dyed and undyed film diminished on prolonged irradiation, secondary reactions becoming relatively important.

To disrupt the H-OH bond, as in (12*b*), it is unlikely that wavelengths longer than the near-ultraviolet can provide sufficient energy. The Cell-H bond, however, if assumed to have a bond energy similar to that of O-H in simple sugars, could be broken in reaction (12*a*) by fluorescence emission wavelengths λ ca. 500 m μ . None of the subsequent reactions is energetically impossible. Of the 19 dyes listed in Table 2 of Part II²¹ as having $\epsilon_b > \epsilon_a$ in the range 430–500 m μ , all but six (1-aminoanthraquinone, Caledon Gold Orange 3G, Cibanone Brilliant Green 2B, Caledon Yellow 2R and 3RF, Cibanone Red FBB) are accepted as tendering-active or have been shown²¹ to cause degradation of dyed cellulose films or to decompose in light. On the other hand, of 20 dyes listed as not showing $\epsilon_b > \epsilon_a$ in this range, only two (Caledon Yellow 5GK, Cibanone Yellow 2GR) are active tenderers, and three (Caledon Yellow 4G, Cibanone Brilliant Orange GK and RK) are mildly active. Since the region where $\epsilon_b > \epsilon_a$ only roughly corresponds with the fluorescence emission band, the correlation is reasonably good.

(iv) *Protective Action of Inactive Dyes.*—The absorption spectra of cellulose films dyed with a mixture of a tendering-active and a protective inactive dye were found to be simply the result of superimposing the spectra of the separate dyes for all mixtures examined. The unperturbed constituent-dye spectra indicate that the two dye molecule species are not bonded by strong chemical or physical forces. However, the dyed films appeared completely homogeneous under the microscope. We may thus assume that mixed dye crystals rather than single-component dye crystals are present, but the component dyes retain their own unperturbed energy bands. If the fluorescence-level band of the active dye (in which light energy may be stored and subsequently used to initiate fading or tendering) overlaps the absorption-level band of the inactive dye, a radiationless energy transfer may occur from the active to the inactive dye, the transferred energy being finally dissipated as heat. Such a process, if efficient, could explain protective action. If, however, the transferred energy, after slight degradation to vibrational energy, is sufficient to promote electrons of the inactive dye to the normally inaccessible fluorescence-band level (a “forbidden” transition), the inactive dye may become active and undergo enhanced fading, a photosensitisation phenomenon often observed.

(v) *Conclusion.*—Although the tentative reaction schemes proposed above account for many of the observed facts, the complexity of the phenomena renders these schemes hypothetical. More work is needed to elucidate completely the reactions involved. A systematic study of the fluorescence emission of the dyes is desirable, especially in rigid solutions at low temperatures,¹⁴ in order to obtain information on the existence of excited triplet states. Further study of the reactivity and general properties of the semiquinones, especially in relation to the kinetics of polymerisation catalysis, would permit an assessment of the feasibility of some of the proposed reactions. The elucidation of the mode of coupling of dye to substrate and its dependence on the physical state of the dye as affected by after-treatments would positively identify the point of initial attack of the substrate. A study of the emitting properties of pure and mixed dyeings might help in explaining the mechanism of protective action of certain dyes. Lastly, work on the photodegradation of dyed and undyed cellulose, particularly in regard to the mobility of H \cdot and OH \cdot radicals, in the cellulose chain, would be of interest.

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