STUDIES IN THE PHYSICAL STATE OF ADSORBED DYESTUFFS

Part I Adsorption at Inorganic Surfaces

Part II Adsorption at Organic Substrates and in Solution
- A Beer's law and Absorption Spectra Measurements
- B Reflectivity Measurement

Part III Relation between Light Fastness and Aggregation of Adsorbed Dyes

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PUBLICATIONS

The work described in this thesis has been embodied in the following publications:

In print

"Adsorption at Inorganic Surfaces." Part IV. Cummings, Garven, Giles, Rahman, Snedden, and Stewart, J.C.S., 1959, 535.

"Adsorption at Inorganic Surfaces." Part V. Giles, Mehta, Rahman, and Stewart, J.Appl.Chem., 1959, 9, 457.

"Optical Investigations into the Physical State of Dyes". Part 2, Trans.Far.Soc., 1959, 55, 1631, Campbell, Cathcart, Giles and Rahman.

"Effect of Fluorescent Brightening Agents on the Light Fastness of Dyed Cellulose". Giles and Rahman, J.S.D.C., 76, 681.

"Light fastness and Surface Activity of Dyes." Giles, Baxter, Macaulay, and Rahman, Textile Res.J., 1960, 30, 934.

"Studies in the Light Absorption of Dyes." Part III. Giles, Rahman, and Smith. J.C.S., 1961 (probably April).

Submitted

Papers on high light fastness and its relation to dye aggregation and on reflectivity of coloured surfaces (both to Textile Res.J.).

In preparation

Papers on fastness and molecular shape, fading on polyester fibres, light fastness (review).

SUMMARY

The main purpose of the research was to gain a better understanding of the state of dyes when adsorbed by a variety of organic and inorganic substrates, with the view to providing a solid experimental basis for any new quantitative treatment of the mechanism of dyeing, and of solution adsorption in general.

Broadly the work is classified into three main sections, dealing respectively with adsorption at the surface of anodic alumina film and of alumina powder; aggregation in adsorption at organic surfaces and by solution in water, and the relation between the state of aggregation of dyes and their light fastness.

The adsorption of organic dyes from solution by the two forms of alumina is studied to find out whether the dyes are adsorbed as associated particles. The specific surface area values of the alumina calculated from the adsorption isotherms of various dyes are compared, with the value obtained by phenol adsorption, and it is concluded that a proportion of dye is adsorbed as micelles. A unique effect has been observed in the adsorption of dyes by anodic alumina: the amount adsorbed varies greatly with the volume of solution used, in apparent contradiction of thermodynamic principles. This is discussed, and an explanation given.

Spectrophotometric tests have also been made to determine whether dyes adsorbed in solid films of regenerated cellulose and gelatin used as models, of cellulosic and protein fibres respectively, are mono-disperse or heterodisperse. The method used was a study of "Beer's law curves" (optical density against concentration) for a large number of dyes at high dye concentration, with and without disaggregating agents.

The absorption spectra in the visible region of a number of dyes have been examined when in solution and adsorbed in transparent films, and the presence of the x and y bands in nearly all cases has been demonstrated and used to detect aggregation and disaggregation effects.

The application of Beer's law is extended to the relationship between light reflectance and concentration of colour in a mass of coloured particles and fibres. The theoretical reason for Beer's law failure in transmission and reflection systems is discussed and it is shown that a more generally true relation is obtained by substituting for c, the colour concentration factor in the Beer's law formula, the empirical factor $\frac{cl}{1 + ac^{x}}$, where a and x are constants ($x < 1$), probably functions of the refractive index difference between the dye and surrounding medium, and x is a simple fraction. From an examination of absorption spectra and fading rate curves of many types of dye of high light fastness it was found that micelles are present in the substrate, and this probably accounts for the high light-fastness. The effects of various treatments used commercially to improve the light-fastness properties of dyes, have been studied and it is shown that aggregation of the dye is the probable cause of the improvement. It is shown that on irradiation the aggregates often break up, probably because of the heat of the lamp. This phenomenon, which can be minimised by keeping the irradiated pattern cool, actually has an opposite effect to fading, i.e. it tends to increase the apparent depth of colour.

Change in the surface activity of dyes, produced by changes in the size and form of their hydrophobic residues and the position of the ionic groups is shown to affect light fastness by virtue of an influence upon the physical form of the adsorbed dye. A statistical investigation of the relation between the molecular shape of dyes and their light-fastness shows that there is a tendency for fastness to rise with fall in axial ratio, i.e. the more nearly square is the dye molecule the higher is its light fastness.

Next the effect of fluorescent brightening agents on the light fastness of dyed cellulose is examined and it is shown that these agents do not usefully alter light fastness.

Some work proceeding is described in which the light fastness of disperse dyes adsorbed in hydrophobic substrates, especially polyesters, is shown to depend partly upon the state of aggregation of the dye, but mainly upon the low moisture content of the substrate. This low moisture content has the effect of raising the light fastness as the crystallinity of the substrate increases. This is the reverse of the normal rule for hydrophilic substrates.

INTRODUCTION

At the beginning of this century a "colloidal theory" was favoured to account for dyeing phenomena. Amongst many investigators, Krafft, Wood, Pelet-Jolivet, and Anderson (quoted by Wood) studied the properties of dye solutions and concluded that water-soluble dyes often exist in solution not as single ions or molecules, but in colloidal aggregates. They discovered that the direct cotton dyes display pronounced aggregation effects, and that the aggregation increases with increase in concentration or with addition of an electrolyte. These effects were supposed to be closely related to the phenomena of the dyeing of cellulose. But with the development of modern physico-chemical methods of studying dyeing, these early ideas were superseded by more precise ones expressed in mathematical terms, in which the possibility of association between dye molecules was at first discarded because by doing this the mathematical treatment was simplified, and then was forgotten or considered discredited. It will be seen from the account of the present author's work given in this thesis that "the wheel has come full circle", and that the early ideas of the presence of large assemblages of dye molecules in fibres must be reconsidered. Ideas on the physical chemistry of the adsorption of dyes have undergone a great change since about 1930, largely as a result of the pioneering work of Neale and the Manchester school and Rideal and Gilbert at Cambridge, and later, of Vickerstaff, R.H. Peters and collaborators in the I.C.I. Manchester laboratories. Neale was the first investigator to make detailed studies of the kinetics of dyeing, and Rideal and Gilbert were the first to apply thermodynamic principles to a study of the equilibrium state. Neale worked with direct dyes on cellulose and Rideal and Gilbert with acid dyes and with acids alone on wool. Gilbert and Rideal assumed that adsorbed anions are located at specific sites in wool. They assumed that if the fibre is compact, the most likely sites for the adsorbed anions are positively charged basic groups, almost all of which, in wool keratin, are usually supposed to be paired with carboxyl groups. All the positive groups have identical properties, as far as their interaction with anions is concerned, and all the carboxyl groups are alike in their affinity for protons. An anion is free to occupy any positive site whether or not the site is next to a carboxyl group that has been neutralised by a proton. Only one anion can however be adsorbed by any one site, just as the adsorption of one proton makes a carboxyl site no longer available. Anions and protons are regarded as being adsorbed independently; except in so far as they influence one another through their contribution to the net charge of the fibre. Thus nearly all the anions in the fibre will be adsorbed in this way and may be regarded as being adsorbed upon a limited number of positively charged sites.

The activity of anions in the fibre is represented by the fraction $\frac{\theta_x}{1-\theta_x}$; $\theta_x = X_a / S_x$; where X_a is the total concentration of anions within the fibre, the amount of uncommitted anion being regarded as negligible; and S_x is the concentration of anion sites, also within the fibre.

This theory of Gilbert and Rideal provided a satisfactory explanation of the titration of wool by hydrochloric acid. For the purpose of a quantitative treatment of wool dyeing, it was assumed that association of dye ions with proteins would be almost complete, so that the amount of uncommitted dye ions within the fibres might be neglected. The activity of anions will then be represented by the expression $\frac{\theta_x}{1 - \theta_x}$, but the value of θ_x will depend upon the number of sites available for the anions.

When wool is placed in a dyebath, the hydrogen ions are adsorbed by the carboxyl groups in the fibre. This process takes place only if there is a simultaneous adsorption of an equivalent number of anions. The dyebath however contains a mixture of anions, but in general the dye anions will be very much larger than the inorganic anions and will diffuse much more slowly. Hence inorganic ions are adsorbed before the dye ions. Elöd has examined the rate of adsorption of chloride, hydrogen, and dye ions by wool from a dyebath containing the sodium salt of the dye, together with hydrochloric acid. Equilibrium with hydrogen ions was quickly attained, but the chloride ions after reaching a maximum adsorption then left the fibre as the more slowly moving dye ions were adsorbed. The fact that the dye ions enter the wool fibre, which already contains equivalent quantities of anions and cations, is considered most significant by the supporters of this theory.

This work was mainly concerned with the acid wool levelling types of dye, which are not colloidal in aqueous solution. Acid milling dyes are often colloidal in solution in the cold. Goodall, in explaining the migrating properties of dyes in wool, considered that acid milling dyes are aggregated even at the boil, in solution, and that they differ considerably in general kinetic behaviour from acid levelling dyes. Moreover L. Peters considered that combination of unionised dye molecules takes place with the amide group of protein, leading to a very large number of sites for dye ions. Both these factors would complicate or invalidate the treatment discussed above.

Speakman and Elliott examined the setting power of fibres by X-ray diffraction, and reached the conclusion that the dye molecules do not as a rule penetrate the internal fibre micelles, but remain on the surface of these micelles in numbers equivalent to the micellar charge. Where the micelles are large, they considered that the dye molecules may force their way in and cause micellar subdivision, with a reduction in fibre tensile strength, but little change in the X-ray diagram. Therefore there are some grounds for the belief that in wool saturated with dye, the dye ions are not always in close proximity to charged amino groups.

Vickerstaff suggests that interaction between amide groups in wool and the non-ionic residue of a dye molecule must occur, and in neutral solution such interaction must be the main attraction between the two. In acid solution however, the electrical forces between dye anions and basic groups in the protein must be highly important, for many dyes of level dyeing type are adsorbed by wool from acid solution, but leave the fibre unstained in neutral solution. It is suggested that amide combination is the main source of the higher affinity of acid dyes in comparison with inorganic anions, but the sites in the fibres are of two types, namely those which are adjacent to positively charged basic groups and those which are not.

Parallel with the work of Gilbert and Rideal, a quantitative theory for the dyeing of cellulose was developed by Neale and his collaborators to account for the dye and electrolyte concentrations found in the fibre. They assumed that the direct dyes exist in solution as fully dissociated salts of type Na_zD, and that of all the ions present only the dye anions are specifically adsorbed at the cellulose-water interface. The distribution of all other ions is determined by the need for electrical neutrality in any finite volume of the system. In the case of cellulose, unlike wool, there are no ionic sites for adsorption.

Neale has also shown that the maximum amount of Chlorazol Sky Blue FF (C.I. Direct Blue 1) which is adsorbed by cellulose corresponds roughly with the available internal surface area if the dye is assumed to form a unimolecular layer thereon. Thus it appears that the dye is adsorbed upon a finite number of sites of a non-ionic type. Its activity would thus be represented by the fraction $\frac{\theta}{1-\theta}$.

R.H. Peters and Vickerstaff have cast doubt on the above line of reasoning, since the saturation value of a cellulosic fibre towards different direct dyes varies by a factor of at least five from dye to dye, and it has no apparent connection with the molecular size or constitution of the dye. This behaviour is in distinct contrast to that of acid levelling dyes on wool, where those examined give almost exactly equivalent saturation values.

Furthermore, in the case e.g. of the direct dye Chrysophenine G on Cellophane, the estimated saturation value appears to vary with the concentration of sodium chloride present in the system. Consequently it is not possible to represent the activity of the dye anions in the cellulose fibre as a function of the fraction of sites occupied unless it is assumed that the type and number of available sites differ from dye to dye. The cations which must accompany the dye into the fibre, to maintain electrical neutrality, similarly cannot be represented by any function of this type, as no sites for the adsorption of such ions exist.

Consequently, Peters and Vickerstaff, while assuming the dye to be completely dissociated in solution, modify Hanson, Neale and Stringfellow's arguments by introducing a volume term V (expressed as litres per kg. of fibre) which represents the volume of a thin layer of solution, near the fibre-water interface, which contains all the variations in ionic concentration.

All the above mentioned arguments are mostly in favour of the assumption that dyes exist in monodisperse form in solution and in the adsorbed state. However the work carried out in recent years in this laboratory on the adsorption of dyes at both organic and inorganic substrates, and on light fastness, has cast doubt on the correctness of this assumption, and as stated at the beginning of this Introduction, it appears that it will be necessary to reconsider the whole theoretical basis of the chemistry of dyeing processes.

The following paragraphs give a short review of the previous literature, mainly describing work in this laboratory, in which it is suggested that adsorbed dyes exist in a heterogeneous state; i.e. that they exist largely as micelles or aggregates in a range of sizes, but perhaps with some molecularly disperse material as well.

Adsorption of dyes as micelles has of course long been known in the case of cyanine dyes on silver halides (for a survey, see Dickinson). Pankhurst also has shown that micellar complexes are formed, in aqueous solution, between gelatin and long chain alkyl sulphates, a system which may be considered as a model of acid dyes and protein fibres.

The basic dye Methylene Blue when adsorbed on silica (Allingham <u>et al</u>., 1958) or on gelatin (Campbell and Giles) clearly shows the presence of an aggregated state in the substrates. This dye is particularly appropriate for this type of examination since Lemin and Vickerstaff have shown that its light absorption peaks at ca. 6700 Å and 6100 Å in concentrated aqueous solutions correspond with monomeric and polymeric forms respectively. The presence of aggregated material is therefore readily detected by spectrophotometry. By this means Allingham <u>et al</u>. have found that a dye solution after shaking with silica contained a lower proportion of aggregated dye than one of similar concentration, which had not been so treated; and further, the reflectance of the dyed silica itself showed the aggregated dye waveband. Similar results have been obtained by the same authors with silica and a cyanine dye. Gelatin films dyed with Methylene Blue also show both monomer and aggregate peaks in the absorption spectrum. These are given by the material which has not been dried after removal from the dyebath, so that aggregates must be formed during the actual dyeing process and not during the subsequent drying out of water. Campbell et al. found that disaggregating agents (phenol or urea) added to the dyebath, reduce the proportion of the aggregate present.

In the adsorption of basic dyes by graphite Galbraith et al. found that the maxima obtained are much higher than can be accounted for by a normal monolayer of monodisperse dye, and they attributed this to the formation of monolayers of ionic micelles or aggregates.

Hansen, Fu and Bartell give evidence of multilayer adsorption of small aromatic and aliphatic molecules, e.g. aniline, phenol, or valeric acid on various forms of carbon, from aqueous solutions approaching saturation concentration.

Cameron, Giles and MacEwan, found that a particular polyhydroxy anthraquinone dye has a marked condensing action on a casein monolayer; and Giles and MacEwan found that metal-complex dyes with strong hydrogen-bonding groups at opposite ends of the molecule, also have condensing action on monolayers of the protein edestin. These effects seem to be much more marked than would be expected from the size of these dye molecules. Tannic acid, which behaves similarly, has a very large molecule. These authors suggested that micelles of dyes are present and when adsorbed by the protein monolayer are responsible for the effects observed.

Recently absorptiometric measurements of dyes in aqueous solution, or in transparent films of gelatin or Cellophane, have been made up to high optical densities, and evidence has been found of the micellar nature of mostof the adsorbed dyes. This is discussed in the Introduction to Part II of this thesis.

Another line of evidence pointing to similar conclusions is obtained from work on photochemical action. Dyes which are aggregated take considerably longer to fade in light than those which are monomeric. Thus, Baxter et al. have studied the relationship between light fastness and dye concentration, and have drawn conclusions regarding the physical state of dyes in air-dry substrates. They found that in most substrates the dye appears to exist at least partly in the form of aggregates. A detailed discussion is given in Part III of this thesis.

PART I

ADSORPTION AT INORGANIC SURFACES

The adsorption of organic dyes from solution by two forms of alumina, viz. the anodic oxide film on aluminium and acidified chromatographic alumina powder is nowadays carried out very extensively. The aim of the present work was to find out whether the dyes are adsorbed as associated particles as in the case of the other inorganic substrates mentioned in the Introduction above or as monodisperse molecules. The method employed was to estimate specific surface area values of the alumina from the adsorption isotherms of various dyes and to compare the data so obtained with the specific surface area value obtained by phenol adsorption; it being assumed that phenol is adsorbed monomolecularly, so that the value obtained is a "true" specific surface area.

Any specific surface area values higher than those obtained by phenol were considered as evidence for dye aggregates, adsorbed on the surface of the substrates.

EXPERIMENTAL

Preparation of the Oxide Film.

(a) Anodising equipment

The anodising cell was a 2 l. beaker immersed in a thermostat. The cathode was a lead plate (6" x 3½" x 1/6") and the anode a strip of aluminium foil of the same area. Any variation in temperature over the metal surface was minimised by agitating the electrolyte with an electrically driven stirrer. The cell was connected to the a.c. mains through a rectifier, with a voltmeter across the electrodes, an ammeter in series with the main circuit and a variable resistance to adjust the output from the rectifier.

The electrolyte used was a 3% solution of "Analar" chromium trioxide in distilled water.

(b) Anodising procedure

The aluminium foil was cut to size (6" x 3½") and lightly marked into strips (3½" x 1/4"). It was degreased by wiping over with cotton wool soaked in carbon tetrachloride. After rinsing with water the foil was inserted as anode in the cell. Anodising was carried out for two hours at constant temperature at an applied voltage of 45 v. This ensured a current density of 6 amps./sq.ft. On completion of anodising the anode was removed from the cell and washed with water. The anodising foil was dried by pressing between two filter papers to remove loose water, followed by oven drying at 130° for one hour. Prior to use in adsorption experiments the foil was kept in a desiccator, but never for more than 24 hours after anodising as the adsorptive capacity of the film deteriorates if a longer period is allowed to elapse.

Analysis of the Oxide Film

The method suggested by Edwards was used to determine the weight of oxide on a strip (3½" x 1/4") cut from the anode. Each strip was immersed in 50 ml. of a boiling solution containing phosphoric acid (85%, 35 ml.) and chromium trioxide (20 g. per litre). By weighing the strip before and after immersion, the amount of oxide present was obtained by difference. In practice, a 5-minute treatment was found sufficient. The average weight of oxide on a strip of 0.875 sq.in. area was ca. 0.015 g.

Analysis of aluminium in aqueous solution.

The concentrations of aqueous solutions containing aluminium were determined using "aluminon" reagent. This reagent forms a bright red lake with aluminium. It was prepared by dissolving 0.2 g. of ammonium aurin tricarboxylate in 100 ml. of distilled water. Small concentrations of aluminium (up to 0.05 g. in 50 ml.) give pink to red coloured solutions which are suitable for colorimetric estimation.

The method of estimation used is described by Vogel. 8 ml. of 2% hydrochloric acid, 10 ml. of 25% acetic acid and 5 ml. of the reagent were added to 2 ml. test solution. The volume was finally made up to 50 ml. by addition of a 10% solution of ammonium carbonate in 30% aqueous ammonia (0.880 S.G.) solution. The colour produced was compared with that of standard solutions prepared by dilution of an aqueous solution containing 1.759 g./l. "Analar" potassium aluminium sulphate, of which 1 ml. contained 0.1 ml. of aluminium.

Preparation of alumina powder

The substrate was mainly from a single sample of chromatographic alumina (Type H, Savory and Moore), but a few tests were made on a rather coarser sample (B.D.H.).

The powder was found to be alkaline in character, 20 ml. of distilled water, shaken up with 1 g. at room temperature, had a pH of 9.5. Alkaline alumina does not adsorb acid dyes, acidified alumina adsorbs them freely; therefore the powder was acidified before use by washing 100 g. twice with 200 ml. 2 N-hydrochloric acid, followed by several rinsings in water. It was then dried in an oven at 150° for two days. The pH of this alumina in distilled water was 4.4.

Both samples of the alumina powder when standardised were found to correspond to Brockmann's grade II. They were kept in separate desiccators during the course of the work.

Dyes etc.

Pure dye samples prepared by the writer's predecessors were used in these experiments. A list is given in Table I.[1]

Adsorption procedure

(a) Oxide Film

5 ml. of a solution of the compound under investigation was placed in a test tube together with a weighed strip of anodised foil. The tube was then completely sealed in a Bunsen flame and immersed in a thermostat tank at the required experimental temperature.

TABLE I.1

The following dyes were used for specific surface area measurement.

	Base	Coupling component
		Monosulphonates
I	Sulphanilic Acid	1-naphthol
II	"	" (O-methylated)
III	"	2-naphthol
IV	1-Naphthylamine-4-sulphonic acid	"
		Disulphonates
V	Aniline	R-acid
VI	1-Naphthylamine	"
VII	p-n-Butylamiline	"
VIII	p-n-Dodecylaniline	"
IX	Sulphanilic acid	Schaeffer acid
X	1-Naphthylamine-4-sulphonic acid	"
XI	Aniline	N-acetyl H-acid
XII	p-n-Butylaniline	"
XIII	p-n-Dodecylaniline	"
XIV	Aniline	H-acid
XV	p-n-Butylaniline	"
		Trisulphonates
XVI	Sulphanilic acid	R-acid
XVII	1-Naphthylamine-4-sulphonic acid	G-acid
		Tetrasulphonate
XVIII	Diamisidine	2S acid
XIX	Lissamine Green V (C.I.44025)	

For measurement of the rate of adsorption several tubes containing 5 ml. portions of a solution of one concentration, usually 0.02% by weight of solute, were placed in a thermostat. These were removed and their contents analysed at various time intervals measured from the instant of immersion. The state of the solution/oxide film system could thus be specified after the adsorption process had continued for different periods of time. Analysis of contents of tubes removed after a period of immersion which varied with solute and experimental temperature from 2 hr. to 24 hr. showed constant distribution of the solute between film and solution. This indicates that the system has reached the equilibrium state.

Adsorption isotherms were plotted from results obtained by immersing a number of tubes in the thermostat each containing one of a range of concentrations of the solute, usually 0.02% to 0.2% by weight. The tubes were allowed to remain in the thermostat until equilibrium was attained.

The amount of solute adsorbed by the oxide was determined by noting the difference between the initial and final concentration of the test solutions.

The amount of oxide film was calculated by weighing the film before immersion and then subtracting from this the value obtained by stripping the oxide from the film after completion of adsorption.

(b) Alumina powder

The adsorption in this case was found to be complete in less than five minutes, and hence there was no need to obtain details of adsorption rate.

0.1 g. of dry acidified alumina was used with 5 ml. test solution, giving a solution/oxide weight ratio of 50:1 compared with 300:1 in the case of adsorption experiments on the anodic oxide film.

Estimation of concentration of solutions of compounds studied.

The concentrations of solutions of the compounds under investigation were determined by photoelectric absorptiometry at the wavelength most highly absorbed by the solute. The Unicam SP 500 and 600 instruments were employed.

RESULTS AND DISCUSSION

Effect of Change in Volume of Solution

Examination of isotherms for the adsorption of Orange I by anodic film (Fig.I.1) shows that at a given temperature they depend markedly on the ratio of solution volume to film weight. It is clear from the data obtained for the dyes, Orange II (Dye III), 1-naphthylamine → R acid (Dye VI) and sulphanilic acid → R acid (Dye XVI) at various ratios (Figs.1-3), that the amount of adsorbed solute in equilibrium with a given concentration in solution varies considerably with the solution : film weight ratio used. Stewart has found that the effect is not confined to the adsorption of sulphonated compounds, because it is also shown in the case of an aqueous solution of 2:4-dinitrophenol.

An explanation of this phenomenon is suggested by the fact that the anodic film was found to be slightly soluble in water. A series of experiments was carried out by using distilled water in place of dye solution in order to determine the relation between the amount of film dissolved and the solution : film weight ratio. The aluminium content of the water after contact with the anodised foil was determined by means of Aluminon reagent as described above; and the amount of film corresponding to this was calculated. The results of these experiments (Table I.2)show that, as would be expected, the higher the solution : film weight ratio, the greater is the amount of film dissolved. It is also evident from Table I.2 that the dissolution appears to be independent of temperature, and to be very rapid compared with adsorption. In fact it seems to be complete in less than five minutes.

The films were usually dried, after electrolysis and rinsing, at 130°-140°C. It was thought that possibly the drying process might produce a water-soluble surface layer. Hence tests were made with undried films; these were rinsed and used immediately for adsorption of Orange II (Dye III).

TABLE I.2

Water solubility of chromic acid anodic film. Means of triplicate results, initial wt. of film, 0.015 g.; anodising temperature, $53 \pm 2^{\circ}$, but $45 \pm 0.5^{\circ}$ for test marked*.

Liquid: film weight ratio	% Original film* dissolved Temp and time (min.)						
	30°	40°			59°	60°	
	15	5	10	25	600	15	300
150:1					0.49*		
300:1	0.91	0.96	0.98	0.98	0.81*	0.98	0.93
460:1		1.2					
1400:1					2.19*		

* The film solubility falls with the anodising temperature, c.f. the reported decrease of film porosity with fall in anodising temperature, and Fig.3.

However, the "volume effect" was still observed, although the specific surface area was thereby reduced in all liquor volumes to less than half its normal value.

It appears that the increase in adsorption with increase in solution : film weight ratio is a result of increase in the surface area of the film due to some of the original surface being dissolved. (The normal effect of solvents on crystals is to increase the surface by etching).

The data given by Greenberg for calcium hydroxide adsorption on silica from water also show evidence of a slight increase in amount adsorbed with increase in volume of solution. This effect is not observed in adsorption on graphite and chromatographic alumina, both water-insoluble. Fig.I.3 shows the relation between the volume of solution and adsorption of sulphonated dyes. When the logarithm of liquid : film ratio (log v) and the logarithm of concentration of dye in the initial monolayer (log C_F) are plotted against each other, then the curves for Dyes VI and XVI at the anodising temperature of 45°C., run parallel. This shows that the increase of specific surface area depends only on the volume of liquid, and does not depend on the nature of the dye; again suggesting that the effect is due to water dissolution of film surface. When the anodising temperature is increased, the specific surface area available at any given liquid : film ratio also increases. Thus it is seen from Fig.I.2 that an increase in anodising temperature (to 59° for Orange I) has the same effect on adsorption that an increase in liquid : film ratio does.

'Sealing' Effect

The anodic film when pretreated in a large volume of cold water for five minutes adsorbed more Orange II than it would otherwise have done (FigI.4). On the other hand, pretreatment in hot water (166:1) at 60° for two hours and then dyeing normally, reduced the adsorption. This is evidence of the well-known "sealing" effect, a slow process whereby the film pores are closed by the growth of aluminium hydroxide crystals (see e.g. Spooner, also Giles, Mehta *et al*., 1954). This is used commercially to fix dyes against degradation by light or by wet processes. The treatment is carried out in hot water or steam. The rate at which the sealing becomes effective depends on temperature. That the results of the normal adsorption tests are not influenced, is shown by the fact that the maxima of the rate curves are independent of temperature (Fig.I.4). Some isotherms are also independent of temperature (Fig.I.5a). The higher the temperature the more pronounced is the sealing effect. If sealing did influence adsorption, it is difficult to understand how adsorption isotherms can give maxima that are independent of temperature. It seems that adsorption is the more rapid procedure and is competitive with "sealing"; further, that adsorption at constant liquid : solid ratio can be considered virtually unaffected by the much slower subsequent sealing process.

Estimation of Specific Surface Area.

Many methods are used for estimating the specific surface areas of powders and porous solids, several of them requiring use of complex equipment. One of the most reliable methods is gas (usually nitrogen) adsorption at low temperatures. The specific surface area is readily calculated from the isotherms. Liquid-phase adsorption of solutes is much simpler and often a more rapid procedure. The adsorption of basic dyes, especially Methylene Blue (C.I.52015), has been used for finding the specific surface area of silica, but the results are probably unreliable because of the ease with which the dye is adsorbed as micelles, thus giving fictitiously large values. The use of any substances having large aromatic molecules is probably undesirable, unless the exact mode of attachment to the surface is known or can be inferred with confidence.

It seems that a solute for surface area determination should have a molecule with the following characteristics. (Giles, MacEwan *et al*., 1960).

a) Reasonable solubility, in common solvents, especially water.

b) Small size with no surface activity (so that micelle formation is unlikely).

c) Planar shape, for ease of estimation of its surface coverage.

d) Ease of analysis.

In the present work, phenol was chosen for estimating specific surface area measurements of both anodic and chromatographic alumina, since all the requirements listed above are met by this compound.

Specific Surface Area of Anodic Alumina Film.

This discussion also covers work done by the writer's predecessors as indicated in Table I.3.

Since the position of isotherms in all cases varies with solution : film weight ratio and also with anodisation temperature, all results in Table I.3 refer to equilibrium data obtained at a fixed volume : weight ratio of 300:1 and an anodisation temperature of 45°C.

The dimensions of the anions studied were determined by measuring the sides of the smallest rectangular box, in which the anion could be enclosed, using Catalin (Stuart type) models.

The surface area of the film available for adsorption of the anions was determined from the isotherms of phenol at 46°C. In the film the phenol molecule may be expected to be standing normal to the surface, forming a close-packed monolayer. The molecular area is then assumed to be 24 Å, as for surface-active phenols on water. The surface area of the film was then estimated by multiplying the number of anions comprising the monolayer by the area of the anion, which gave a value of 11.5 $cm^2./g. \times 10^{-5}$. The specific surface area was then calculated from adsorption data for the other compounds, tabulated in Table I.~~II~~3. The values obtained for the cross-sectional area of the anion, measured from the models in the three positions shown are recorded in Table I.3, and also the values for the surface covered by each anion assuming it is adsorbed end-on, edge-on or flat respectively.

It is evident that most of the compounds are adsorbed as monolayers. The smaller values given by most of the di- and tri-sulphonated dyes may be due to the presence of associated water around the sulphonate groups.

Orange II (Dye III), the C_{12} homologue of Azo Geranine (Dye XIII) and Sky Blue FF (Dye XVII) however give values rather higher than phenol. Their high adsorption values can reasonably be assumed to indicate that some aggregates or micelles of these dyes are adsorbed on the surface of the films.

Specific Surface Area of Alumina Powder

To find out the reliability of the value obtained for specific surface area measurement by solution adsorption, comparison was made of the data obtained for the specific surface area by other methods using different samples of alumina. The two different materials were (a) a sample of chromatographic alumina (Type H, Savory and Moore) and (b) a coarser material supplied by B.D.H. Three different methods (a) phenol adsorption, (b) air permeability test and (c) microscopic counts were employed. The results are shown in Table I.4. Several of

TABLE 1.3

Measurements of specific surface area* on chromic acid anodic film

Solute (in aq. solution, except where shown)	Area of mol. or anion (Å^2)			Max. adsorption (mmole/kg.)	Temp.(°C)	Surface covered (cm.^{2}/g. x 10^{-5}) Assumed orientation**		
	End-on	Edge-on	Flat			End-on	Edge-on	Flat
Phenol	24**	-	40	800	46	11.5	-	-
Monosulphonated								
Dye I (Orange I)	50	72	150	350	50	10.5	-	-
Dye III	50	80	150	400	50	12	-	-
Dye IV	50	75	150	350	50	10.5	-	-
Disulphonated								
Dye V	65	80	200	180	52	-	9	-
Dye VIII	65	80	250	215	50	-	10.5	-
Dye VI	65	80	190	180††	50	-	9.0	-
Dye IX	65	85	160	100	50	-	-	10
Dye X	60	80	190	125	50	-	-	(15)
Dye XI	60	85	195	200	50	-	-	9
Dye XIII	60	85	250	260	33	-	12	-
‡Dye XIX	55	85	210	115	36.5	-	6	-
Trisulphonated								
Dye XVI	65	85	225	65	50	-	-	9
Dye XVII	55	80	190	65	50	-	-	7.5
Tetrasulphonated								
‡Dye XVIII	55	145	380	65	50	-	-	15

*All data for solution vol./film wt. ratio, 300:1 except where otherwise stated. Anodisation temp. 45°.

**Water solvated.

†† By interpolation from data at other solution vol./film wt. ratios.

‡ Expt. not by author.

these tests were made by the writer's predecessors.

Table I.4

	Type H	Coarse Powder
Loss on ignition	6.5	5.9
Sieve grading (%) + 100	0.6	8.8
-100, +150	67.0	57.7
-150, +200	14.3	8.0
pH of 5% w/v solution	8.7	9.2
Activity	I-II	II
Temp. of activation		
normal	600	-
maximum	700°	-
Specific surface area, $cm.^2 g^{-1}$ (approx.), by:-		
phenol adsorption	5.0×10^5	0.5×10^5
air permeability	0.027×10^5	0.04×10^5
microscopic count	0.035×10^5	0.15×10^5

Thus, air permeability and microscopic count gave specific surface areas less by factors of <u>ca</u>.100 and 10 respectively, than those given by phenol adsorption. The discrepancies between the values could be explained by assuming (a) that the H type powder has a much rougher surface than the other, and perhaps a higher content of extremely fine particles (as shown by fine sieve grading), (b) that in the air permeability test fine particles tend to lodge in cracks in the rough surface of coarse ones.

All the sulphonated azo dyes studied were found to be strongly adsorbed on acidified alumina from aqueous solution. The amount adsorbed at equilibrium is independent of time and temperature (Fig.I,6,6a)The isotherms have well defined plateaux which, for the purpose of specific surface area measurements, may be taken as representing the existence of monomolecular layers of adsorbed solute on the substrate.

Specific surface areas were calculated as in the case of the anodised alumina, see Table I.5. The amount of the dye adsorbed in a few cases is too high for monomolecular adsorption, and therefore micellar adsorption may be occurring.

Table I.5- Adsorption on alumina powder

Solute	Area of mol. or anion (A^{o})			Max.adsorp.	Surface covered ($cm^2 g.^{-1}$, x 10^{-5})		
	End-on	Edge-on	Flat	m.mole/kg.	End-on	Edge-on	Flat
			Monosulphonates				
Dye (III)	50	80	150	166	5.2	-	-
Dye (IV)	50	75	150	175	5.5	-	-
			Disulphonates				
Dye (VI)	65	80	190	104	-	5.2	-
Dye (X)	60	80	190	100	-	5.0	-
Dye (XI)	60	85	195	80	-	4.25	-
Dye (XII)	60	85	220	132	-	7.0	-
Dye (XIII)	60	85	250	124	-	6.5	-
Orange *	65	140	375	106	-	9.5	-
Ponceau *	55	110	235	62	-	4.3	-
			Trisulphonates				
Dye (XVI)	65	85	225	58	-	-	8.1
Dye (XVII)	55	80	190	68	-	-	8.1

*These two dyes are not included in Table I.~~II~~1; they are Congo Orange R (C.I.23605) and Poncean 6RB (C.I.27165) respectively.

PART II

ADSORPTION AT ORGANIC SUBSTRATES AND IN SOLUTION.

IIA BEER'S LAW AND ABSORPTION SPECTRA MEASUREMENTS

INTRODUCTION

Lewis and Calvin have suggested that the absorption spectrum of a substance with a planar or almost planar molecule should consist of bands corresponding to electronic oscillations along the three perpendicular axes of the molecule respectively. The shorter the axis the shorter the wavelength of its band. This suggestion was confirmed experimentally by Lewis and Bigeleisen in the case of several basic dyes. When the molecules aggregate, they may pack face to face, and the axis normal to the face is lengthened. Thus the aggregates should have an intensified short wave-band. This was in fact found with a number of dyes which display two well defined absorption bands.

Lemin and Vickerstaff, studying the aggregation of Methylene Blue (C.I.52015), confirmed that its absorption spectrum consists of two peaks, ~~the~~ one at the lower wavelength due to polymer, and the one at the higher wavelength due to monomer. By making use of this fact Lemin and Vickerstaff were able to estimate approximately the proportion of monomer and aggregate present from the relative heights of the peaks.

Recently Campbell and Giles have examined the absorption spectra of Methylene Blue in various organic substrates, e.g. gelatin and Cellofas A (ethylmethyl cellulose). They confirmed the presence of the aggregate peak. Phenol and urea acted as disaggregating agents, and lowered this peak.

The cyanine dyes, which have been studied exhaustively (see e.g. Dickinson), show the main absorption band of the monomeric form of the dye (often termed the "M" band), in dilute aqueous solution or in non-aggregating solvents such as pyridine. A shoulder on the short-wave side of the band becomes more pronounced ("D" band) as the concentration in water increases, and is usually attributed to a dimeric form. At high concentrations a new long-wave band may appear. This is known as the "J" band, and is attributed to chain-like aggregates in which the planar dye molecules are packed face-to-face with a layer of water molecules between each pair of dye molecules.

Katheder has used the decay of fluorescence to determine the degree of polymerisation of methin-cyanines. Davey and Dickinson give evidence that some cyanines in solution exist as both single and aggregated molecules.

Lewis and Bigeleisen have also detected second order x-bands in absorption spectra of dyes. These bands are about half the wavelength of the first-order bands, whereas the y-bands have usually only slightly shorter wavelengths than the x-bands.

Holmes, as early as 1924, studied the absorption spectra of a great number of dyes at varying concentrations. He noted that the wavelength of maximum absorption changed as the concentration changed, but he did not attribute this change to the formation of aggregate at higher concentrations.

Forster and Konig, by examining the concentration dependence of the absorption spectra of aqueous solutions of C.I. Acid Yellow 73, C.I. Acid Red 87 and C.I. Basic Violet 10, have deduced that the dyes exist in solution as dimers. The monomer absorption band upon dimerisation splits into two bands, one at a slightly longer, the other at appreciably shorter wavelengths.

Little is known about the occurrence of these bands in the spectra of other dyes, except vat dyes in some solvents, and apart from investigations upon cyanine dyes in silver halide-gelatin emulsions (see e.g. Dickinson), little previous work on the occurrence of x and y-bands in spectra of adsorbed dyes has apparently been reported. In connection with the study of the photo-tendering properties of anthraquinone dyes Moran and Stonehill have described the x- and y-bands in spectra of vat dyes dyed on cellulose films but they did not discuss the effect of changing the concentrations.

Deviation from Beer's law

Schubert and Levine have studied deviations from Beer's law. They maintain that not all deviations from Beer's law can be explained by dye polymerisation. According to them the location of the permanent charge of the dye ion is more important. In those dyes that conform to Beer's law the charge group is part of the chromophoric system, whereas those that do not conform to Beer's law the charged group is not part of the chromophoric system.

Previous evidence of aggregation at organic substrates

Besides the case of Methylene Blue on gelatin and Cellofas, discussed above, dyes have previously been found to be adsorbed in aggregated states in the case of (a) acid dyes in wool (Astbury and Dawson), and basic dyes in oxidised cellulose and alginic acid (Warwicker). Schiebe has found that "polymerisation" of certain dyes occurs more readily at surfaces than in solution.

Effect of disaggregating agents

It is well known (Vickerstaff) that the degree of aggregation of dyes in aqueous solution usually rises with the addition of electrolytes or with fall in temperature, and falls with addition of certain hydrogen bonding agents, e.g. alcohols, phenol, ethylene glycol, pyridine or urea. Thus Alexander and Stacey have shown that aggregation of Benzopurpurine 4B (C.I. 23500) and Coomassie Milling Scarlet 5B (C.I.23910) can be substantially reduced by the addition of high concentrations of urea and relatively smaller concentrations of phenol. The aggregation of Benzopurpurin was also examined by Martin and Standing, who found that sodium chloride causes aggregation, but in the presence of pyridine aggregation is prevented. Aryan has also studied the prevention or dispersion of dye aggregates. He examined the absorption spectra of a series of dyes in mixtures of water and an organic solvent, e.g. alcohols, pyridine. The ratio of maxima of longwave and shortwave bands indicated the degree of association, which was found to depend on the nature of the solvents.

Present work

This work was carried out to determine qualitatively the physical state of dyes in solution and adsorbed by organic substrates. First a detailed examination of the absorption spectra of the direct cotton dye Benzopurpurin 4B (C.I.23500) in solution and in adsorbed solid phases was carried out. The state of aggregation of this dye has been studied previously by other means (Alexander and Stacey). It is also a dye of low light fastness, so that it is probably adsorbed by the cellulose in monodisperse form (due to strong dye-fibre associative forces). Hence if a state of aggregation is found for this case, it is reasonable to assume that it occurs with most other dyes. Alexander and Stacey's data on dye aggregation are compared with "Beer's law curves" (optical density against concentration) for this dye and others (II, III) with the aim of establishing the value of these curves for detecting micelles in solid substrates. Later a series of such Beer's law curves for a number of dyes in different solid substrates e.g. gelatin, cellulose triacetate, regenerated cellulose, were obtained to discover whether dye aggregates exist in these solids.

Finally the absorption spectra in the visible region of a number of dyes of a variety of chemical classes (anthraquinone; monoazo, unsulphonated and sulphonated; dis- and trisazo, sulphonated; metal-complex; reactive; and triphenylmethane) have been examined in solution, in water and other solvents, and adsorbed in various transparent films. From the relative heights of the x and y absorption peaks, as discussed in the Introduction above, the conclusion is reached that the dyes always exist both in monomeric and aggregated states in most solutions and substrates, and the proportion of aggregate increases with concentration.

EXPERIMENTAL

Preparation of Films

a) Gelatin.- A 6% aqueous solution of gelatin (pure inert photographic quality) was evenly spread on a "subbed" photographic plate (4" x 2" x 5") on a screw-levelled platform. The film was then air dried and hardened by soaking in dilute formaldehyde (10 ml. of 40% 'formalin' solution in 100 ml.) for two hours, after which it was washed with cold water and dried.

For dyeing, the hardened films were cut to 4.7 x 1 cm., and placed in a series of test tubes containing 15 c.c. of graded concentrations of dye (0.0002 - 0.01 M) in distilled water. These were heated to 50-60°C., usually for 15-30 minutes. Where phenol was used a slight molar excess was added to each bath.

b) Cellophane.- The regenerated cellulose film used was normal commercial Cellophane of 0.001" thickness. The film was wrapped around a glass cage (1.5" x 1.5" x 2.75") and was securely fastened by means of small alloy metal staples. The unit was connected to the motor as shown in Fig. II.1. The cage was then immersed in a dyebath containing 300 c.c. of 0.05% dye solution. The unit revolved in the dyebath at 20 r.p.m., the temperature of the bath being maintained at about 85°, for approximately one hour. The different depths of colour were obtained by varying the time of dyeing. After dyeing the glass cage was removed, the film thoroughly washed with water and allowed to dry in the air still attached to the glass cage. Phenol or cetyltrimethylammonium bromide (CTAB), where required, were added to the dyebath (1-2 mol.per mol.dye).

c) Cellulose triacetate.- Film (0.003") containing 15% by weight of triphenyl phosphate as plasticiser was dyed from a hot suspension of dye.

Mounting of transparent films

The films were carefully cut to 4.7 x 1 cm. and bound between two glass plates of the same size, suitable for direct insertion in the cell-carrier of the spectrophotometer. In the case of gelatin slides, the film surface was covered with a second equal sized portion of similar glass.

Optical density and absorption spectra measurements

These were made on a Unicam spectrophotometer (SP 600 or SP 500). For absorption spectra, readings were taken at intervals of 50 A; for Beer's law curves, the optical density was measured at peak absorption wavelengths.

Differential Analysis

This is the name given to the method used in this investigation to enable high optical densities to be read with good precision. In place of the usual reference blank, one of a known solution of the substance under test is used, of concentration close (ca. 0.5 unit of optical density) to the unknown. The resulting optical density reading is then added to the optical density of the coloured blank used. This gives the optical density of the test solution, since optical densities are additive. For fuller discussion of the method and its theory see e.g. Giles and Shaw.

Extraction of dyes

After reading the optical density of the films the slides (gelatin, Cellophane or cellulose triacetate) were placed in a test tube with 10 c.c. of 50% (v/v) aqueous pyridine to extract the dye completely. After extraction the optical density of the extract was found by using a 10 m.m. cell in the spectrophotometer.

The examination of wet films was made by placing them in a 10 mm. cell in distilled water immediately after removal from the dyebath, and rinsing.

The two sets of optical density values were then plotted against each other, film optical density on the y-axis and extract optical density on the x-axis. If Beer's law is obeyed in the films a straight line should be obtained through the points.

The same procedure was carried out with the addition of certain agents to the dyebaths. When the results are plotted the curve should rise if disaggregation takes place or fall if there is increased aggregation. This can be seen from the tests with dyes in the known different aggregation states shown by Alexander and Stacey.

To show that no instrument error was likely to occur two experiments were carried out with Caledon Brown R and Duranol Brilliant Blue G300. These are insoluble, very finely powdered, dyes with quite different absorption peaks. These were used as suspensions in water, so that their particle size would be the same at all concentrations. Both suspensions obeyed Beer's law up to the highest measurable densities ~~(Fig. II.6)~~ (Campbell et al, 1959, Fig. 1) and instrument error is therefore negligible. (These experiments were made by the writer's predecessors).

Dyes.- The list of dyes used in this work is given below in Table II.1. Most of the dyes were purified from ethanol-water mixture. The basic dye Malachite Green (C.I.42000) was recrystallised from 10% aqueous hydrochloric acid.

Table II.1

Dyes used in Part II

i. Benzopurpurin 4B (C.I.23500)
ii. Coomassie Milling Scarlet 5B (C.I.23910)
iii. Polar Yellow R
iv. Orange II (C.I.15510)
v. Naphthalene Scarlet 4R (C.I.16255)
vi. Azogeramine 2G (C.I.18050)
vii. p-n-Butylaniline→N-acetyl-H-acid
viii. p-n-Dodecylaniline→N-acetyl-H-acid
ix. Cibalan Red 2 GL
x. Chlorazol Sky Blue FF (C.I.24410)
xi. Chrysophenine G (C.I.24895)
xii. Chlorantine Fast Green BLL (C.I.34045)
xiii. Duranol Brilliant Blue CB (C.I.64500)
xiv. Solway Blue BN (C.I.62085)
xv. Solway Blue RN (C.I.63010)
xvi. p-n-Dodecylaniline→2 naphthol
xvii. Aniline→Naphthionic acid
xviii Aniline→R Acid
xix. p-n-Dodecylaniline→ R acid
xx. Dye IV, see Cameron and Giles
xxi. Dye V, " "
xxii. Dye VI, " "
xxiii Dye VII, " "
xxiv Chlorarol Azurine G (C.I.24140)
xxv. Copper complex of C.I.24410
xxvi. Durazol Blue 4G
xxvii Irganol Blue BS (Geigy)
xxviii Irglan Orange RL (Geigy)
xxix. Cibacron Rubine R (Ciba)
xxx. Cibacron Scarlet 2G
xxxi. Procion Brilliant Blue 7HG (I.C.I.)
xxxii Malchite Green (C.I.42000)

RESULTS AND DISCUSSION

Light absorption data for Benzopurpurin 4B (C.I.23500)

The absorption curve for this dye gives only one noticeable peak. The position of this peak however changes its position in different media. In Fig.II2 a series of absorption curves for Benzopurpurin 4B determined in various solution and solid phases are shown. In solution λ_{max} moves from 5200 A in pyridine to 4850 A in salt solution. The maximum peak in wet cellulose is at 5200 A, while in dry cellulose it is at 5150 A. The maximum shift to short wavelengths is in the crystalline state, at 4650 A (Table II.2). The effect of light fading would probably be to destroy the more disperse dye more easily, and thus, as expected, after irradiation the peak tends to move to shorter wavelengths.

When the data from Table II.1 are plotted as wavelength of maximum absorption vs. extinction ratio, Fig.II.3, there appears to be a linear relation between all states. The points fall on two lines, representing solution and solid absorbed phases respectively. If the proportion of monodisperse dye decreases, the points will be further to the left. Upward movement also suggests a tendency in the same direction. The effect of light fading would be the progressive and preferential destruction of monodisperse dye, which would gradually shift the peak to the left.

It is assumed that this dye is always and in all media present in heterodisperse form, partly monodisperse, partly aggregated.

TABLE II.2 Spectral Absorption data for Benzopurpurine 4B

Solvent	max (A^{o})	Optical density (1 cm. cell)	Ratio of densities at 4650 and 5200Å
pyridine	5200	0.360	0.51:1
pyridine	5200	1.020	0.54:1
pyridine	5150	2.010	0.62:1
50% (V/V) aqueous pyridine	5100	0.804	0.67:1
1.0M aqueous phenol	5000	0.734	0.84:1
0.2M aqueous phenol	5000	0.307	0.90:1
0.2M aqueous phenol	5000	0.802	0.92:1
5.0M aqueous urea	5000	0.900	0.87:1
1.3M aqueous urea	4920	1.100	0.97:1
water	4975	0.255	0.94:1
water	4950	0.762	1.00:1
water	4950	3.000	0.97:1
0.01M NaCl	4900	1.040	1.11:1
	solid phases		
substrate			
cellulose wet*	5200	0.328	0.67:1
cellulose wet	5200	0.500	0.68:1
cellulose wet	5200	1.000	0.64:1
cellulose dry	5200	0.326	0.62:1
cellulose dry	5150	0.775	0.70:1
cellulose dry	5150	1.190	0.69:1
cellulose dry	5150	2.750	o.65:1
cellulose film after irradiation 8 in. from 400W Hg-vapour Lamp (unfiltered) for			
1 h	5120	0.710	0.75:1
20 h	5100	0.620	0.83:1
20 h	5100	0.924	0.83:1
93 h	5070	0.510	0.85:1
288 h	5070	0.373	0.85:1
cellulose (dyed in 1% aqueous CTAB)	5100	2.140	0.69:1
gelatin film (dyed in 0.004M phenol solution)	5090	1.050	0.79:1
gelatin film (no addition)	4900	3.278	1.03:1
gelatin film (dyed in 0.2M phenol)	4900	2.855	1.13:1
dry crystals (by evaporation of EtOH solution on glass)	4650		very high

*examined in water immediately after removal from dye bath.

Possibly in its most highly disperse form it gives λ_{max} at 5200 A; this value falls with increase in micelle size. Hence the results show that in dyed cellulose and gelatin films Benzopurpurin 4B is present both as monodisperse and associated form.

The dye, aniline → naphthionic acid, is a homologue of the "half molecule" of Benzopurpurin 4B. A series of absorption curves for this dye were also determined in different solutions. The absorption peaks are at 4550 A and 4620 A respectively. The peak of the "half molecule"dye in water is broader than in pyridine. The peak also does not shift with aggregation. Beer's law is not obeyed in aqueous solution, the curve is nonlinear at concentrations above 0.001 gm./l. This is attributed to aggregation.

The dyes used are listed in Table II.1.

Effect of disaggregating agents in solution and in films.

Alexander and Stacey made a number of tests on the light scattering properties of dyes. They found that dyes I-III are highly aggregated in aqueous solutions up to $60^{o}C.$, containing low concentrations of salt. Apparent molecular weights were as follows i 2.8×10^{-4} ($0.05 - 0.30$ $g.l^{-1}$; 0.01 M. NaCl $20^{o}C$) ; ii 2.9×10^{-4} ($0.1 - 0.5$ $g.l^{-1}$; 0.01 M. NaCl, $4^{o}C.$); iii 11×10^{-4} ($0.38 - 0.50$ $g.l^{-1}$ ($0.05 - 0.20$ M. NaCl $20 - 60^{o}C.$), respectively.

They also reported that the addition of a small amount of phenol or urea to solutions of i and ii substantially reduced aggregation. Thus, a solution of ii (o.12 g.l^{-1}, at 20°C.), which was completely flocculated by addition of 0.025 M. NaCl., had only a small turbidity in presence of phenol (0.04 M. However dye iii was not disaggregated by the addition of phenol or urea.

In the present work aqueous solutions of Dyes i-iii were examined with and without phenol. The apparent extinction of i and ii is markedly increased, i.e. the degree of dispersion is increased, by phenol and still more so by pyridine (Fig.IL3) and that of iii is increased only very slightly (Fig.IL4). This is in agreement with Alexander and Stacey's results, obtained by a totally different method (light scattering).

Dye I was also applied to Cellophane and dyes ii and iii, which are acid wool dyes, were applied to protein (gelatin film). Similar tests were then carried out as with solutions. The results obtained in each case are qualitatively exactly similar to those obtained with solutions. Phenol increases the apparent extinction of i and ii but not (or only very slightly) that of iii. The most reasonable explanation for this behaviour appears to be that the dyes are aggregated in the adsorbed state in the films, as they are in the respective solutions.

Further interesting comparisons can be made by examining the position of equivalence lines[*]. In Fig.II.4 all the curves of dyes I and II in films lie below the equivalance lines. This suggests that transference to solution in pyridine increases the apparent extinction. In the case of dye III, both curves are coincident with the equivalence line, so that phenol or pyridine have no effect on the extinction and probably neither is very effective as a disaggregating agent.

Examination of optical density - concentration relations in other dyed systems.

A variety of other dyes were next examined by similar methods to those just described. These included sulphonated acid wool dyes (IV-VIII) and an unsulphonated metal-complex dye, (IX) all applied to gelatin; three sulphonated direct cotton dyes two (X, XI) of low and one (XII) of high light fastness, applied to Cellophane, and a non-ionic disperse dye applied to cellulose acetate[**]. Results are shown in Figs.(II.5,6 All the dyes in this series are affected by disaggregating agents, having their extinction in the dyed substrate raised by the

[*] Showing the theoretical relation if the extinction were the same in film or pyridine; calculated from dimensions of film and spectrometer cell, and volume of extract.

[**] A number of these curves were determined by Campbell and Cathcart.

agents. These dyes include several with small highly sulphonated molecules. The evidence therefore suggests that all the dyes exist partly in an associated form in the adsorbed state.

The one exception in this series is that shown by Cibalan Red 2GL (IA) on gelatin. The behaviour of this dye is similar to that of Polar Yellow R (III) discussed above. It is unaffected by phenol and belongs to a class of dyes known to be highly aggregated in aqueous solution. Giles and McEwan have shown that this class of dye is probably adsorbed by proteins in the form of stable micelles, held together largely by Van der Waals forces. It appears that adsorbed aggregates of both dyes III and IA are stable to phenol.

Absorption spectra of dyes.

From a study of Figs. 7-9 it is evident that most dyes of all classes have two absorption bands in the visible region. These bands are tentatively identified with Lewis and Calvin's x and y bands, because they are close together and, with increase in dye concentration either in solution or adsorbed in solid films, or on changing from a non-associating solvent (e.g. methanol or pyridine), to an associating one (e.g. water), the band of shorter wavelength almost always increases in height relative to that at longer wavelength. In a very few cases it remains constant, but in almost no case does it decrease. In a few cases, e.g. Irganol Orange RL or Cibacron Scarlet 2G, the bands are so close as to make one of them difficult to locate with precision; it appears as a very slight bulge on the short wave side, occasionally on the long wave side, of the main peak. In Fig.II.D is shown the method used to estimate the approximate position of this type of band.

The azo dyes used are *ortho*aminoazo or *ortho*hydroxyazo compounds, and therefore cannot show (a) azo-quinoneimine or (b) *cis-trans* changes. This was confirmed by the examination of Orange II (Sulphanilic acid → 2-naphthol) in solution. Here the x:y band ratio did not change either with variation in pH (a) or on prolonged exposure to high intensity illumination (b).

Both bands persist in all media, but there is in most cases a "solvo-chromatic" shift of both bands with change of solvent, according to Kundt's rule. This rule states that an increase in refractive index of solvent causes the absorption waveband to move to longer wavelengths. However this rule is not always followed and opposite effects are sometimes found among dyes of closely similar structure. For example, Sky Blue FF obeys the rule in water and pyridine, but Benzopurpurine behaves in the opposite sense.

The similarity in behaviour of each dye is solutions or adsorbed in films, with increase in concentration, is evidence that the adsorbed dye is at least partly aggregated. The result of the examinations of "Beer's law curves" of dyed film discussed previously is thus confirmed.

The change in the height of the y band relative to the x band, with increase in concentration, was quite small, about 5% for a hundredfold increase in concentration.

Krasovitskii and Pereyaslova have found that λ_{max} for benzidine cotton dyes is frequently much higher on regenerated cellulose sheet, than in solutions. They attributed this to increased conjugation in the dye molecules, caused by improved planarity. From the data in Table II.3, it is evident that λ_{max} for many dyes shifts to longer wavelengths when the dye is adsorbed on cellulose. It now appears that in the adsorbed state, the dye molecules are probably aligned parallel to the cellulose chains, and separated therefrom by a layer of water molecules (Giles and Hassan).

Reactive dyes.

These new dyes react directly with the fibre, forming covalent bonds, and thus they differ from all other types of dye, which are adsorbed by reversible physical forces. That they are aggregated in solid substrates has been suggested previously by Baxter *et al*. (1957) after a study of light fading rates. Further studies of light fading rates of two reactive (Procion)

Table II.3 Absorption spectra data (x and y-bands) for dyes in various media.

Dye	medium	max band[x] y	max band[x] x	O.D at max (x) in 1 cm. cell conc(g)	O.D Ratio y:x
XIV	pyridine:water (50% v/v)	5800	6250	0.602	0.92
	pyridine:water (50% v/v)	5800	6250	1.300	0.93
	pyridine:water (50% v/v)	5800	6250	1.460	0.94
	0.2 M-phenol	5800	6200	0.264	0.95
	0.2 M-phenol	5800	6200	1.276	0.97
	Water	5800	6100	0.277	0.96
	Water	5800	6100	0.349	0.96
	Water	5800	6100	0.918	0.99
	Water	5800	6100	1.259	0.98
	gelatin	5850	6250	0.125	0.92
	gelatin	5850	6250	0.270	0.96
	gelatin	5850	6250	0.804	1.02
	gelatin	5850	6250	1.08	1.05
XV	pyridine:water (50% v/v)	600	6450	0.167	0.91
	pyridine:water (50% v/v)	600	6450	0.749	0.91
	gelatin	6100	6500	0.108	0.93
	gelatin	6100	6500	0.250	0.94
	gelatin	6100	6450	0.355	0.95

[x] Wavelengths are given in parenthesis where the peak is flat or in the form of a "shoulder"; a query indicates very undefinite peak.

Monoazodye, unsulphonated

XVI	Ethyl Methyl cellulose film	4200	4800	0.315	0.80
	Colloidon film	4200	5000	0.920	0.65

This dye is more highly aggregated in the hydrophilic than in the hydrophobic film.

Monoazodyes, sulphonated

XVII	pyridine	4400	4750	0.344	0.89
	methanol	(4200)	4600	0.447	0.76
	water	(4200)	4600	0.459	0.80
	water	(4200)	4600	1.760	0.85
	water	(4200)	4600	2.46	0.91
	1M-Nacl	(4200)	4600	0.557	0.83
V	methanol	5100	(5300?)	1.150	1.11
	gelatin (dyed in 0.25M-phenol)	5150	(5450)	1.000	1.28
	gelatin (dyed in 0.25M-phenol)	5150	(5450)	2.910	1.29
	gelatin	5150	(5450)	1.580	1.30
VI	water	5050	5300	0.447	1.01
	water	5050	5300	0.720	1.01
	water	5050	5300	0.955	1.01
	water	5050	5300	3.048	1.03
VII	water	5150	5450	0.110	1.00
	water	5150	5450	0.902	1.02
	water	5150	5450	3.480	1.09

	gelatin	4950	(5300)	0.168	1.42

CTAB = cetyl trimethylammonium bromide; this cationic agent increases the association of the dye.

Dis- and trisazo dyes sulphonated

II	0.2M-phenol	5050	(5450)	0.162	1.23
	0.2M-phenol	5050	(5450)	0.730	1.49
	water	5100	(5450)	0.165	1.34
	water	5100	(5450)	0.780	1.60
XXIV	pyridine	(5500)	5930	0.760	0.77
	methanol	5500	5750	0.680	0.93
	cellulose	5850	(6350)	0.690	1.27
X	pyridine:water (50% v/v)	(5900)	6300	0.160	0.83
	pyridine:water (50% v/v)	(5900)	6300	0.771	0.83
	pyridine:water (50% v/v)	(5900)	6300	1.520	0.84
	water	(5900)	6200	0.061	0.87
	water	(5900)	6200	0.084	0.89
	water	(5900)	6200	0.346	0.89
	water	(5900)	6200	1.250	0.89
	water	(5900)	6200	1.490	0.94
	cellulose	6100	6600	0.294	0.80
	cellulose	6100	6600	0.820	0.80
	cellulose	6100	6550	1.900	0.89
	gelatin	(6100)	6250	0.165	0.96
	gelatin	(6100)	6250	0.552	0.98
	gelatin	(6100)	6250	0.956	0.98
	gelatin (dyed in 2M-phenol)	5200	5550	0.825	1.13

	gelatin	5200	5550	0.081	1.10
	gelatin	5200	5550	0.435	1.16
	gelatin	4950	5550	0.880	1.23
XVIII	methanol	4850	5050	0.305	1.03
	water	4950	5050	0.580	1.04
	gelatin	4950	(5150)	0.280	1.09
XIX	methanol	4950	(5200)	0.200	1.12
	water	5000	(5270)	0.280	1.10
	0.2M-phenol	4950	(5350)	0.190	1.14
	gelatin	5050	(5350)	0.190	1.08
XX	water	4100	(4400)	0.349	1.27
	water	4000	(4400)	0.569	1.50
	gelatin	4000	(4400)	0.086	1.38
XXI	water	4050	(4400)	0.182	1.59
	water	4050	(4400)	0.445	1.66
	gelatin	4000	(4400)	0.185	1.75
XXII	pyridine:water (50% v/v)	4800	(5300)	0.137	2.31
	water	4800	(5300)	0.165	2.54
	gelatin	4800	(5300)	0.147	2.56
XXIII	pyridine:water (50% v/v)	4900	(5300)	0.078	1.46
	gelatin (+CTAB)	4800	(5300)	0.135	1.74
	water	5000	5300	6.211	1.13
	gelatin	(6100)	6250	1.800	1.04
XXV	pyridine:water (50% v/v)	(6200)	(6600)	0.139	1.01
	pyridine:water (50% v/v)	(6200)	(6600)	0.561	1.03
	pyridine:water (50% v/v)	(6200)	(6600)	1.480	1.07

	water	(6150)	(6750)	0.133	1.40
	water	(6250)	(6750)	0.424	1.35
	water	(6250)	(6750)	1.260	1.36
	cellulose	(6300)	(6650)	0.137	0.99
	cellulose	(6300)	(6650)	0.555	1.00
	cellulose	(6300)	(6650)	0.678	1.06
XXVI	pyridine:water (50% v/v)	(5900?)	6400	0.118	0.67
	pyridine:water (50% v/v)	(5900?)	6500	0.540	0.70
	pyridine:water (50% v/v)	(5900?)	6500	1.49	0.70
	water	(6000?)	(6300?)	0.102	0.90
	water	(6000?)	(6300?)	0.554	0.91
	water	(6000?)	(6300?)	1.680	0.96
	cellulose	(5900?)	6400	0.218	0.69
	cellulose	(5900?)	6400	1.100	0.71
	cellulose	(5900?)	6400	2.230	0.79
	gelatin	(5900?)	6350	0.222	0.80
	gelatin	(5900?)	6350	0.355	0.82
	gelatin	(5900?)	6350	1.000	0.86
III	0.2M-phenol	(4100)	(4400)	0.150	0.97
	0.2M-phenol	(4100)	(4400)	1.370	1.06
	cellulose	(4100)	(4400)	0.420	0.98
	water	(4100)	(4400)	0.245	1.02
	water	(4100)	(4400)	1.150	1.02
	gelatin	(4100)	(4400)	0.323	1.03
	gelatin	(4100)	(4400)	1.370	1.06

Metal-unsulphonated Ligand (1:2) Dyes

XXVII	water	(5750)	6200	0.091	0.85
	water	(5750)	6200	0.364	0.86
	water	(5750)	6200	1.400	0.88
	pyridine	(5850)	6250	0.116	0.85
	pyridine	(5850)	6250	0.414	0.90
	pyridine	(5850)	6250	1.060	0.91
	gelatin	(5850)	6250	0.104	0.93
	gelatin	(5850)	6250	0.310	0.94
	gelatin	(5850)	6250	1.430	0.96
XXVIII	water	4800	(5300?)	0.062	1.65
	water	4800	(5300?)	0.283	1.73
	water	4800	(5300?)	1.105	1.70
	gelatin	4900	(5400?)	0.475	1.54
	gelatin	4900	(5400?)	0.980	1.54
	gelatin	4900	(5400?)	1.720	1.56
	pyridine	5000	(5400?)	0.590	1.40
	pyridine	5000	(5400?)	1.370	1.43

Reactive Dyes for Cellulose

XXIX	water	4950	5250	0.125	0.76
	water	4950	5250	0.498	0.80
	water	4950	5250	0.995	0.83
	water	4950	5250	1.990	0.86
	cellulose (after alkali treatment)	(5050?)	(5500?)	0.111	0.91
	cellulose (after alkali treatment)	(5050?)	(5500?)	0.545	1.01
	cellulose (after alkali treatment)	(5050?)	(5500?)	1.300	1.08
XXX	water	5000	(5200?)	0.172	1.10

	water	5000	(5200?)	0.585	1.14
	water	5000	(5200?)	1.760	1.14
	2% Na_2CO_3 soln. (cooled after boiling 30 min)	4950	(5200?)	0.204	1.23
	2% Na_2CO_3 soln. (cooled after boiling 30 min)	4950	(5250?)	0.541	1.28
	cellulose (after alkali treatment)	5100	(5350)	0.068	1.02
	cellulose (after alkali treatment)	5100	(5350)	0.73	1.12
	cellulose (after alkali treatment)	5100	(5350)	1.46	1.12
XXXI	water	6200	6600	0.074	0.43
	water	6200	6600	0.382	0.68
	water	6200	6600	1.340	0.81
	cellulose	6250	6630	0.494	0.65
	cellulose	6250	6630	1.460	0.66
	2% Na_2CO_3 soln. (after boiling 30 min.)	6300	6630	0.106	0.68
	2% Na_2CO_3 soln. (after boiling 30 min.)	6300	6630	0.410	0.71
	pyridine	6070	6700	0.162	0.25
	pyridine	6070	6700	0.632	0.28
	pyridine	6070	6700	1.300	0.34

Triphenylmethane Dye

XXII	water	(5750)	6200	0.098	0.47
	water	(5750)	6200	0.368	0.46
	water	(5750)	6200	2.460	0.53
	cellulose	(5750)	6300	0.790	0.45
	cellulose acetate	(5750)	6300	0.363	0.33
	gelatin	(5750)	6300	0.361	0.39
	gelatin	(5750)	6200	1.080	0.39

dyes are discussed, with the same conclusion, in section III of this thesis.

The absorption spectra for these dyes and the change in the height of the y band relative to the x band with increase in concentration, whether in solution or in a solid substrate, appears to confirm the existence of aggregates. Their intermolecular forces are therefore sufficiently powerful to cause aggregation even when one point on the dye molecule is covalently attached to the fibre molecular chain. During the reaction with the fibre the system is of course in an aqueous medium, and the fibre molecules accessible to dye will be solvated by water and quite flexible enough to accommodate themselves to the position taken up by the aggregated dye molecules.

Ageing effects*

For most of the dyes, aqueous solutions were prepared by dissolving the dye first in a minimum of cold distilled water. But for a few dyes of difficult solubility such as metal-complex

[*] It has been reported by Choei Sito, that for methylene Blue, the spectrum of the dye adsorbed on montomorillonite changes gradually with lapse of time. In potassium and ammonium bentonites, the band at 5700A decreases its intensity remarkably and the broad bands at 6000-6200A increase their absorbance markedly with lapse of time. This, the author assumes, is due to the dyes being adsorbed in the associated form on the outer surfaces of the dye.

dyes it was necessary to boil for a few minutes until the solution became clear. The solutions were then diluted as required with cold water. Readings were then taken as soon as possible, usually within 30 minutes of dilution. Hence tests were made to determine whether there are any ageing effects, by examining the solutions, kept in a cold place, at different periods up to 24 hr. after dilution. In the case of the sulphonated dyes there was no change, except in one or two cases, where, over a period of several hours, the y:x peak ratio increased by ca. 2%. The metal-complex dye solutions, however, which had been prepared by diluting the hot solutions, showed a slight decrease in aggregation with time; the weakest solution changed at the lowest rate. Thus a weak solution of Irgalan Orange RL with optical density 0.119 at 4800A decreased in y:x ratio about 15% over 24 hr.

To discover whether any of the spectral changes recorded could be caused by traces of metal ions, two dyes (C.I.18050,24410) were examined in 0.1% aqueous ethylene diamine tetraacetic acid solution. The spectra were the same as in water.

Examination of reliability of spectrophotometric data

The variance test

All the experiments in the above section were carried out by a single person since it was discovered that the readings obtained on the Unicam SP 500 instrument differed slightly from person to person. Furthermore the optical density reading for a dye at any concentration was different in the third decimal place if determined subsequently.

Since the significance of the optical density ratio was the basis of this section, one dye (C.I.18050) was examined in three concentrations of solution, the ratios of optical density at the two λ_{max} for each solution being determined three times. The whole operation was repeated by four operators. The writer is indebte to Mr. David Smith of this Department, for making the statistical analysis; details are given in the appropriate publication. It is there shown that differences in optical density, if found by one operator, are significant down to 0.01 unit.

The analysis of variance gives $\sigma^2 = 0.000025$ and hence the standard deviation for each ratio is $\pm$ 0.005.

$\therefore$ The average percent error of each ratio is 0.05.

To find if the difference $(x_1 - x_2)$ in the ratio for two concentrations of a dye is significant at the 5% level, when the x's are the average of two readings, the t test can be used.

Thus,

$$t = \frac{x_1 - x_2}{\left(\frac{\sigma^2}{2} \quad \frac{\sigma^2}{2}\right)^{\frac{1}{2}}} = \frac{x_1 - x_2}{\sigma} \qquad \text{with 24 degrees of freedom}$$

Table II.4

Operator	A		B	
Concentration	Ratio*	Sum	Ratio	Sum
a	1.067,1.067,1.064	3.198	1.058,1.059,1.062	3.179
b	0.987,0.985,0.987	2.959	0.987,0.987,0.987	2.951
c	0.970,0.955,0.955	2.880	0.969,0.970,0.985	2.873

	C		D		Total
a	1.079,1.079,1.079	3.237	1.055,1.056,1.056	3.167	12.781
b	0.983,0.983,0.985	2.951	0.978,0.963,0.970	2.911	11.782
c	0.952,0.968,0.953	2.873	0.955,0.955,0.955	2.865	11.542

*optical density ratio, y-band/x-band maxima.

An analysis of variances was carried out on these data, with the following results:

Source of variance	Degree of Freedom	Sum of Squares	Mean Square	Component of variance
(1) Between concentration	$p-1 = 2$	0.071965	0.035982	$\sigma_0^2+3\sigma_1^2+12\sigma^2$
(2) Between operators within concentrations of dye	$p(m-1) = 9$	0.002183	0.000243	$\sigma_0^2 + 3\sigma_1^2$
(3) Error	$pm(n-1) = 24$	0.000603	0.000025	σ_0^2
Total	$npm - 1 = 35$	0.074751		

where

p = number of concentrations = 3

m = number of operators = 4

n = number of readings of one concentration taken by one operator = 3

σ_0^2 = variance of error

σ_1^2 = variance between operators

σ_2^2 = variance between concentrations.

At the 5 percent level of significance the difference in ratio is significant if $t \geqslant 2.06$

$\therefore$ x_1 is significantly different from x_2 if $x_1 - x_2 \geqslant \sigma\sigma t$ $\geqslant 0.005 \times 2.06 \geqslant 0.01$

IIB REFLECTIVITY MEASUREMENT

INTRODUCTION

In the previous section it has been shown that Beer's law is strictly not obeyed by dyed films, probably on account of the presence of dye aggregates. It is in fact only obeyed by true solutions or by suspensions of particles of constant size distribution.

In this section the application of Beer's law has been extended to the relationship between light reflectance and concentration of colour in a mass of coloured particles and fibres.

Previous work

The relationship between the intensity of incident and reflected light for diffusing surfaces has been the subject of many investigations from 1860, onwards (Stokes, Channon et al.). Apparently the first investigators to examine the relationship between reflected light intensity from a coloured surface and the concentration of colour were Cunliffe and Lambert in 1929. They found empirically a linear relationship between reflection density of certain dyed fabrics, and the log of their dye concentration, but only up to concentrations of 1-1.5%; beyond this the curve bent towards the concentration axis. This observation was a small part of an exhaustive investigation of the light fading of dyes on wool. It was limited to two dyes (C.I.15620, 16150) on one fibre (wool). It appears that no further examination of this relation was made until it was rediscovered by Baxter et al., who found a linear relation between reflection density and log concentration of some dyes, on viscose rayon, over the whole range of concentration measured. Cunliffe and Lambert had used a visual spectrophotometer. The departure from linearity they observed may have been caused by the difficulty of visually assessing low intensity reflected light. Baxter et al. used a photoelectric instrument.

Meanwhile several other authors (Kubelka and Munk, Pineo, Guelke and Fitzsimons, Preston and Tsien, Atherton) have examined the subject theoretically, and have produced a number of functions, often complex, of reflectance which vary linearly with colour concentration in a diffusely reflecting surface. The simple relation first suggested by Cunliffe and Lambert seemed however to offer some advantages over the others. It enables the effect of change in physical state of dyes in fabrics to be compared directly with corresponding effects in solution or transparent films, it uses a function of reflectance read directly on the measuring apparatus, and it can be plotted directly. It was therefore examined here more exhaustively, and a theoretical basis was derived by D. Smith.

EXPERIMENTAL

Dyes.

The following normal commercial dyes were used.

Chlorantine Fast Red BL (C.I.35780)
Azo Geranine 2G (C.I.18050)
Naphthalene Scarlet 4R (C.I.16255)
Naphthalene Orange GC (C.I.16230)
Chlorazol Rose B (C.I.29100)
Chlorazol Yellow 6G (C.I.13920)
Chlorazol Sky Blue FF (C.I.24410)
Polar Yellow R

Rayons.

The rayon fabrics for direct dyes, Chlorazol Yellow 6G (C.I.13920), Chlorazol Sky Blue FF (C.I.24410) and Chlorantine Fast Red BL (C.I.35780) were dyed in 5 gm. portions for 90 min. at 85-90°C. in 50-volume baths containing different amounts of dyes, and 10% Glauber's salt was added while dyeing. Finally they were well rinsed and dried in air.

The amount of dye on each of the samples was measured by extraction in pure pyridine or 50% (v/v) aqueous pyridine. The amount of Chlorantine Fast Red BL (C.I.35780) on the fabric was determined directly from the change in bath concentration.

Wool.

5 gm. patterns of scoured worsted flannel were dyed in different depths with Naphthalene Orange GC (C.I.16230) and Polar Yellow R as described for rayon, with 1% addition of acetic acid (w/v).

The dye on the fabric was estimated photometrically from the solution obtained by boiling 0.1 gm. of fabric in 50 c.c. of 10% aqueous sodium hydroxide solution. A similar piece of undyed wool was treated likewise to be used as control.

Optical and reflection densities were measured on the Unicam Spectrophotometers SP 500 and SP 600. Reflectances were measured using four layers of fabric. It was found that addition of further layers produced no change in readings.

RESULTS AND DISCUSSION*

It is assumed that any light, diffused or parallel, illuminates a mass of material composed of coloured particles or fibres. The mass may be suspended in a liquid or a solid medium, or laid out on a plain surface as in a painted material or fabric. The emergent light consists of a very large number of individual rays, each of which after striking a single particle is either scattered, reflected or refracted according to its angle relative to the surface of the individual particles and outside medium.

In Fig.II.1 a step wedge is shown as a model of the general system. In this system there are a very large number of very small steps, nearly all coloured, but a few uncoloured, representing light which has been specularly reflected from the outer surfaces and has not penetrated any particle.

The absorption of light suffered by each individual coloured ray varies with the concentration of colouring matter in the particle in accordance with Beer's law (Fig.II.2) and is independent of the actual path the ray may have taken in its devious course into and out of the surface.

While each individual ray obey's Beer's law, the emergent ray as a whole does not do so, and in fact its optical density - concentration graph is a curve. This can be seen simply from a numerical example, in which two emergent rays are assumed to have 1% and 10% of the original light intensity, i.e. optical densities of 2 and 1 respectively. The mean transmission is 5.5 and corresponds to an optical density of 1.26. If the concentration of colouring matter is doubled, then the optical density values become double, i.e. 4 and 2, according to Beer's law. But the percentage transmissions become0.01% and 0.1%. An instrument will measure mean transmission, which is now 0.05%, corresponding to an optical density of 2.4%. Thus in a system of transparent coloured particles Beer's law is never obeyed. The optical density of the emergent light is therefore increasingly less than proportional to the concentration of colouring matter. This is illustrated by Fig.II.12, where the curves of optical or reflection density <u>vs</u>. concentration in aqueous solution and in viscose rayon fabric are shown.

Quantitative Treatment.

On the basis of the suggested model a ray can take an infinite number of paths. In the step wedge diagram (Fig.II.11) the thickness of each step (cl_i) corresponds to the length of path of the light through a material containing a monodisperse colouring matter with molar extinction coefficient (ϵ) and in concentration c and the width (a), to the probability that the ray will take the respective path, where l_i is the path length at unit concentration. It is assumed that Beer's law can be applied to the light passing through any step or path , and.by a process of integration over an infinite number of paths, each of which is assumed to be equally probable, it has been shown by the writer's colleague, Mr. David Smith, that

$$\frac{I_T}{I_o} = \frac{1}{\epsilon c L \log_e 10}\left[1 - 10^{-\epsilon c L}\right] \qquad \ldots \qquad (1)$$

where $L = \alpha W$ = the longest path length at unit concentration. Now the value of ϵ for organic colouring matters is very high, of the order of 10^4, and L is of the order of 10^{-1}, so that the above equation, for all except very low values of c, approximates to

$$\log \frac{I_T}{I_o} = -\log c + A, \qquad \ldots \qquad (2)$$

where A is a constant. $\log \frac{I_T}{I_o}$ is of course the optical density, if the light is measured by transmission, and it may be called reflection density if measured by reflectance.

Therefore there should be a linear relationship between density and (log) concentration of colouring matter.

After this treatment, then believed novel, had been worked out, it was discovered that Pineo had used a similar treatment, but had obtained a more cumbersome final expression.

Comparison with broad-band spectrophotometry.

On the above reasoning, there should be a resemblance between the reflection density-concentration relation in diffusely reflecting surfaces and the optical density-concentration relation for solutions of a dye having a symmetrical absorption band, and measured with light of continuous spectrum.

The measured optical density can be considered the result of an integration of transmissions through an infinite number of light paths of continuously varying lengths, i.e. the absorption band behaves as a step wedge with infinitely small steps. Fig.II.13 shows that up to a density of 0.5 this relation holds for white light measurements. Thereafter the density rises more steeply with concentration. This could be due to the variation of spectral sensitivity of the photo-cell. The sensitivity is at a maximum near the middle of the spectrum, and falls towards each end; at 4500 A and at 6200 A it has fallen to about half the maximum, and at 4000 A and 7000 A to about 30 and 10 per cent, respectively (Giles). Higher densities (>0.5) can be obtained without filter with highly concentrated dye solution. These almost completely absorb the mid-spectrum light (the optical density is too high for measurement with the optimum filter), and the optical response would then increasingly depend on the marginal wave-bands at each end of the spectrum, so that the sensitivity falls steadily, and the apparent optical density rises more rapidly than it would with a photocell of uniform sensitivity across the whole spectrum. These concentrated solutions also show light scattering effects, which will also contribute to the anomalous increase of optical density.

Effect of physical state of colouring matter

Failure of Beer's law

Eqn. 2 shows that the graph of reflection density against the (log) concentration of colour should have a slope of unity. But from Figs.II.14-16 it is evident that the slope measured at maximum wavelength is less than unity. (In the Figs. unit slope is 45°). It has been established (see above) that soluble dyes adsorbed in solid substrate are probably partly aggregated. Hence it appears that the slope being less than unity may also be due to the aggregated state of the dye. From the law of mass action the degree of aggregation increases with concentration, i.e. the proportion of higher aggregates rises. Since there is a different value of ϵ for each state of aggregation, this leads to a failure of Beer's law. This law therefore does not apply to the value of each individual ray as in eqn. 1 above, since it has there been assumed that the colouring matter in the dyed fibre is monodisperse and obeys Beer's law.

Since the observed or "apparent" molar extinction coefficient (see below) varies with the state of aggregation of dye and therefore with dye concentration (Campbell <u>et al</u>) the value of $c\ell$ in equation (1) is replaced by a term $\frac{c\ell}{1 + ac^{x}}$.

The effect of the introduction of the $\left(\frac{\epsilon c\ell}{1 - ac^{x}}\right)$ term in place of the simple extinction coefficient, in the normal Beer's law relation is now to be considered. With uniformly dyed films the optical density *vs*. concentration curves lies below the line to be expected for a truly monodisperse dye. The curve is linear over the lower concentration range, but with increase in concentration, it becomes convex to the concentration axis. (Fig. II.17).

Probably the only liquid systems that obey Beer's law are true monodisperse solutions and suspensions of particle size distribution.

If the above hypothesis is correct, then a reduction in the degree of aggregation of colouring matter should raise the slope of the log. reflection *vs*. log c curve and an increase in aggregation should lower it. This was checked by examining two types of system, both of which behaved as predicted above.

In confirmation that this effect is correctly attributed, a parallel test was made on wool fabric dyed with a dye (Polar Yellow R) which has previously been shown (see above) *not* to be disaggregated by phenol. Consistent with this, Fig.II.16 shows that the reflectance curve of the dye on wool is unaffected by phenol.

It is therefore concluded that the lower than theoretical slopes of all the curves obtained may reasonably be attributed to the failure of Beer's law caused by aggregation of dye.

Conformity with Beer's law

It appears that the only solid substrate systems likely to obey Beer's law and so give reflection density/log c curves of unit slope~~d~~, would be those prepared by a process not involving adsorption, e.g. by mixing insoluble pigment particles so as to ensure constant particle size distribution at all concentrations. In practice this condition is difficult to achieve because of changes in distribution caused by capillary effects in the drying process.

In the previous section, it is shown that Benzopurpurine 4B (C.I.23500) and Coomassie Milling Scarlet 5B (C.I.23910) remain in aggregated form both in aqueous solution and in films Fig.II.4, and that phenol acts as disaggregating agent for these dyes. Cellulose fabrics dyed with these two dyes show (Fig.II.16) the same result, only more satisfactorily. In both cases the presence of phenol increases the slope.

The causes of Beer's law failure

The real extinction coefficient varies from one type of molecule to another, but is constant for each type. But the apparent molar extinction coefficient is not constant and is a function of particle size.

It might seem that an increase in particle size of a solute would increase its optical density since an increase in scatter will occur, raising the optical density by diverting some of the light which would otherwise reach the photocell.

But the experiments described in the previous section and shown in Fig.II.4 indicate that instead, an increase in particle size decreases the optical density of both dissolved and suspended materials. This contradiction can be resolved by assuming that with increase in the scatter of the light, some of the transmitted rays take shorter paths than they would otherwise do, since the rays are more often reflected from the particle surfaces, and whenever they do so they do not suffer selective absorption. The photocell receiving the emergent beam receives both directly transmitted light and scattered light resulting in decrease in the optical density.

Amount of Surface Reflection from Fabrics

Pineo compared actual results with the theoretical formula first obtained for the variation of reflectance from a diffusing coloured material, with concentration of colouring matter. He concluded that long paths of the rays in diffusing material must be more effective than he had at first assumed, i.e. that light might perhaps penetrate some distance into the surface before being reflected back. This would imply that diffuse or specular reflection from the surface of the outer-most particles or fibres in unimportant.

This hypothesis was examined, by measuring the reflectance of a series of dyed viscose rayon fabrics before and after wetting with ethyl salicylate. This liquid has almost the same refractive index as viscose rayon, and thus is an "optical dissolving agent", and so would be expected almost to eliminate surface reflections. Fig.II.14 shows that the reflectance of most of the dyed fabrics used was reduced by some 20 per cent. This reduction falls with dye concentration, until for the heaviest shades it is only about 5 per cent.

This effect can be explained by the presence of aggregates of dye in the fibre. With rise in concentration aggregates increase in size, and therefore their refractive index rises. Thus the difference in refractive index between the dyed fibres and liquid in contact with it increases and the "optical dissolving effect" begins to fail. Thus for the particular fabric discussed above, about 20 per cent of incident light appears to be reflected from the surfaces of the outermost fibres.

Reflectance measurements at various wavelengths

Measurements were made at different wavelengths increasingly removed from that of the absorption maximum. The value of the extinction coefficient may become so low that the factor $10^{-\epsilon cl}$ in eqn.(1) becomes less than unity and the relation of log $\frac{I_T}{I_o}$ to log c then would be a curve. This would obviously occur more at low values of c than at high values. Fig.II.18 shows that in fact this is so, at low concentrations the lines for wavelengths well away from λ_{max} are curved, but at higher concentration values the lines for all wavelengths are parallel.

Effect of fibre orientation

The long axes of direct cotton dye molecules in dyed cellulose are oriented parallel to the cellulose molecular chains. The light absorption of a dye is less intense across the molecule than in the direction along it. Hence the better the fibre molecules are oriented parallel to the fibre length the weaker the colour appears (Preston and Tsien, Fothergill, Morton). Baxter <u>et al</u> (Fig.II.15) found that direct cotton dyes on very crystalline viscose rayon fabrics gave higher apparent reflectance values, at the same dye concentration, than on rayon of two lower values of crystallinity. (The relative effects shown on the latter vary a little according to condition and nature of dye).

In some cases the orientation effect appears to produce no change in slope of the curve, in others the curve for more crystalline fibre has slightly lower slopes. This shows that at low concentrations the adsorbed dye molecules in fibres of different crystallinities tend to be oriented parallel with the fibres, but with increasing concentration this is less possible in the amorphous than in the more crystalline fibres.

PART III

Relation between Light Fastness and Aggregation of Dyes

Theoretical Background

Influence of state of aggregation of dye.

If the fading reaction involves oxygen and/or water vapour, as it certainly appears to do (see e.g. Cumming *et al* (1956) and references therein), then it clearly must be influenced by the size and the nature of the air-dye interface. The smaller the surface area exposed the less rapid should be the fading. It has long been recognised that this must be so in a general way, and Bean and Rowe stated that aftertreatments e.g., soapboiling or steaming, which cause microscopically visible crystal growth of insoluble azoic dyes on cellulose fibres, and therefore reduce the surface area of the dye, at the same time improve the light fastness. Giles and Macaulay have confirmed this result, using an azoic dye on Cellophane film.

The very low light fastness of vat dyes on nylon, compared with their fastness on cellulose, has likewise been attributed by Smith and Douglas to their much smaller particle size on the former substrate, occasioned by the restriction of dye crystal growth by the greater compactness of the fibre.

Sumner, Vickerstaff and Waters examined the effect of soaping on vat dyeings on Cellophane. No significant increase in light fastness was obtained, but electron photo-micrographs of aged colloidal suspensions (dyed film did not show the effect) showed that the treatment changed the dye from amorphous particles to long needle-shaped crystals.

Astbury and Dawson, in a study of the setting properties of wool fibre, examined by X-ray diffraction samples of dry fibre dyed with a few acid dyes, and detected evidence of dye (Solway Blue, C.I. No.62085) crystallites; some other acid dyes gave no positive result.

The influence of dye concentration on light fading.

Barker, Hirst and Lambert examined the fading of wool cloth dyed to different percentage depths of shade with a number of dyes, measuring the loss of colour by the Lovibond Tintometer. They found in each case that when the amount of dye remaining after the exposure, was plotted against the amount originally present, a straight line was obtained, of slope approximately 1.0, but not passing through the origin. (The line of no fading would be a line of slope 1.0 passing through the origin). The actual loss of colour is thus approximately the same whatever the original amount present. They explained this by saying that a given amount of absorbed energy can cause only the same destruction of dye, whatever the amount originally present. This, of course is the condition normally obtaining in photochemical reactions when the whole of the active radiation is absorbed, the number of molecules decomposed then becoming proportional to the time of exposure. This is known as a reaction mechanism of zero order, so that if the dyed fabrics do absorb the whole of the active radiation, the relationship established by Barker, Hirst and Lambert is normal.

Cunliffe and Lambert found an empirical relationship between fading and the square root of the time of exposure. These workers used the Guild trichromatic colorimeter. As a measure of degree of fading they used the percentage decrease in the distance of the point on the colour-chart, representing the dyed pattern, from that representing the undyed material. They discovered that this point in most cases moved steadily towards "white" with the progress of fading. They obtained the relation

$$F = \underline{a}\sqrt{t} + \underline{b} \qquad \text{.........} \qquad \text{(i)}$$

where F = amount of dye faded and $\underline{a}$ and $\underline{b}$ are constants; this applied to the stages of fading up to 60%, and the relation

$$F = \underline{c}\log b + \underline{d} \qquad \text{........} \qquad \text{(ii)}$$

where $\underline{c}$ and $\underline{d}$ are constants, applied also to the fading at about 25% loss. In addition they found empirical equations of other types to hold over a limited range.

Sommer studied the same subject and noticed an empirical linear relation between amount of fading and square root of exposure time.

Eaton, Giles and Gordon (1952) have found that a linear relation exists between light fastness grade number, and logarithm of dye concentration on the fibre. The lines so obtained were later termed "characteristic fastness grade" (CFG) curves (Giles, 1957). The light fastness numbers represent a geometrically graded series of patterns of increasing light fastness. The test sample is given the grade number of the standard which shows the same degree of fade under equal exposure conditions, the fading being judged in the early stages. If it is to be assumed that the percentage colour loss for a pattern to be judged "faded" is the same no matter what the grade number, then it follows that there should be a linear relation between the logarithm of time (t_F) required to produce a given percentage loss of any dye and the logarithm of its initial concentration (C_o) i.e.

$$\log t_F = \underline{a}' \log C_o + \underline{b}'$$

where $\underline{a}'$ and $\underline{b}'$ are constants. Thus the linearity of the CFG curves is explained.

Baxter et al (1955) first described the method of plotting the log. of the time (t_F) required for a given percentage loss of dye by fading (conveniently 10%), against the log. of the initial dye concentration (C_o). The linear curves so obtained ("characteristic fading", or "CF" curves) were shown by Giles (1957) to be equivalent to the CFG curves just described, since t_F is equivalent to a fastness grade on a geometrical scale.

Theoretical model of the light fading of a dye deposited on a solid substrate, as set out by Baxter, Giles, McKee and Macaulay.

As mentioned previously (page 75) the fading rate of a dye is probably determined by the extent of the air-dye interface, i.e. the surface/weight ratio of the dye. The dye is considered to be present in the substrate as a series of discrete particles freely exposed to air and water vapour and evenly irradiated by either directional or diffuse illumination.

The manner in which the fading rate of the dye in the model system now to be considered, changes with increase in concentration will be discussed with respect to three types of idealised systems (Fig.III.IA).

a) Uniform Particle size distribution system.

This system may consist of any number of sizes or shapes provided that at each concentration of dye the proportion of particles of each given size or shape remains the same. Thus the total number of particles and the surface area both increase in direct proportion to the total weight, i.e. the surface area/weight ratio is constant, and hence the time taken for a given proportion of dye to fade is also constant. The CF curve is a horizontal line.

b) Constant particle size system.

The dye particle may expand symmetrically as more dye is added, thus retaining the same shape (say, a cube). The total number of particles thus remains constant as the dye concentration increases, but the total surface area grows as the 2/3 power of the total weight of the particles.

If it is assumed that the total loss of dye in a given period is proportional to the total surface area of the cube and that the photochemical reaction at the surface is of the first order, the CF curve has a positive slope.

c) Unsymmetrical particle growth system.

In the system each particle is considered to grow with increase in total dye concentration, but only in one direction. In the extreme case, where the illumination and the oxygen and water vapour reach only the side of the particle which does not increase in size, the total surface area of dye being irradiated remains the same at all dye concentrations, and hence the total amount of dye faded is constant, and the fading reaction is then zero order.

Relation between fading and aggregation.

Fig.III.1B shows hypothetical curves relating dye concentration to fading time in the manner already discussed. Let C_a, C_b be two values of dye/fibre concentration and t_a, t_b, the corresponding fading times. The curve I, drawn through the point a,b is thus characteristic of that dye-substrate system.

Now suppose some treatment is applied to the system which causes the dye to aggregate into larger particles, in which the surface area of any given quantity of dye is reduced, in relation to its weight. The fading time for C_a will now be, say t_a', the fastness being increased. What will happen to the curve as a whole, i.e. by how much will the fastness of C_b be increased? The answer to this question will depend upon what effect aggregation has upon the rate of increase of surface area of dye relative to its total weight. If the aggregation takes place in such a manner that the surface area/total dye weight ratio, though less than before, still remains constant at all concentrations, the curve II will be obtained, which is parallel to curve I. On the other hand if the treatment makes this ratio lower as the concentration is raised, i.e. if the tendency to coalesce becomes greater the higher the concentration, then we may obtain curve III, while an opposite effect will produce curve IV.

In general, then any form of aggregation which decreases the surface area of the dye will improve the light fastness, but its effect on the slope of the curve will depend upon the exact physical nature of the aggregation. The slope may rise, fall, or remain unchanged. An exactly similar argument may be applied to a process which disaggregates the dye, though in this case the fastness, and hence the height of the curve will be lowered.

In the following cases the position of the curve was found by

Baxter at al. to be raised:-

a) Soaping of insoluble azo dyes in Cellophane. This visibly increases aggregation, and the slope may be increased or decreased.

b) Substituting viscose rayon for cotton as substrate with direct cotton dyes. Viscose rayon is less crystalline and would allow larger aggregates to grow.

Statistical treatment of fastness data.

Eaton, Giles and Gordon have examined a large number of light-fastness gradings published in trade literature of various manufacturers in pale, medium and heavy shade depths of given relative values. When the data for each dye-fibre system are averaged, a linear relation appears between (mean) log C_o (initial concentration on the fibre) and (mean) n, the light-fastness grade. Furthermore, the curves for each dye-fibre system differ in slope and the slope differences are statistically significant. It seems probable, therefore, that each dye-fibre system has a characteristic mean slope, about which the slopes for the individual dyes in the system may be grouped.

EXPERIMENTAL

The illuminant for light fastness determination.

An artificial light source is necessary for light fastness determination where results have to be obtained much more rapidly than if exposures are made only in daylight, which, as a fading agent, is slow and highly variable in intensity.

In the present work, a General Electric "Osira" high pressure mercury vapour lamp of power 400 w. was used, with the appropriate choke in series, but without a condenser. The lamp was chosen for its relatively constant emission over long periods, and low running cost, and because it requires virtually no attention. The lamp is held in a porcelain lamp-holder screwed to a wooden base-board and surrounded by a cylindrical sheet aluminium screen (17" diameter x 15" high), fitted at vapour stream level with a 3/4" wide aluminium shelf, on which the patterns are rested during exposure (see Fig.III.2). As the source of illumination is a vertical incandescent vapour the intensity of emission was considered to be relatively constant in any lateral direction, hence the construction of a rotating pattern holding device was considered to be unnecessary.

The lamp has a weak continuous spectrum as a background with a number of superimposed strong monochromatic bands. The five major emission lines in its spectrum are at 3650 A, 4047 A, 4358 A, 5461 A, and 5780 A.

The air temperature within the screen was found to be constant, for continuous running, at 56°C.

For tests in different degrees of humidity, the slides for exposure were hung in hard glass test tubes (10" high and 1.5" in diameter) containing either a small amount of water or calcium chloride. The slides were held about 1.5" from the surface of the water or calcium chloride, care being taken not to wet the films. The test tubes were then clamped to the aluminium wall so that the slides always faced towards the lamp (see Fig.III2). From time to time it was checked that the slides had not moved from their original position due to torsion in the supporting thread. For a cooling effect, water-jacketted tubes were used as shown in Fig.III.2, fed with a stream of cold mains water.

Some experiments were also made by using a high pressure Xenon arc discharge lamp (Type FA, A.E.I. Lamp and Lighting Co. Ltd.) of 150 w. output. The fading was slow, but the patterns appear to remain at room temperature, whereas in the more powerful mercury lamp they become warm. McLaren (1959) has recently given a full account of different types of Xenon arc lamp suitable for fading.

The visual assessment of fading.

A series of blue patterns developed by the Society of Dyers and Colourists has been adopted by the British Standards Institution as light-fastness standards. The standards increase in fastness from No.1-8 and are spaced evenly on a geometric scale from Nos.1-6, each one fading at about half the rate of the one lower in the scale. Standards 7 and 8 are more widely spaced. The change which occurs in a light fading test may be a change in depth of colour, a change in hue, a change in brightness or any combination of these. The light-fastness evaluation is based upon the contrast between the original material andthe faded specimen, regardless of the character of the change. A visual comparison of contrast can be made with use of the five pairs of neutral shade patterns in the Standard Grey Scale, developed by the Society of Dyers and Colourists, for evaluating the changes of colour in textiles, leading to a more accurate and reproducible evaluation of light fastness.

In the work described below, on the effect of fluorescent brightening agents on fading, some fabrics were tested by this standard procedure, in the laboratories of Hickson and Welch Ltd., Castleford, Yorks., by Mr. D.J. Stamp.

<u>The calculation of relative fading rate from fading curves</u>.

It was found that initial fading in large numbers of cases (especially pigments and azoic dyes), was rather irregular, and it is assumed that this is due to purely physical changes, perhaps to some form of rearrangement of dye particles occasioned by heat and some loss of moisture. Changes of this sort may perhaps account for the irregularities noticed in practice in the early stages of fading of some dyed fabrics when under test for light-fastness. Consequently, the decrease in concentration ΔD, was measured over an interval of time T from D_1 to D_2, the selected initial and final concentration respectively, D_1 being taken as the first suitable point on the fading curve after the dye assumes a steady rate of fading. The time for equivalent fade t_F was taken as time of exposure, calculated on the mean of fading between D_1 and D_2, required to give a 10% decrease in value of D_1. The value of t_F is obtained for a number of optical density values and is then plotted on a log. log graph with optical density as x-axis and t_F as y-axis. The curve passing through these points, usually a straight line, is referred to as a CF curve, as already mentioned.

RESULTS AND DISCUSSION

a) High fastness to light in colouring matters

In this section some of the factors contributing to the improvement of light fastness of organic colouring matters are examined in detail. Previously (Baxter et al., 1955, 1957, Giles 1957), it has been emphasised that the fastness is largely determined by the physical form of the dye, and results have suggested that dyes of high light-fastness are likely to be more highly aggregated than those of low fastness. This suggestion has been confirmed by Weissbein and Coven in electron microscopic tests on a number of direct cotton dyes in regenerated cellulose film; they found that dyes of high fastness are present as aggregates, but those of low fastness are not, or at least if aggregates are present, they are too small to be seen. In the present work a number of light-fast dyes of different types are examined to determine whether aggregation is responsible for their fastness; and factors other than aggregation which influence fastness are also considered.

Three general methods are here used to detect qualitatively the presence of particulate dye.

(i.) Spectrophotometric absorption tests: the absorption spectra of most dyes show two bands, the short-wave (y) band representing associated dye, and the long-wave (x) band, representing monodisperse dye. An increase in the ratio of the y/x extinctions represents an increase in degree of association.

(ii) Examination of CF curves: The slope of the CF (Characteristic Fading) curve gives qualitative information on the state of association of dyes in the substrate, as discussed above (p.78).

(iii) Examination of fading rate curves: The slope of the fading rate curve is also informative upon the physical state of the dye. (Baxter *et al*., 1957). Thus if the rate decreases exponentially with time (Fig.III.3a) there is a first order reaction and the dye is probably molecularly dispersed. Harashima *et al*. (private communication) have observed that some direct cotton dyes fade according to the second order law (linear relation between time and reciprocal of optical density, or nearly constant curvature of the graph of optical density against time) (Fig.III.3c). Few fading curves of this type were observed in the present work. A possible cause of this type of fade may be that the destruction of a rapidly fading molecularly disperse dye is retarded by a low moisture content of the substrate. A constant rate, i.e. a zero order reaction, represents a dye present in large particles (Fig.III.3b).

In practice the type of curve shown in Fig.III.3d is often obtained. Here there is dye both in molecular dispersion, giving the initial rapid fade, and also in larger aggregates, giving the subsequent constant rate of fade. An initial "negative fade" in which the extinction at first increases, i.e.

the amount of dye apparently increases (Fig.III.3e) is sometimes observed. This also represents dye present as large particles. The increase in extinction is probably due to the splitting up of particles in the heat of the illumination. (Extinction rises with decrease in particle size of dyes (Campbell et al., 1959)). Indeed this type of curve is probably a more certain indication of the presence of large aggregates of dye than is (b); because a fading curve of first order with a very slow rate (type a) might be difficult to distinguish from a true zero-order curve.

Pigments.

Giles (1957) pointed out that the CF or CFG curves of a pigment should be horizontal, i.e. the light-fastness should be the same at all depths, because the particle size distribution is constant. Fig.III.4a shows that in practice a colouring matter applied as a pigment gives a CF curve which, while not actually horizontal, has a lower slope than that given when it is applied from a solution and afterwards insolubilised on the substrate (cf. also Fig.4, Baxter et al., 1955).

The same principle appears in many cases to apply to technical systems. Thus CFG curves for fading of fabrics coloured with commercially resin-bonded pigments have lower slope than those for fading of fabrics dyed with insoluble dyes of the same manufacturer. (cf. Fig.19, Giles, 1957). Other similar information (supplied in confidence by another manufacturer) is given in Table III.1. One

Table III.1. Characteristic Fastness Grade (CFG) curve Slopes of an Identical Series of Colouring Matters Applied to Cellulose by Different Methods.

Application by	Exposure by		
	Fadometer	Daylight	
Padding and resin bonding	0.5	1.9(?)	0.25
Dyeing by vat method	1.3	1.1	

Bracketed data are from the tests run simultaneously.

daylight figure in these data appears to be anomalous. This may be the result of changes in atmospheric humidity (which was not controlled). In the author's test however the CF curve slope for vat dyeings was not significantly affected by change in humidity.

Capillary effects and pigment fastness.

The meaning of the positive slope of the CF curve for pigments is that the particle size distribution is not constant over all concentrations; the proportion of larger particles increases with concentration. The author's experiments show that the probable cause is capillary attraction between pigment particles. This draws together individual particles to form clusters before the substrate has set solid, and obviously the nearer the particles are together at first, i.e. the higher the concentration, the greater is the tendency for this to happen (Fig.III.5). This was confirmed by tests with an azoic pigment exposed in cast films of different mobilities (Fig.III.6). For films of ethylmethylcellulose the curve is steepest; this material does not set until quite dry, and therefore the pigment particles have the longest period of time to migrate and have the best chance of forming clusters. For gelatin films the curve is less steep. These films set rapidly after pouring out, and remain as gels while being dried, thus migration is retarded and clustering is reduced. When the gelatin films are frozen, however, immediately after pouring, so that the particle migration is almost prevented, the CF curve is nearly horizontal. The CF curve for normal gelatin film at low concentrations appears to fall below that for frozen films. This may be due to slow penetration of gelatin solution between compressed masses of particles, which are thereby wetted and partly separated. Thus there are two opposing effects tending to alter particle size distribution and complicate the light fading effects in systems of this type.

Complex lakes of basic dyes.

Baxter et al. (1955) have suggested, on the evidence of CF curves, that the improvement in fastness of basic dyes produced by laking them with certain complex inorganic acids, may be due to a resultant increase in particle size. This process, which is of considerable technical importance in enabling the bright shades of basic dyes to be taken advantage of in preparing printing inks, had not hitherto been satisfactorily explained. The suggestion is now confirmed by examination of absorption spectra (Fig.III.7) and by fading rate measurements (Fig.III.8). After laking the extinction of the y-band of the spectrum is increased relative to that of the x-band, indicative of increased association of the dye molecules.

The fading rate curves of the lakes show the rise in optical density characteristic of some particulate dyes. The fading rate curves are non-linear for the uncomplexed dye, indicating the presence of some monodisperse dye; and mainly linear for complexed dye, indicating the presence of aggregated material.

Water-soluble dyes of high light fastness (Figs. 9, 9a, 10, 11, 16).

Metal-complex dyes.

These are of considerable importance for wool and for cotton dyeing, and usually have very good light fastness. Giles and MacEwan have given evidence, from linear fading-rate curves, and other tests that the neutral-dyeing type of metal-complex dyes for wool are highly aggregated when adsorbed. Weisbein and Coven (Fig. 9a) have confirmed, by electron micrography, that there are aggregates of the copper complex of the cotton dye Sky Blue FF (C.I.24410) in dyed regenerated cellulose film. In the present work this observation is supported by the characteristic shape of the fading rate curve of this dye (Fig.III.9), in comparison with that of its uncomplexed form. The true zero-order curve is obtained when the dye is first given a severe after-treatment with copper sulphate; if this is not done, there is a small rapid initial fade, presumably due to the presence of a small proportion of uncomplexed dye.

Light-fast direct cotton dye, not of metal-complex type.

A typical dye of this class, Solar Green BL (C.I.34045), shows a fading curve characteristic of aggregated dye (Fig.III.10).

Acid wool dyes.

Fading rate curves for two anthraquinone acid wool dyes were given elsewhere (Fig.7, Baxter et al., 1957) and show evidence of aggregated particles. X-ray diffraction examination of some dyes of this class in wool (Astbury and Dawson) also showed the presence of crystalline aggregates.

Reactive dyes in cellulose

In Part II, Section I, above, it was shown that the absorption spectra of reactive dyes on regenerated cellulose (Fig.II,9) have the y/x band extinction ratio increased with increase in concentration (Table III.2). This almost certainly indicates that these dyes exist in associated form in cellulose. Baxter et al. (1955, Figs.14,15) have also reached the same conclusion by studying fading rate curves. In the present work fading rate curves for the reactive dyes Procion Blue HB and Procion Brilliant Blue 7HB have been obtained (Fig.III.11) and these also show that particulate dye is present.

The influence of temperature and humidity on light fading.

A reduction in moisture content of a dyed fibre decreases the fading rate, hence the importance of the temperature and humidity of the atmosphere in determining light fastness (an increase in temperature decreases the moisture content of the fibre).

Hedges, who was probably the first investigator to study the effect quantitatively, exposed dyed fabrics under atmospheres having various humidity values, by placing aqueous solutions of glycerol or certain salts in small boxes containing horizontally

TABLE III.2

Change of absorption spectra of dyes when faded

a. Water-soluble dyes

Dye	Time of exposure (hrs.)	max	(x-band) optical density	y/x extinction ratio
Benzopurpurine 4B(C.I.23500)	0	5200	0.775	0.70
	1.0	5120	0.710	0.75
	20	5100	0.620	0.83
	93	5070	0.516	0.85
	288	5070	0.373	0.85
Methylene Blue 2B(C.I.52015)	0	6300	0.690	0.81
	0.5	6300	0.750	0.61
	1.0	6300	0.580	0.63
	2.0	6300	0.460	0.74
	3.0	6300	0.380	0.83
Chlorazol Azurine G (C.I.24140)	0	6300	0.684	1.24
	0.17	6300	0.649	1.29
	0.50	6300	0.649	1.29
	48	6300	0.272	1.51
Victoria Pure Blue BO (C.I.4259)	0	6250	0.276	1.15
	2.0	6250	0.226	1.19
	4.0	6250	0.184	1.22
	6.0	6250	0.142	1.26
Chlorazol Sky Blue FF (C.I.24410)	0	6600	1.440	0.89
	0.8	6600	1.36	0.93
	5.0	6600	1.15	1.08
	46.0	6600	1.01	1.12
Chlorazol Sky Blue FF (C.I.24410)	0	6600	0.800	0.60
	5.0*	6600	0.770	0.60
	15.0*	6600	0.740	0.65
	25.0*	6600	0.725	0.76
Azogeranine 2G (C.I.1805)	0	5400	0.162	0.95
	24	5400	0.157	0.95
	48	5400	0.154	0.97
	96	5400	0.158	0.98

b. Water-insoluble dyes

Base 2 + Naphthol 4	0	5400	0.31	1.16
	35	5400	0.32	1.14
	55	5400	0.295	1.20
Base 2 - Naphthol 10	0	5300	0.261	1.17
	18.5	5300	0.271	1.17
	42.0	5300	0.260	1.16
	75.0	5300	0.248	1.14
	165.0	5300	0.177	1.13
Base 2 + Naphthol 19	0	5300	0.181	1.21
	18.5	5300	0.194	1.21
	48.5	5300	0.185	1.23
Base 2 + Naphthol 4	0	5300	0.258	1.17
	24.0*	5300	0.261	1.17
	48.0*	5300	0.263	1.17
Acridine Orange	0	5150	0.67	1.08
R (C.I.46005)	2.3*	5150	0.54	1.17
(Phospho-molylidic lake)	11.6*	5150	0.51	1.17
Victoria Pure Blue	0	6250	0.757	1.2
BO (C.I.42595)	24*	6250	0.84	1.09
(Phospho-tungstic lake)	72*	6250	0.84	1.06

*Xenon lamp; all other exposed to mercury vapour lamp.

†Base = C.I. Azoic Diazo Component;
Naphthol = C.I. Azoic Coupling Component.

fixed dyed patterns behind a Vita-glass window, for exposure to a "Hanovia" quartz mercury vapour lamp. The degree of fading was determined by a Lovibond Tintometer. The moisture content and the effect of temperature change at various humidities were observed and the temperature coefficients calculated at various temperatures over the range 10-50°C. The values obtained were small, lying between 1.03 and 1.12.

Fading was found to be accelerated by a rise in humidity in all cases; a linear relationship appeared to hold between percentage loss of dye and the moisture content of the sample, at least down to 5% moisture content, for a number of dyes on cotton or wool. Evidence of sharp change in the relationship for dyes on silk was noted, at about 10% moisture content, beyond which the curve of colour loss against moisture content becomes much more steep.

Hedges proposed the formula $F = \frac{K}{T(R + C)}$, as a means of predicting fading under different conditions. (F = percentage loss of dye; K, C are constants, T is the temperature, and R is the regain of the fabric). It has however been pointed out by Lead that the moisture content of exposed fabric cannot directly be determined from the humidity of the surrounding atmosphere. This has been confirmed by Nordhammer, who found that the temperature of the samples in the Fadeometer fluctuated around a temperature as high as 90°C., with a fabric humidity much lower than to be expected from the condition of the atmosphere inside the lamp.

Later Morris et al studied the effect, on a variety of fibres, and McLaren (1959) has recently examined the effect in the fading of dyes on cellulose, and has found that the fading of some azoic dyes is markedly accelerated by a rise in humidity.

In general trend these observations agree with expectation. They may simply be due to a mass-action effect. It is known that water takes part in fading reactions (see e.g. Cumming et al., 1956) and therefore this reaction should occur more rapidly at high humidity than low. Unfortunately the data given by the earlier investigators are not in a suitable form for a direct test of this hypothesis.

Tests made in the present work show that reduction of humidity affects fading rate in two ways: (a) in most cases it reduces fading to a constant degree throughout the period of test, no doubt a normal mass action effect (Figs.III.12,13); (b) in cases where an initial increase in density occurs due to breakdown of aggregates, the increase is greater under dry conditions than under wet; and it is favoured by heat (Fig.III.12a,b). (Bean and Rowe noticed that heat breaks down azoic dye aggregates). Dry conditions therefore improve light-fastness by a two-fold action, viz. by retarding access of moisture to the dye, and by facilitating breakdown of large dye aggregates, whereby the apparent depth of colour tends to increase. Not all aggregated dyes however are affected in the second manner, thus the direct blue C.I.24410 (see above, Fig.III.9) is not so affected.

Evidence of nature of fading from absorption spectra.

It has already been described in Part II, Section I, how nearly all water-soluble dyes in transparent dyed substrates give an increased y/x band extinction ratio with increase in concentration. This was attributed to aggregation. If monodisperse dye fades more rapidly than aggregated or micellar dye, then the y/x band ratio should increase when the dye is faded. Data in Table III.2 show that it does so, with water-soluble dyes. With insolubilised dyes the opposite effect usually occurs, the y/x band ratio falling with exposure. Presumably this is the result of the breakdown, in the heat of the illumination, of some of the large dye crystals to give a small proportion of monodisperse dye, possibly a vaporisation or sublimation process.

Mordanted dyes.

The high light fastness which most mordanted dyes have, might be due either to high photochemical resistance of dye-metal chelate molecules in general or to a marked tendency for them to aggregate.

The light fastness of mordanted dyes has not previously been examined in detail, but it seems reasonable to envisage the building up of large aggregates of mordanted dyes, because of the possibility of polymerisation of the dye-mordant complex (Arshid, Desai, et al.).

In the present work, fading rate curves of some acid mordant dyes on gelatin, and after-coppered direct dyes on cellulose, show that the dye is partly monodisperse before treatment with the metal, but after treatment it is almost certainly aggregated (Fig.III.14,16). The yellow mordant dye is improved in fastness by aftertreatment with aluminium, and its absorption spectrum gives evidence of increased aggregation (Fig.III.15) by the rise in y/x band extinction ratio. (It is assumed that chelation alone does not affect this ratio). Not all mordanted dyes behave in this way however. In the case of Alizarin Red S (C.I.58005) in gelatin, unmordanted or mordanted with aluminium or with chromium, fading rate curves demonstrate that some monodisperse dye is present. Moreover, the CF curves show that this dye is actually less fast to light when chromed than when unmordanted. This seems to show that chelation with a metal does not necessarily increase light fastness. In this case the hues of the mordanted and the unmordanted dye were different, and monochromatic light (mercury light) was used for exposure, This might account for some of the difference in fastness, but by no means all, because the extinction of the dye in the two forms differs very little in the region of maximum emission of the lamp.

(b) Improvement in light fastness by changes in the surface activity of dyes

The effect of Alkylation and Sulphonation pattern.

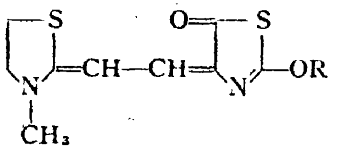
This work, a continuation of that of the author's predecessors, was designed to examine the influence on light fastness of changes in the surface activity of dyes, produced by alteration in the size and form of their hydrophobic residues, and the position of their ionic groups. The dyes used were selected in series of two or more of the same fundamental constitution, but differing in the relative size or position of the hydrophobic portion of their molecules, and thus in surface activity. In certain cases a surface active cationic agent was added to the dye, to act as a disaggregating agent.

The complete series of dyes used by the writer and his predecessers is shown in Table III.3.

III.3

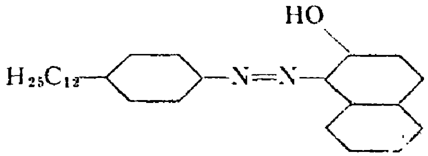
TABLE ~~I~~. Dyes Used

(X–XIII are color formers from which color-developed dyes were made.)

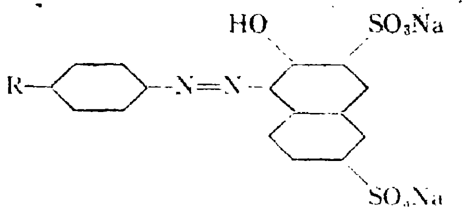


I

R = $-C_2H_5$; b, R = $-CH(CH_3)_2$; c, R = $n-C_4H_9$;
R = $n-C_5H_{11}$; e, R = $-CH_2C(CH_3)_3$; f, R = $n-C_6H_{13}$;
R = $n-C_7H_{15}$; h, R = $n-C_8H_{17}$; i, R = $n-C_{10}H_{21}$;
R = $n-C_{12}H_{25}$; k, R = $n-C_{14}H_{29}$; l, R = $n-C_{16}H_{33}$;
, R = $-(CH_2)_3Ph$.

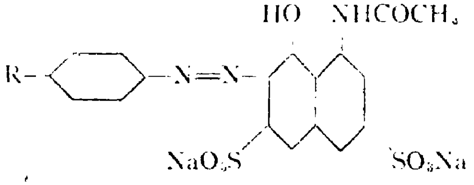


II



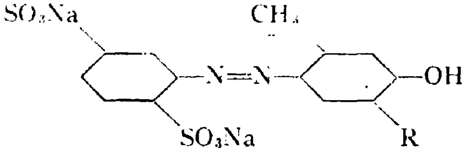
III

a, R = $-H$; b, R = $-CH_3$; c, R = $n-C_4H_9$;
d, R = $n-C_{12}H_{25}$; e, R = $n-C_{16}H_{33}$.



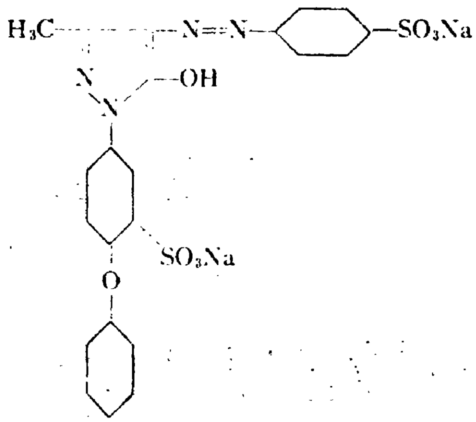
IV

a, R = $-H$; b, R = $n-C_4H_9$; c, R = $n-C_{12}H_{25}$.

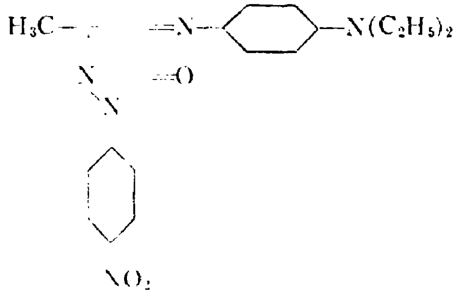


V

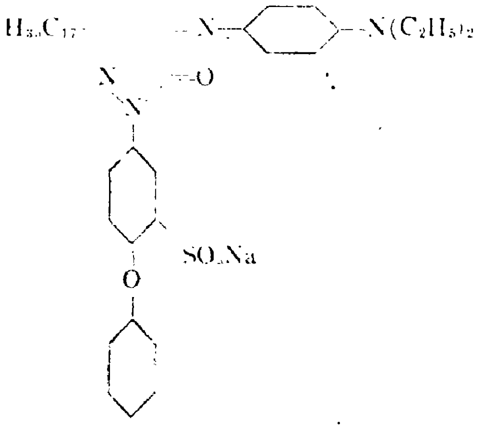
a, R = $-H$; b, R = $-CH_3$; c, R = $-CH(CH_3)_2$;
d, R = $-C(CH_3)_3$.



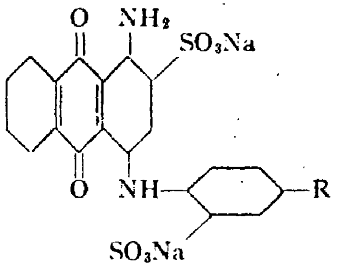
IX



X

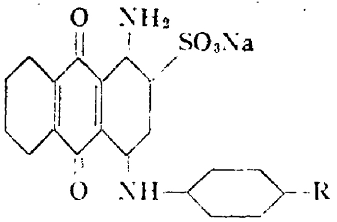


XI



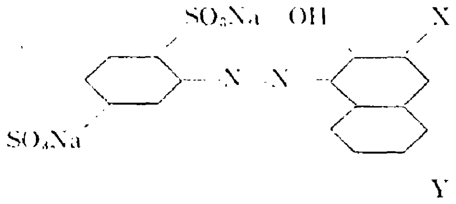
XV

a, R = $-CH_3$; b, R = $n-C_{12}H_{25}$.



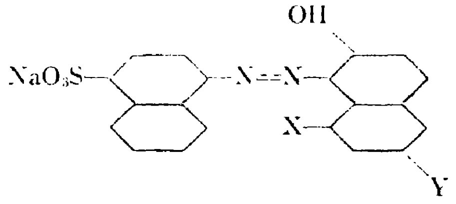
XVI

a, R = $-H$; b, R = $n-C_4H_9$.



XVII

a, X = $-H$; Y = $-SO_3Na$; b, X = $-SO_3Na$, Y = SO_3Na.

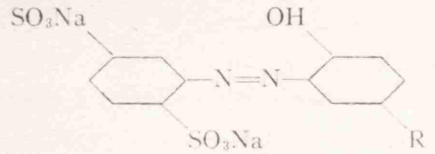


XVIII

a, X = $-H$, Y = $-H$; b, X = $-SO_3Na$, Y = $-SO_3Na$.

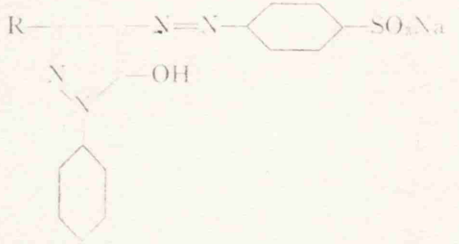
III 3.

TABLE ~~I~~ Continued



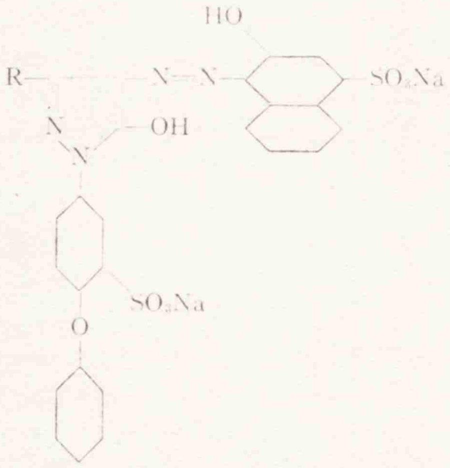
a, R = —CH_3; b, R = —$C(CH_3)_3$;
c, R = —$C(CH_3)_2CH_2C(CH_3)_3$.

VI



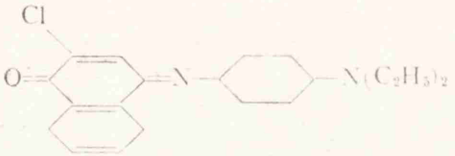
a, R = —CH_3; b, R = n—$C_{17}H_{35}$.

VII

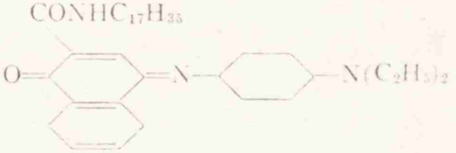


a, R = —CH_3; b, R = n—$C_{17}H_{35}$.

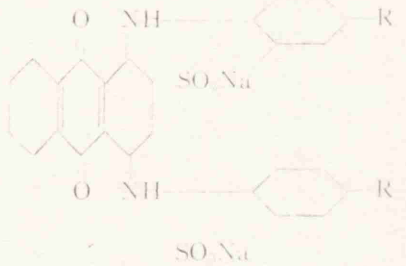
VIII



XII

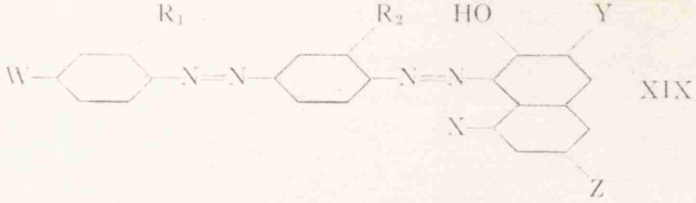


XIII



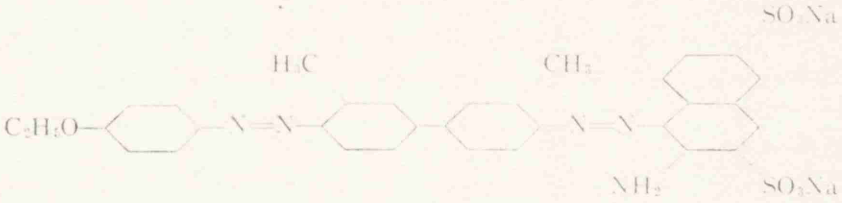
a, R = —CH_3; b, R = n—C_4H_9.

XIV

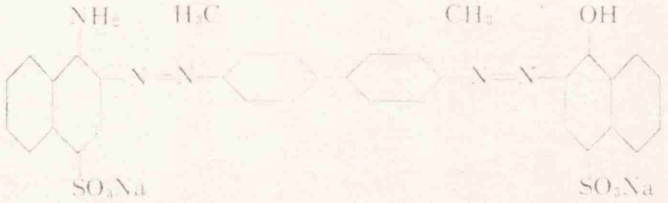


a, W = —SO_3Na, X = —SO_3Na, Y = —H, Z = —H,
R_1 = —CH_3, R_2 = —CH_3; b, W = —H, X = —H,
Y = —SO_3Na, Z = —SO_3Na, R_1 = —CH_3, R_2 = —CH_3;
c, W = —H, X = —H, Y = —SO_3Na, Z = —SO_3Na,
R_1 = —H, R_2 = —H.

XIX



XX



XXI

Effect of increase in length of an attached paraffin chain.

The addition of an alkyl chain to any dye present wholly in monodisperse form in a substrate would be expected either to have no effect on fading, if fading depends only on the photochemical reactivity of the dye molecule, or to retard it, by more effectively blocking the pores of the substrate against entry of air and moisture, if physical state is important. The blockage would either be a result of increased molecular size or perhaps of the enhanced hydrophobic properties of the dye, the retardation of fading then becoming progressively more noticeable with increase in length of the alkyl chain. If however the dyes are present in the substrate as discrete particles, then addition of a hydrophobic residue might have a different effect on fading rate. Thus e.g., a small residue might increase the tendency to aggregate and a larger one might decrease it, by increasing the tendency for the dye to spread as a monolayer.

From the present results (Figs.III.17,18,19; dyes of series II-VI and XVII-XXI)* there appears to be a general tendency for the fastness of anionic dyes to increase with chain length from C_0 up to about C_4, and then to fall. In some cases the high surface activity conferred by a very long chain markedly reduces fastness.

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*Footnote. A number of these tests were made by the author's predecessors.

These effects are probably caused by change in the ratio of molecularly dispersed and aggregated dye. Dye molecules with short chains may be present mainly as aggregated particles or micelles, which increase in size and therefore in light fastness, with increase in chain length. When the chain is lengthened beyond about C_{12}, it can form not only micelles, but also a condensed unimolecular film, which becomes more stable and more uniformly spread in the substrate as the chain length increases (see Table III.4). The dye in this unimolecular film fades more rapidly than in the micelles. Hence the fastness tends to be low with long chain dyes, because of stability of the condensed monolayer on the internal surface of the substrate. Whether the tendency to aggregate would increase or decrease with change in surface-activity in any given series of dyes would perhaps depend on the geometry of the basic constitution of the dye molecule.

Non-ionic dyes.

A series of tests made by the writer's predecessor N. Macaulay with water-insoluble mero-cyanine dyes (series I) in films formed from collodion solutions, showed that the fading rate is not influenced by the length of the attached alkyl chain, thus apparently the substituent does not influence the physical state of the dye. This belief is also supported by a study of the visible light absorption curves of the dyes in the films. They each have a single rather broad symmetrical peak at about 4550 A.

TABLE III.4

Monolayer-forming Data for Sulphonated Dyes (from Cameron and Giles, 1957)

Dye	Molecular cross-sectional Area(A[*]) found on: -		
	Calc. from model	Water alone	4M.NaCl solution
IVa	65	n.f.	n.f.
IVb	65	n.f.	n.f.
IVc	65	17	53
XIXa	120	n.f.	42
XIXc	65	n.f.	61

[*] The nearer the measured value is to the calculated, the more stable is the monolayer; low measured values represent partial solution of film molecules.

n.f. = no film formed.

In gelatin dispersion however there are two peaks, a broad one at 4500 A and a sharp one at 5000 A probably due to presence of aggregated, as well as molecularly dispersed dye. The fading rates are very high.

Effect of position and number of sulphonate groups.

It is evident from Fig.III.19a, obtained by examination of all relevant data for acid dyes on wool in the Colour Index ([illegible]), that light fastness is usually improved by altering the orientation of sulphonate groups, so as to reduce surface activity of the dye, i.e. by placing them more symmetrically around the periphery of the dye molecule.

It also appears that a mere increase in number of sulphonate groups can improve light fastness. In some cases this increase can reduce surface activity (cf. XVIa → XVa; XVIIIa → b) but in other cases the increase cannot reduce surface-activity (e.g. XVII a → b); because neither dye in the pair can be surface-active.

These effects of altering the position of sulphonate groups cannot be due only to variations in susceptibility of the dye molecules to photochemical degradation; if they were, the ranking of the dye in each case would be reversed as between the two substrates (ethylmethylcellulose and gelatin (Cumming et al.)). It must be assumed that increased sulphonation improves the stability or the size of the dye micelles in the substrate. It is probable that the micelles have water associated with ionic groups, as in the "J-aggregates" or giant molecules of photographic sensitising dyes (see e.g. Dickinson), but have not the chain-like structure of the "J-aggregates". A relevant fact in this case, is that layers of basic dyes deposited by sublimation *in vacuo* are usually amorphous, but they appear to take up more ordered arrangement in presence of water vapour (Lyzina and Vartanian).

Effect of cationic surface active agent.

Baxter *et al*. (1955) have reported that the cationic agent, cetylpyridinium bromide, reduces the fastness of direct cotton dyes on Cellophane film. The change was attributed to monolayer formation, the cationic agent tending to form mixed monolayers with the dyes, which are sulphonated and hence anionic. Later, Cameron and Giles showed that cetyltrimethylammonium bromide (CTAB) does promote the formation of mixed monolayers of sulphonated dyes on water, by association between surface active cations and the sulphonated groups. Some dyes thus form monolayers which would not otherwise do so. It is also well known in technical practice that any aftertreatment of direct cotton dyes on cellulosic fibres with cationic agents is very liable to reduce their light fastness.

The results here (Figs.III.17,18) show that the effect of CTAB is not always the same. In general it may be said that this agent reduces the fastness in low dye concentrations, presumably by acting as disaggregation agent. At high dye concentrations it sometimes decreases and sometimes increases fastness, i.e. the CF curve in the latter cases steepens, which indicates that there is an aggregation tendency as well.

(c) A Relation between Molecular Shape and Light Fastness of Dyes and its bearing on Adsorption Mechanisms.

Establishment of Relationship

This investigation was made to examine a prediction that the light fastness of dyes might be related to their molecular geometry. Measurements have been made of the axial ratio of each planar dye molecule where the dye's light fastness is given in the Colour Index[*]. The ratio is defined as that of length to breadth of the smallest rectangle enclosing the molecular model (Catalin, Stuart pattern, see Fig.III.20,21). The sulphonate group was not included in the measurements. When it was included, slightly more scatter was evident in the data, probably because the dimensions to be assigned to this ionised group, when it has associated water are uncertain. All markedly non-planar dyes were excluded, because non-planarity also introduces further uncertainty into the measurements used.

The ratios were then plotted against the respective (Colour Index) light fastness figures for the standard shade depth. In the case of direct and vat dyes on cellulose, and monoazo acid dyes on wool there is a statistically significant correlation between molecular axial ratio and light fastness. (Figs.III.22,23). Light fastness increases with fall in axial ratio, i.e. as the molecule becomes more nearly square in plan. Moreover, the

[*] The complete list of dyes and axial ratios will be given in a paper which it is hoped will be published later.

respective regression lines are almost identical, and the identity is highly significant (see below).

In the case of disazo acid dyes and anthraquinone dyes on wool, and disperse dyes on cellulose acetate, there are not sufficient data for a significant trend to be established. The data for azoic dyes on cellulose gave a random result with no statistical significance (Fig.III.25).

Cause of Relationship

The cause could be either chemical or physical in origin. The longer is the conjugate chain in a molecule the more points are there at which photochemical attack can occur, therefore the lower is its photochemical stability. Thus Jeffreys found that certain cyanine dyes dissolved in methanol, fade more readily as the length of their polymethin chain is increased. In methanol these dyes are largely monodisperse, whereas in a fibre most dyes are partly associated, so that the simple relation observed by Jeffreys will be marked by effects due to the physical state of the dye. Dyes with conjugate chains of similar length (cf.Fig.III.20,21) often appear to have quite different fastness.

Significance in relation to adsorption mechanism

It can be shown* that the regression lines for direct cotton

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*The statistical analysis of the present data, made by the writer's colleague, Mr. D. Smith, is too long to quote here, but it will be given in a paper to be submitted for publication soon.

dyes on cotton and monoazo acid dyes on wool are concurrent. This appears to show that the form of the dye aggregates or micelles depends only upon the shape of the dye molecule rather than on the nature of the substrate. There is already evidence (Part II) that the dye molecules associate during the actual adsorption process. The conclusion to be drawn from the present results is that the substrate molecule acts as a template on which large adsorbed organic solute molecules build up small micelles; but first there must be a mutual attraction between substrate and solute molecules to trigger off the process. (Fig.III.24).

Azoic dyes, as stated, give a random result in the present examination (Fig.III.25). The shape of their molecules is completely altered by the coupling and insolubilisation process after dyeing, and as it is the final form of the particles that determines the fastness, the relation between the original molecular shape and the fastness no longer holds. The vat dyes are not appreciably altered in molecular shape in the insolubilisation process, and the relation does hold for them. Indeed the regression line is significantly parallel with that for the direct cotton and acid wool dyes.

Interrelation of Present effect with effect of spectral regions upon fading.

This work establishes a relation between light fastness and the shape of dye molecules; McLaren (1956) has established a relation between light fastness and the effectiveness of certain wavebands of light in causing fading. Are the two effects inter-related?

McLaren showed that there is a roughly linear inverse relation between the normal light fastness of a dye on a fibre, and the proportion of fading caused by the visible (blue-red) region of the spectrum (Fig.III.26). Thus fugitive dyes are faded mainly by absorbed radiation in this visible region, and fast dyes mainly by absorbed radiation in the ultra-violet and violet region. No explanation for these observations has hitherto been offered. McLaren also found that dyes are faded by absorbed radiation up to a certain critical wavelength, above which radiation is not effective even if strongly absorbed. This critical wavelength decreases as the fastness increases. These observations were made after tests on well over one hundred dyes. These form a random selection and it seems unlikely therefore that the effect can be related to any systematic change in photochemical properties of the dye molecules. This is especially so because the degree of light fastness, as already mentioned, appears to be a function of the physical state of the dye, and not of the photochemical stability of its individual molecule. It has recently been shown, e.g. that dyes of high light fastness, of several classes, including reactive dyes on cellulose, are present in a highly associated state in the substrate, and their high fastness is attributable to this (see above).

This would at first suggest that the relation established by McLaren is fundamentally one between the physical state of dye, regardless of its chemical nature, and its sensitivity to spectral regions, but it is difficult to understand how this could be the case: moreover, if it were, a change in degree of aggregation of a dye would be expected to change its relative sensitivity to different wavebands of the spectrum; yet some preliminary experiments here appear to show that this does not occur.

It must therefore be concluded that there is an <u>indirect</u> connection between the present relation and that established by McLaren, i.e. a low molecular axial ratio in a dye favours both a high degree of association and sensitivity to short-wave radiation. It should be possible to make a direct test of this hypothesis by plotting McLaren's data for the relative spectral sensitivity of dyes against their respective molecular axial ratios. When this is done (Table III.5) it is clear that there is a direct relation between these two parameters (Fig.III.27), the relation is indeed highly significant. We may therefore suggest that "squareness" in plan of a planar dye molecule favours two, possibly independent, effects. It favours sensitivity to short-wave radiation and it also favours, during adsorption, a form of association that ensures high resistance to photochemical breakdown.

Table III.5 Relation between Fading caused by Blue-Red Wavebands (data of McLaren) and Molecular Axial Ratio.

A. Azo Dyes

C.I. Number	Fading Caused by Blue-Red Region %	Molecular Axial Ratio
Basic Brown 1	65	2.92
Acid Violet I	4	1.58
Direct Violet 22	84	2.80
Disperse Black 1	66	2.00
Acid Black 24	11	1.82
Direct Blue 1	87	2.88
Direct Blue 138	65	2.63
Direct Blue 16	84	2.68
Direct Black 51	66	2.48
Acid Green 19	76	2.48
Disperse Black 2	20	2.20
Acid Orange 10	15	1.49
Direct Red 127	64	2.41

B. Anthraquinone Dyes

C.I. Number	Fading Caused by Blue-Red Region %	Molecular Axial Ratio
Vat Blue 5	8	2.06
Vat Violet 2	56	2.00
Vat Brown 5	74	2.44
Vat Violet 17	15	2.36
Vat Violet 14	2	1.12
Vat Violet 9	48	2.46
Vat Green 9	44	2.37
Disperse Blue 7	8	1.13
Disperse Violet 8	26	1.30
Disperse Blue 3	16	1.21
Acid Violet 41	7	1.67
Vat Brown 3	11	1.05
Disperse Blue 24	22	1.07
Disperse Violet 4	18	1.22
Vat Red 1	56	2.06
Vat Red 10	27	1.45
Vat Green 1	24	1.82

(d) Attempted improvement of light fastness by use of fluorescent brightening agents with dyed cellulose.

The use of fluorescent brightening agents for improving the whiteness of fabrics is now common practice, and most soap powders and synthetic detergents have such an agent incorporated. The chemical and physical properties, and the application of these agents have been discussed e.g. by Adams, but no detailed account of their effect on light fastness has previously appeared, though some conflicting statements on their value have been reported. They would presumably retard dye fading, because of their strong absorption of u.v. radiation. McLaren suggests that this radiation is partly responsible for fading. Patents by Agfa and by I.C.I. claim the use of these compounds for improving the light fastness of coloured photographs, and their use for this purpose in plastics and varnishes has been reported by Bradley.

The author, in a thesis for the Post-Graduate Diploma of this College (1957) described work on the effect of these agents upon the light fastness of dyed cellulose. He has continued this work and with the completion of standard fading tests on fabrics, kindly made by Hickson and Welch Ltd. (Mr. D.J. Stamp), a firm conclusion can now be given. In theory, the effectiveness of fluorescent brightening agents on fabrics is reduced by complicating factors. If the agent fades quicker than the dye itself, then it will clearly not have much effect. (Most of these agents have a light fastness between grades 1 and 4). On the other hand too slow fading of the agent might also reduce its effectiveness. The dyed shade appears weaker and brighter in presence of fluorescent agents, and the effect increases as the proportion of agent rises. Therefore if the agent fades more slowly than the dye, its proportion rises during irradiation, and the weakening effect on the shade becomes noticeable. This might mask and even reverse the improvement in fastness due to a reduced fading rate of the dye. The colour of the fading product of the agent may also tend to disguise any improvement in fastness. Light fastness tests were made by the normal method against the B.S.I standards on a series of standard viscose rayon fabrics, dyed in medium depths with the following dyes of different levels of light fastness, C.I. Direct Yellow, 8,12, Reds,2,23,75,80, Blues 1,8,66, Greens 8,22, Vat Yellow 26, and Orange 5. Four sets of dyed fabrics for each dye were prepared a) untreated, (b and c) dyed with addition of C.I. Fluorescent Brightening Agents 15 and 18 to the dyebath (0.1%) and (d) padded, after dyeing, with (0.1%) of C.I. Fluorescent Brightening Agent 17. Exposures were made until standard 4 faded. The examination then showed that with two exceptions no notable change had been produced by the agents. In a few cases a slight improvement (1 grade) and in others a slight deterioration, was noticed in the early stages of the fading only. The two exceptions were direct reds. Red 2 had in all cases considerably deteriorated in fastness; Red 23 had deteriorated after treatment with two agents.

Fluorescence of the fabric

The addition of the brightening agents usually changed the appearance of the fabric, and sometimes considerably. In general the shade became brighter, redder, and weaker, with the exception of C.I. Direct Reds 75 and 80 and Greens 8 and 28. Fluorescence was tested (by Hickson and Welch Ltd.), by using the Harrison Fluorimeter. ~~The results are given in Table III.10.~~ The figure obtained showed that the amount of fluorescence varied from dye to dye and also from agent to agent. Direct Red 75 when treated with Fluorescent Agent 18 showed no fluorescence at all, and it was at first suspected that no brightening agent had been adsorbed by the fabric. Hence a rate test was made to measure the uptake. From the curve obtained it appeared that despite the final dull appearance, the agent is in fact adsorbed by the fabric. The dye appears to have the property of quenching the fluorescence of the agent. A recent investigation by Hayashi showed that there is a "critical quenching concentration" of agent in cellulose above which changes occur in its state of aggregation, light fading rate and fluorescence. There appears to be no relation between the figures given by the Harrison Fluorimeter, and the light-fastness of the dye obtained by exposure until standard 4 faded.

(e) Anomalous light fastness effects in highly hydrophobic substrates.

Note. This section describes work which was proceeding at the time of writing. Because of the shortage of time and the incompleteness of some of the data, only the main conclusions are given. Full details of the experimental data, and figures, will be included in a paper to be submitted for publication when the work is complete.

Many but not all, dyes on the highly hydrophobic fibres (i.e. these with a regain of $<$ca 5%) have much higher light fastness than on other fibres of higher regain. This applies particularly to a number of (a) disperse dyes, which have higher fastness rating on polyester fibres than on cellulose acetate, and (b) basic dyes, which have higher fastness on polyacrylonitrile fibres than on cotton, silk, or wool (Giles, 1957; Schwen and Schmidt). This effect is the reverse of the general rule on the more hydrophilic fibres. On these the general rule is that light fastness rises with fibre regain. This is presumably because the fibres with higher regain have the longer intermolecular spaces and consequently during adsorption the dye molecules can form larger aggregates in them. In general the larger the aggregates, the higher their light fastness. This applies particularly to direct dyes on regenerated cellulose (viscose) of different degrees of crystallinity, either in fibrous or film form (Baxter et al, 1955).

The suggestion was made (Giles, 1957) that on hydrophobic fibres the anomalous effect is due to fading being retarded because of the low moisture content of the fibre, or to the low rate of transport of moisture to the site of fading. The regain instead of the particle size of the dye, thus becomes the rate-controlling factor in fading, not as it is in hydrophilic fibres. The anomaly might of course be due to a reversal in the case of the more hydrophobic fibres of the apparently normal aggregating behaviour of dyes, i.e. they may perhaps aggregate more as the fibre regain falls.

The present investigation was made to examine these suggestions for which no direct experimental evidence had previously been available. Three typical disperse dyes were chosen, two having higher rated fastness on Terylene polyester fibre than on cellulose acetate, and one the reverse. They were applied to polyester fibres and films of different degrees of crystallinity, judged by moisture adsorption, and to (sec.) cellulose acetate film. Also, some tests on regenerated cellulose films of different degrees of crystallinity were included for comparison.

The dyes used were:

C.I.12770, Disperse Yellow 3G (I.C.I.)., aniline→2,4-quinoline diol

C.I.61100, Duranol Violet 2R, 1,4-diaminoanthraquinone

C.I.61105, Duranol Brilliant Violet B, 1,amino-4, methylaminoanthraquinone

Effect of nature of medium

The present results show that - (a) Pyridine does not completely disaggregate any of the disperse dyes. This is shown by the fact that the minimum y/x ratio, i.e. minimum aggregation, for the yellow dye appears in the polyester film, and not in pyridine. Therefore there must be some aggregation in pyridine, even though the y/x ratio does not increase significantly with concentration. (The ratios for the violet dyes in pyridine do increase with concentration).

(b) In all cases where the y/x ratio for a dye is compared on substrates identical except in degree of crystallinity, the degree of dye aggregation rises with fall in crystallinity. This would be expected: aggregates can grow more readily in a substrate as the substrate molecules become less highly ordered. The difference is very marked in the cellulose films, It is much less so in the polyester films, probably because the degree of aggregation in these is low even in the recrystallised film.

(c) Two adsorbed disperse dyes (C.I.12770, 61105) are least aggregated in Melinex film, the third (C.I.61100) is apparently least aggregated in cellulose acetate film, and also shows very little difference between Melinex and recrystallised film.

The reasons for these effects are not obvious, but it may be connected in some way with the fact that the anomalous dye (C.I.61100) is the most symmetrically substituted, and it has recently been pointed out (Giles, 1961) that this condition favours low aqueous solubility and low adsorption in cellulose acetate. Possibly symmetry of substitution in the aromatic nuclei of the dye, in some way favours adsorption and aggregation on the aromatic nuclei of the polyester fibre.

(d) The monomer dye absorption peak of two disperse dyes (C.I.12770, 61105) is at a higher wavelength on polyester than on cellulose acetate, in each case. This probably indicates a closer alignment of dye and substrate molecules in the polyester than in cellulose acetate leading to improved planarity and increased conjugation in the dye molecule. A similar shift of monomer waveband occurs when direct cotton dyes are transferred from water to cellulose, as mentioned in Part II, probably for the same reason.

There is no such change with C.I.61100. This fact conforms to the hypothesis advanced above, that on the polyester fibre aggregation of this particular dye is favoured.

The general impression given by the results, is that the degree of aggregation of the disperse dyes in the hydrophobic substrates is probably quite low, and is generally more uniform over a range of dye concentrations than it usually is in hydrophilic substrates.

Light Fastness Effects[*]

The hypothesis that light fading of dyes on very hydrophobic fibres is retarded by the very low moisture adsorption of the fibre is now confirmed by two facts:

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[*] At the time of writing, the tests on polyester fabric are not complete.

(a) On all the polyester substrates, fastness rises with fall in moisture adsorption.

(b) Fastness falls on all the films when the atmospheric humidity is raised, i.e. when a more abundant supply of moisture is available, but the fall is much more marked on Melinex film* than on cellulose acetate and on recrystallised polyester, presumably because in the last two, there is normally nearly enough moisture for fading not to be retarded.

(c) In all cases the monomeric dye fades more rapidly than the aggregated dye, as would be expected.

(d) Fading rate curves of the violets have the shape characteristic of aggregated dye, in those of the Yellow there is more evidence of monomeric dye**, as indeed there is in the low y/x ratio.

*In the I.C.I. publication(954 EHU) the light fastness figures for disperse dyes on Terylene fibre are all much lower for Fadeometer exposure than for daylight. Presumably a humidified and cooled lamp was used, giving higher moisture regain in the fibre than is obtained in daylight exposure.

**In all cases, though the shape of the fading-rate curve is very similar for both monomer and aggregate peaks. This is attributed to the overlap of the two absorptions i.e. the optical density at each peak is the sum of values for the two forms, the monomer form predominating at the higher wavelength (cf. Campbell and Giles). Thus it is not possible in these cases to obtain a fading curve characteristic of truly monomeric dye, in all cases what is measured is the fading of a mixture of monomer and aggregate.

(e) In all cases, fastness is higher on cellulose acetate than on both polyester films. This is in accordance with the normal rule that fastness rises with regain, for fibres with a regain above ca. 5% (Giles, 1957). It shows that generally the aggregated dye in cellulose acetate is in larger particles than it is in the polyester films[*].

It seems possible from an inspection of the results that when the data for the fabrics are available, they will show that dyes in Terylene fibre, which is more hydrophobic than Melinex film have higher fastness than on the film. Thus C.I.61100 may then be rated higher on Terylene than on cellulose acetate, as in the commercial literature.

The results confirm that in highly hydrophobic fibres, the reversal of the usual rule that higher fibre regain produces higher light fastness (because of higher degree of aggregation) is due to the "moisture diffusion restriction effect", i.e. to the insufficient supply of water to maintain the fading reaction.

[*] C.I.61100 fades, at first, much more rapidly on cellulose acetate than on polyester. This is consistent with its y/x ratio, which is lower, indicating a higher proportion of monomer, on the acetate film. The CF curves show the reverse, i.e. higher fastness on acetate, because they are calculated from data for the later, slow, fading, determined by the state of the main bulk of aggregated dye.

CONCLUSIONS

All normal dye-substrate systems in the air-dry state or the dyes in concentrated aqueous solution, contain some aggregated dye.

Beer's law is seldom strictly obeyed by a dye either in solution or when adsorbed by an organic substrate, at high concentration. This is attributed to aggregation.

High light-fastness exibited by water-soluble dyes is attributed to the presence of large aggregates of the dye in the substrate. The theoretical model described is shown to represent qualitatively the capillary effect causing dye particle growth during drying-out processes with pigment particles suspended in a liquid film.

Those substrate systems prepared by adsorption of a soluble dye from solution, whether it is subsequently insolubilised or not, are heterogeneous, and contain a small proportion of molecularly dispersed dye, presumably adsorbed as a monolayer, with the remainder as aggregates in a range of sizes.

The fading rate of these systems varies with concentration in a manner characteristic of a range of distribution of particle sizes of dye present.

Dye-substrate systems obeying the normal photochemical laws for ideal systems are comparatively rare.

In highly hydrophobic fibres high light fastness of dyes is attributable to the very low moisture content.

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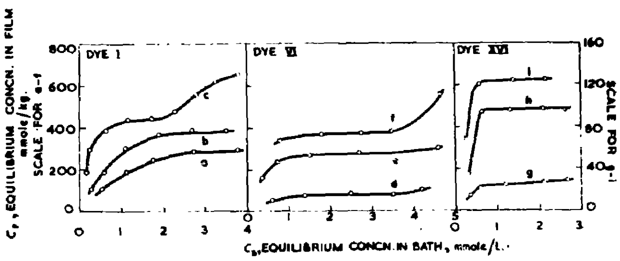


FIG. 1.1 *Adsorption isotherms of sulphonated dyes on anodic film at various liquid/solid ratios*

Dye I, 52°. a 150 : 1, b 300 : 1, c 600 : 1
Dye VI, 45°. d 133 : 1, e 833 : 1, f 1666 : 1
Dye XVI, 45°. g 133 : 1, h 833 : 1, i 1666 : 1

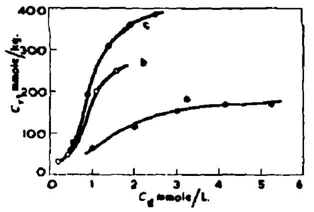


FIG1.2. *Effect of various treatments on adsorption at 59° by Dye III by the anodic film*
(anodisation temp. 52°)

a pretreated in 1666 : 1 bath of water at 60° for 2h., then dyed normally in 300 : 1 bath
b normal dyeing at 300 : 1, no pretreatment
c as a, but pretreated in cold water for 5 min.

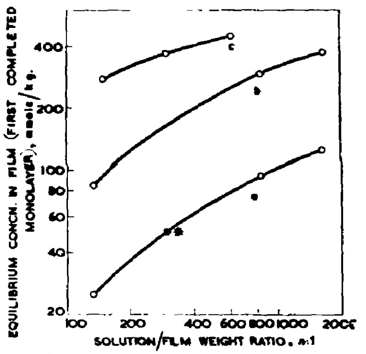


FIG1.3. *Relation between volume of solution and adsorption of sulphonated dyes by the anodic film*

a Dye XVI at 59° (45°). * point obtained by interpolation from isotherms in Fig. 5.
b Dye VI at 59° (45°). c Dye I at 60° (52°)

(figures in parenthesis are anodisation temp.)

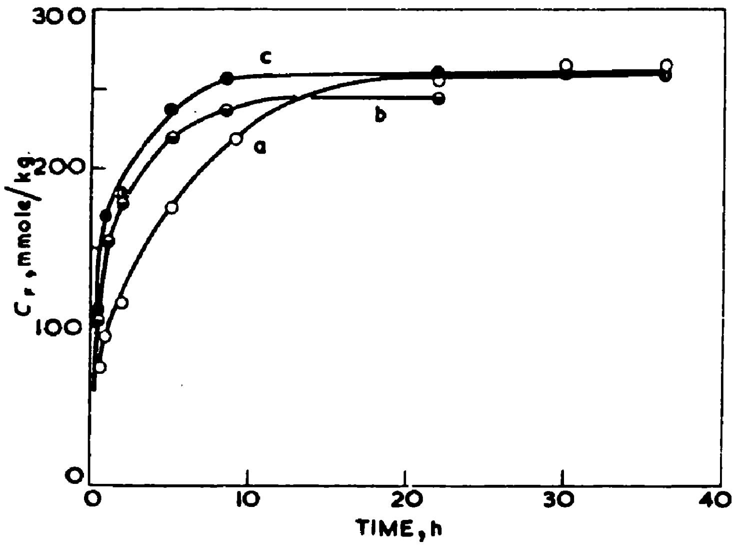


FIG. 14. *Rate of adsorption of sulphate ester dye I*^{8} *by the anodic film*
Solution/film ratio 333 : 1. Initial concentration 1·072 mmoles/l. a at 30° c at 60° b as c but film pretreated in water at 60° for 2 h. (333 : 1 ratio)

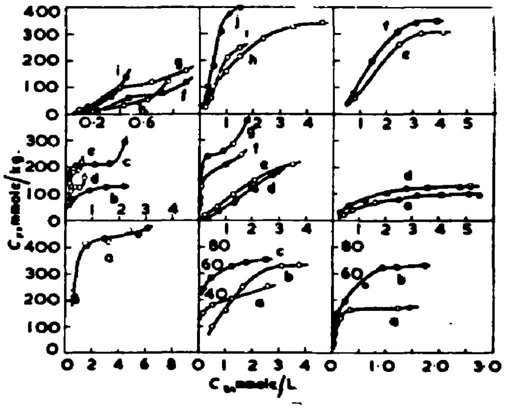


FIG. I.5. *Adsorption isotherms of sulphonated dyes on anodic film*

(all 300 : 1 ratio except where otherwise stated)

Left: Alizarin: a ● 51°, ○ 59°. Dye VIII: b 60°, c 50°. Dye V: d 52°, e 40°. Dye XIX: f 36·5°, g 57°. 2 : 4-dinitrophenol at 59°; h 300 : 1, i 666 : 1

Centre: Dye XVI: a 66°, c 50°. Dye XVII: b 50°. Dye XI: d 60°, e 50°. Dye XIII: f 50°, g 33°. Dye I: h 50°. Dye III: i 60°, j 50°

Right: Dye XVIII: a 60°, b 50°. Dye IX: c 50°. Dye X: d 50°. Dye IV: e 59°, f 50°

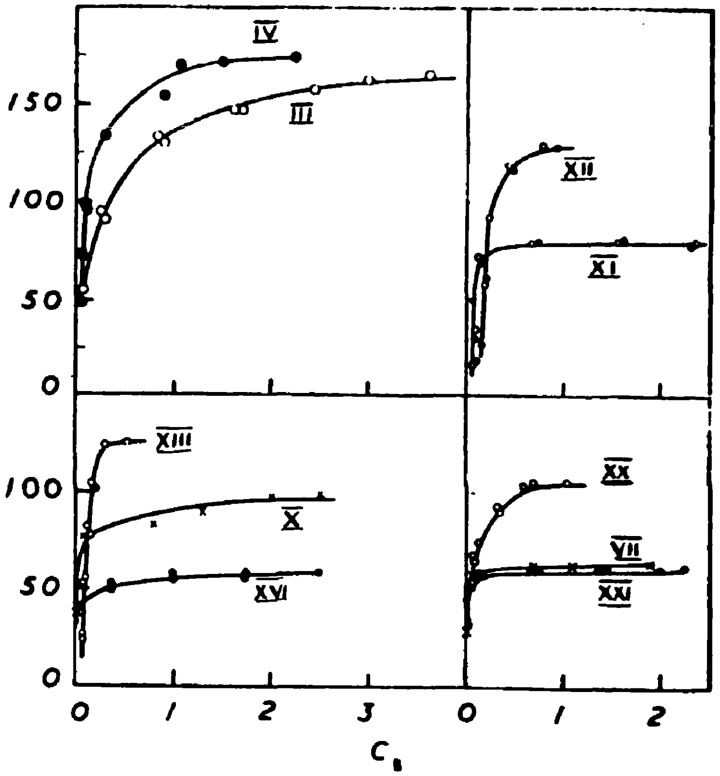
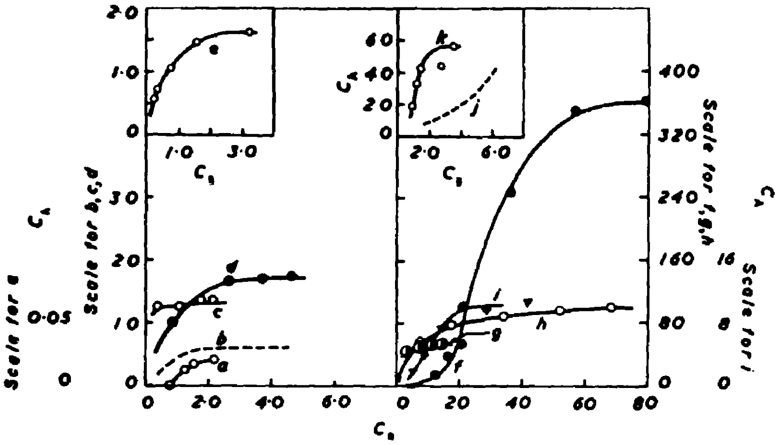


Fig. I.6. Adsorption isotherms of sulphonated azo-dyes from water on chromatographic alumina. Temperatures III,33°,60°; IV,33°; X,26°; XI,50°,60°; XII,51°,61°; XIII,50°,60°; XX,49°,61°; XXI,49°,61°; XVI,49°,60°; VII,26°. For clarity the points for individual temperatures are not differentiated in several cases. Roman numerals refer to dyes.

FIG. 1.6[a] *Adsorption isotherms of non-ionic solutes on chromatographic alumina.*



a,* Nitrobenzene in ethanol-water (1 : 1 v/v), 20°.
b, *cis*-Bis(phenylazo)benzene in ethanol–water (4 : 1 v/v), 30°.
c, 2 : 4-Diacetoxyazobenzene in benzene, 44°.
d, 4-Aminoazobenzene in dioxan, 58°.
e,* Terephthalaldehyde in benzene, 20°.
f, Phenol in water, 58°.
g, Phenylazo-2-naphthylamine in dioxan, 58°.
h, Resorcinol in water, 58°.
i,* 4-Nitroaniline in ethanol water (1 : 1 v/v), 20°.
j, *cis*-Azobenzene in ethanol water (4 : 1 v/v), 30°.
k, Cellobiose in water, 53°.

C_A is the equilibrium concentration on the alumina (mmole/kg.) and C_B that in the bath (mmole l.).
* Coarser alumina; all others chromatographic alumina.

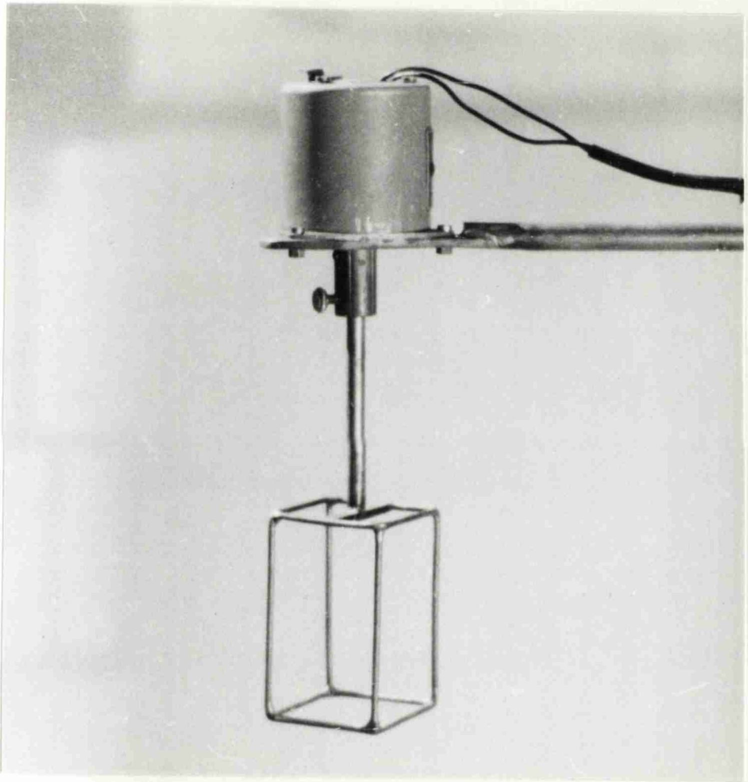
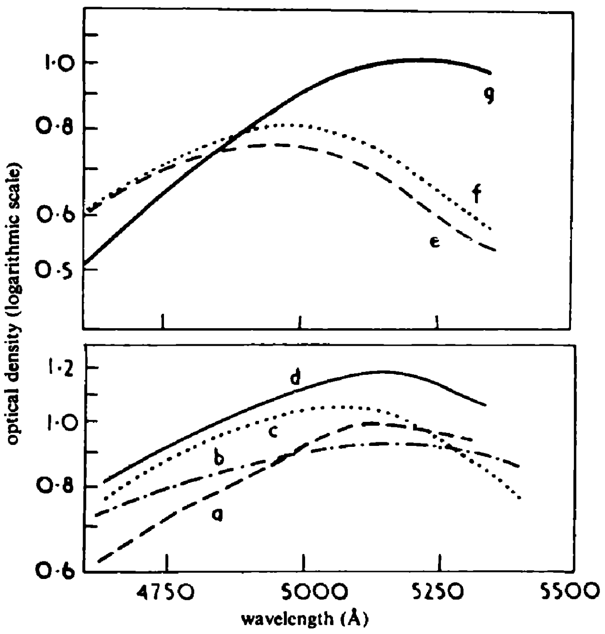


Fig.II.1 Device for dyeing Cellophane film. The film is bound round the lacquered brass wire frame and rotated in the dyebath by slow-speed motor.



FIGII.2.—Absorption spectra of Benzopurpurin 4B in various media.

Media: (*a*) wet cellulose film; (*b*) dry cellulose film (as (*d*)) after irradiation (20 h); (*c*) gelatin film, with phenol; (*d*) dry cellulose film; (*e*) water; (*f*) 0·2 M phenol solution; (*g*) pyridine.

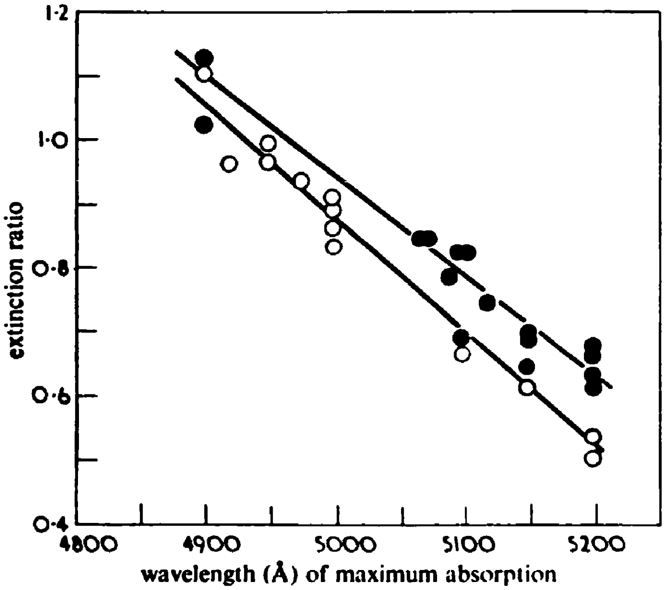


FIG. II-3.—Relation between ratio of extinctions of Benzopurpurin 4B at 4650 and 5200 Å and wavelength of maximum absorption (data from table 1).

Black circles, solid films ; open circles, solutions.

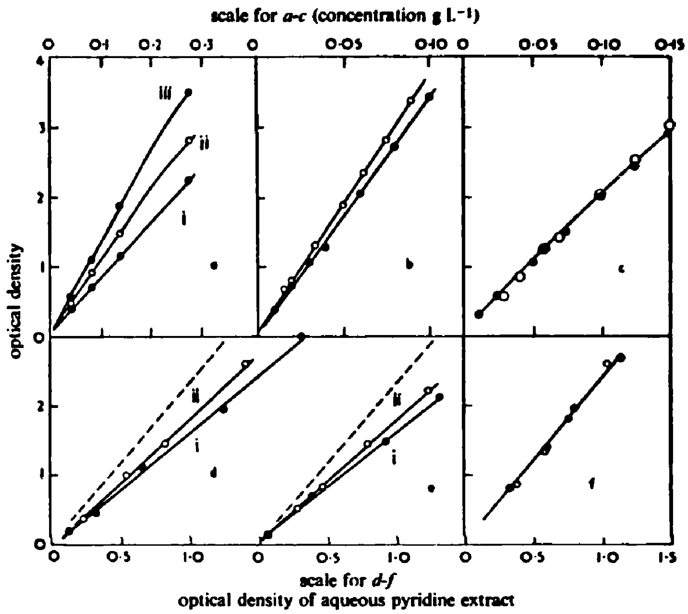


FIG. 4.—Comparison of optical density against concentration relations for dyes in solutions and adsorbed at solid surfaces.

Top curves: aqueous solutions aged 3 days, cold; bottom curves: solid films.

(*a*) (i) water alone; (ii) 0·25 M phenol; (iii) 50 % aqueous pyridine (w/w). densities at λ 5000 Å.

(*b*) (i) water alone: (ii) 0·2 M phenol. Densities at λ 4950 Å.

(*c*) black circles, water alone; open circles, 0·2 M phenol. Densities at λ 4300 Å.

(*d*) Cellophane films: film densities at λ 4900 Å; pyridine extracts at λ 5150 Å.

(*e*) gelatin films. Densities at λ 4950 Å.

(*f*) selatin films. Densities at λ 4300 Å.

Dyes: left, I; centre, II; right, III.

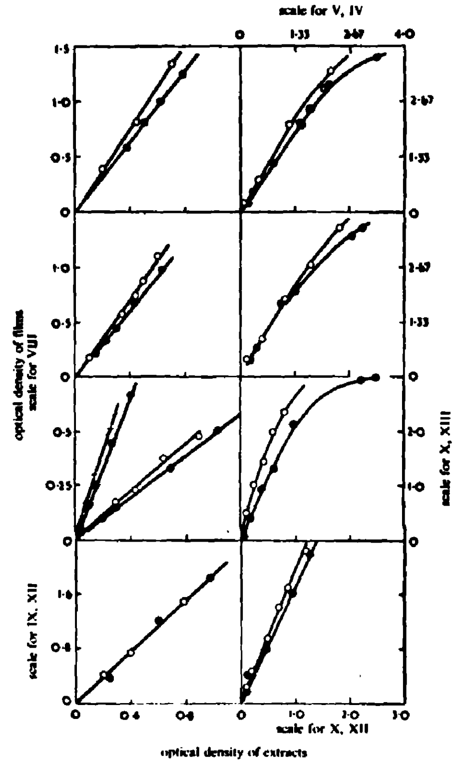


FIG. 5.—Optical density against concentration curves for dyed films, with and without disaggregating agents.

Black circles: no added agent. Open circles: films dyed in presence of phenol. Crosses: films dyed in presence of cetyltrimethylammonium bromide. Half-black circles: films examined in water at 60 immediately on removal from dyebath (no added agent).

Dyes (reading down): 1st column, VI, VII, XIII, IX; 2nd column, V, VI, X, XII.

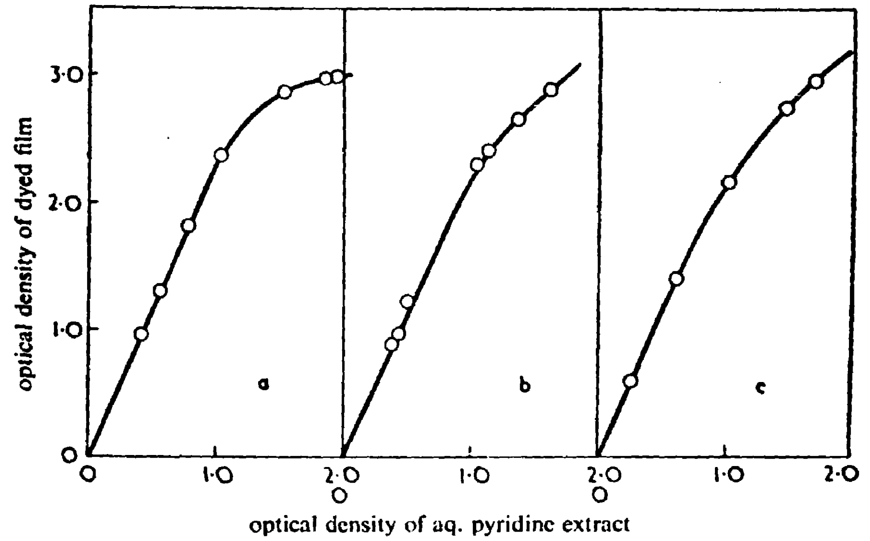
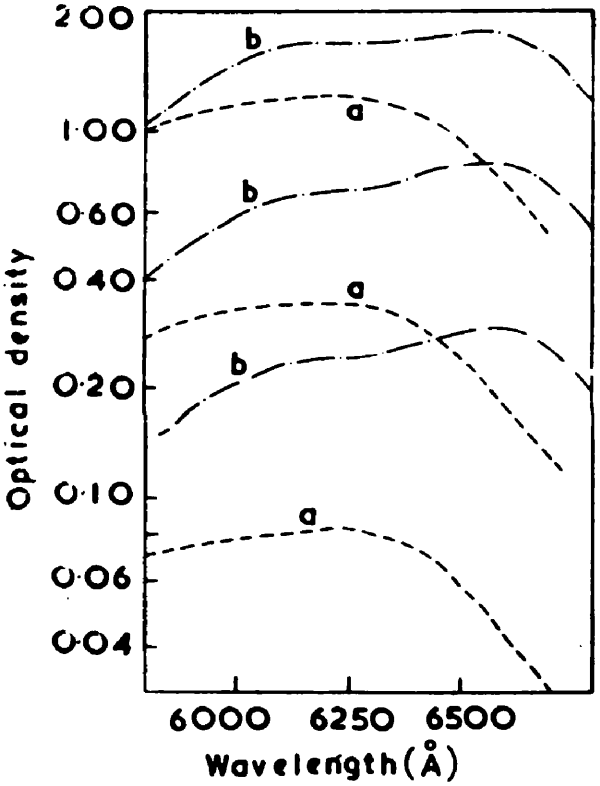


FIG. 6.—Optical density against concentration curves for films dyed with Chrysophenine G(XI), with and without disaggregating agent. (*a*) dye alone; (*b*) phenol in dyebath; (*c*) film pretreated with phenol before dyeing.

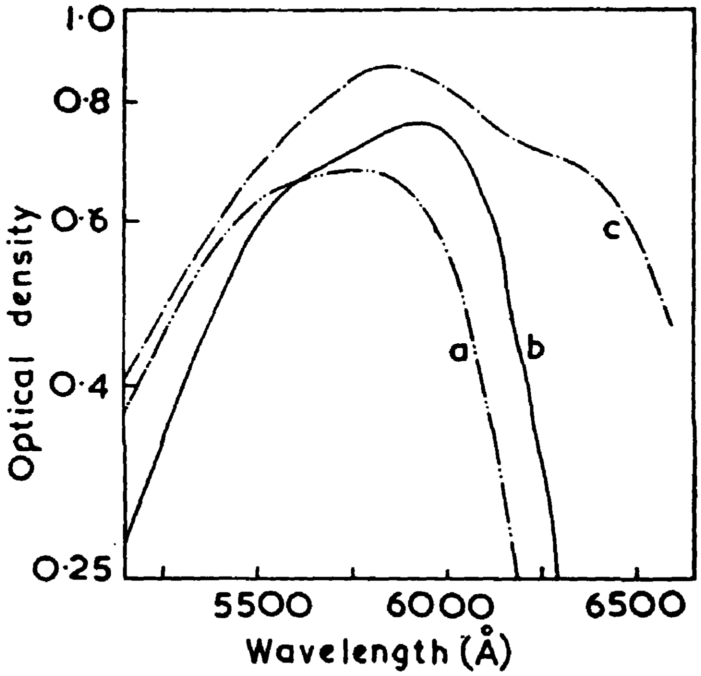
FIG. II.7. *Absorption spectra of a (direct cotton) disazo-dye* (C.I. 24,410, *Sky Blue FF*) *in various media.*



a, *Water*; b, *dyed regenerated cellulose film.*

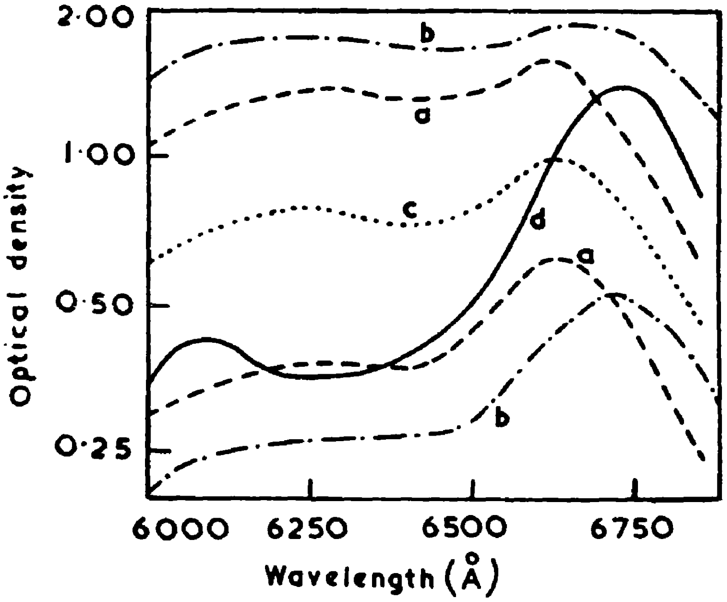
II.8.

FIG. 2. *Absorption spectra of a (direct cotton) disazo-dye* (C.I. 24,140) *in various media.*



a, *Methanol*; b, *pyridine*; c, *dyed regenerated cellulose film.*

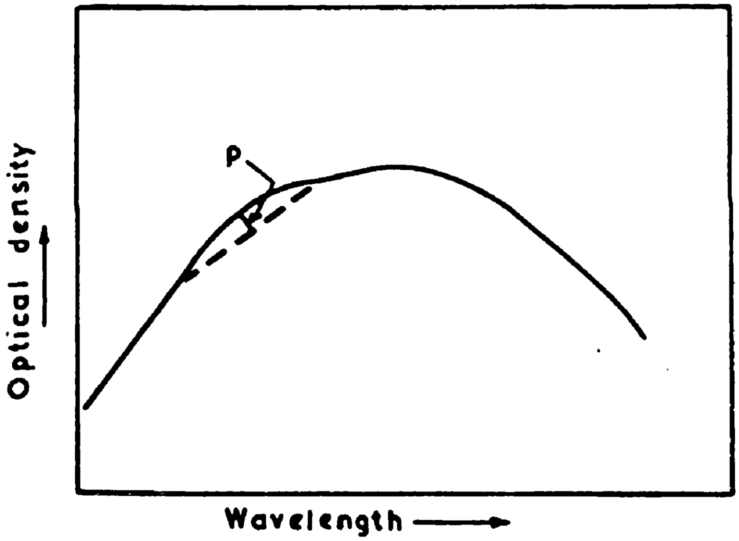
II.9.
FIG. ~~3~~ *Absorption spectra of a reactive dye (Procion Brilliant Blue* H7G) *in various media.*



a, *Water*; b, *dyed regenerated cellulose film*; c, *alkaline solution, after boiling*; d, *pyridine*.

II.10.

FIG. ~~4~~. *Illustrating the method of estimating the position of a subsidiary absorption peak. The peak is at the intersection of the curve with the perpendicular* p. *This method was checked by graphically adding peaks of different heights.*



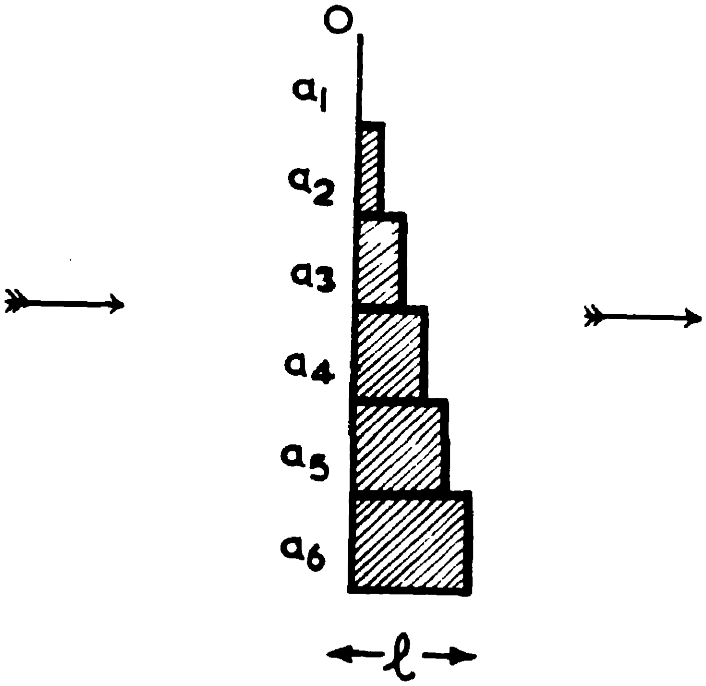


Fig.II.11 Schematic diagram of equivalent paths of a light beam transmitted or reflected by a mass of coloured particles.

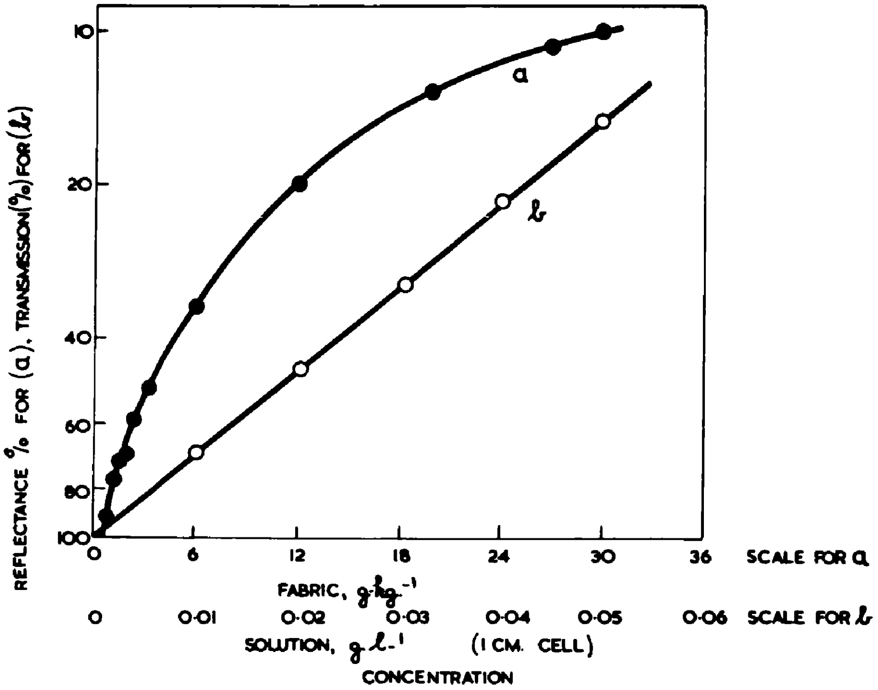


Fig.II.12 Reflectance (at λ 5400A) and transmission-concentration curves for a direct cotton red dye (C.I.35780) (a) on viscose rayon fabric (residual dyebaths measured at λ 5300A) and (b) in aqueous solution (at λ 5300A). Beer's law is obeyed in solution. (The wide difference in length of light path in the two cases accounts for the differences in concentration range).

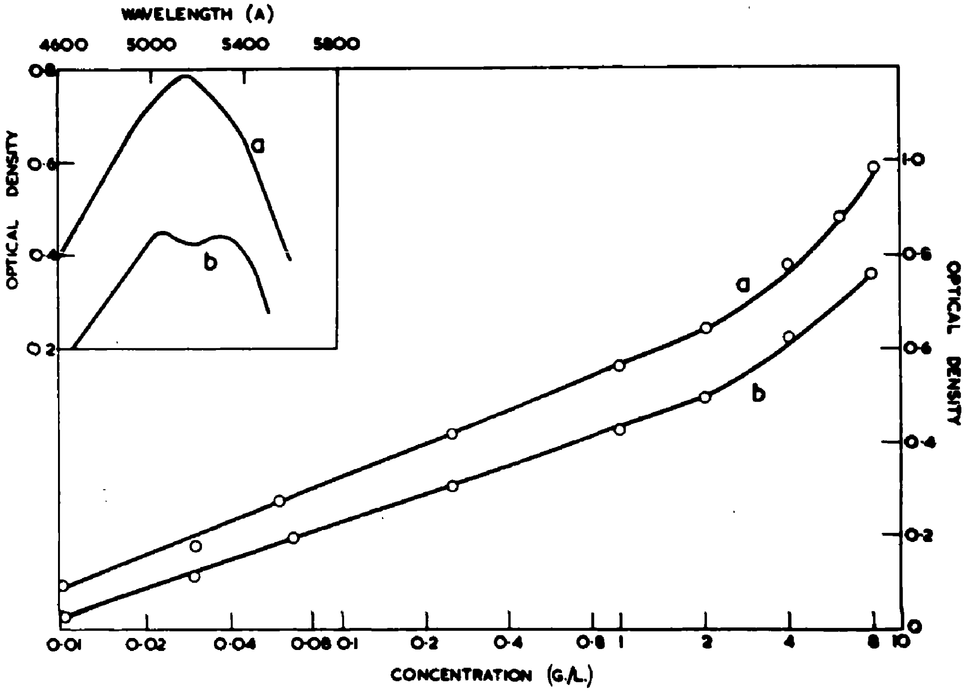


Fig.II.13 Optical density-log. concentration relation for aqueous dye solutions measured using whole visible wave-band (Hilger Spekker absorptimeter, no filter; 1 cm. cells), showing similarity to relation for diffusely reflecting surfaces.

(a) C.I. Acid Red 18 (16255), recrystallised sample.

(b) C.I. Acid Red 1 (18050), commercial sample.

Insert shows respective absorption spectra: a, 0.049 g./1., b, 0.28 g./1. (1 cm. cells).

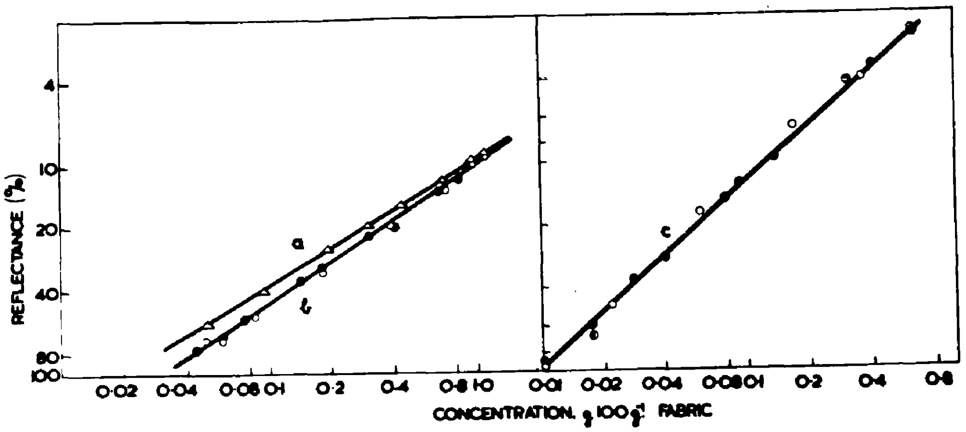


Fig.II.14 Reflectance-concentration curves for dyed fabrics, (a) direct cotton red dye (C.I.35780) on viscose rayon fabric, treated with optical dissolving agent (ethyl salicylate)(λrf, 5400A, residual dyebaths measured at 5300A); (b) the same on untreated fabric; (c) acid wool orange dye (C.I.16230) on wool flannel fabric, λrf, 4950A. Different symbols on curves b,c represent replicate experiments.

λrf = Wavelength of minimum reflection of fabric,

λex = Wavelength of maximum absorption of extracted dye solution (see below).

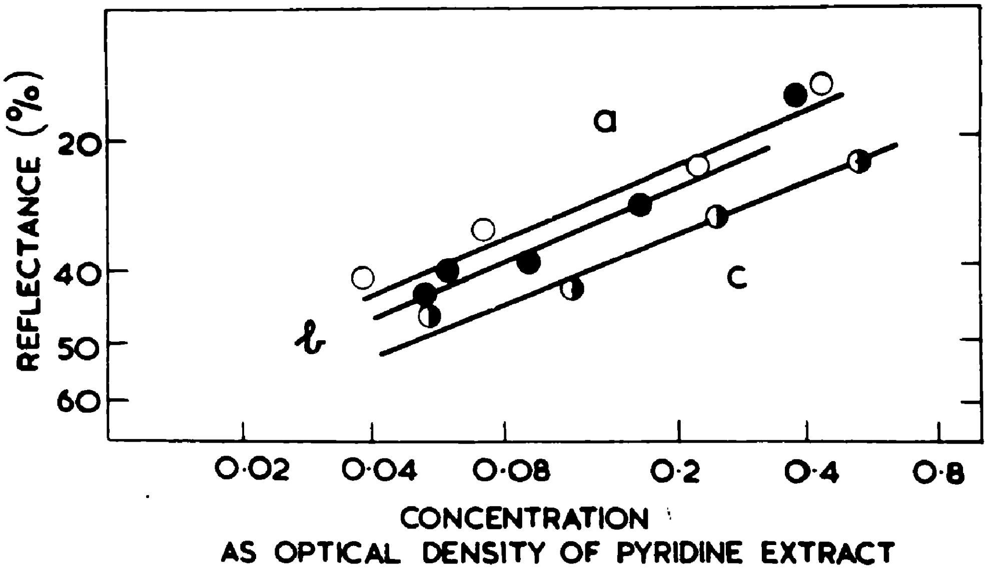


Fig.II.15 Direct cotton red dye (C.I.29100) on viscose rayon fabrics of (a,b,c) different crystallinity, λrf, λex, 5400A; λrf is the same for all three types of dyed fabric, (a) normal fibre, (b) strong (Tenasco) fibre, (c) low swelling (highly crystalline) fibre.

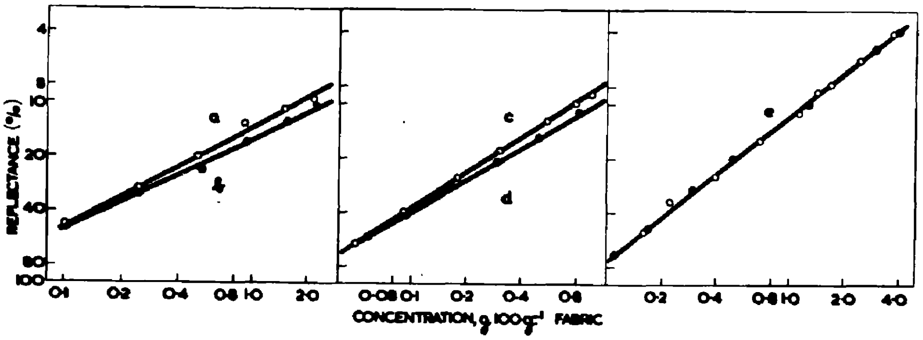


Fig.II.16 Reflectance-concentration curves for fabric dyed with and without disaggregating agent (phenol). (a,b) Direct cotton yellow (C.I.13920) on viscose rayon, λrf. = 4200A, λex 4100A; (c,d) Direct cotton blue (C.I.24410) on viscose rayon, λrf 6250, λex 6600; (e) acid wool dye (Polar Yellow R) on wool flannel fabric, λrf, λex 4300A; (○), Phenol in dyebath; (●) No phenol present. There is no change in λrf in presence of phenol, in any of these cases.

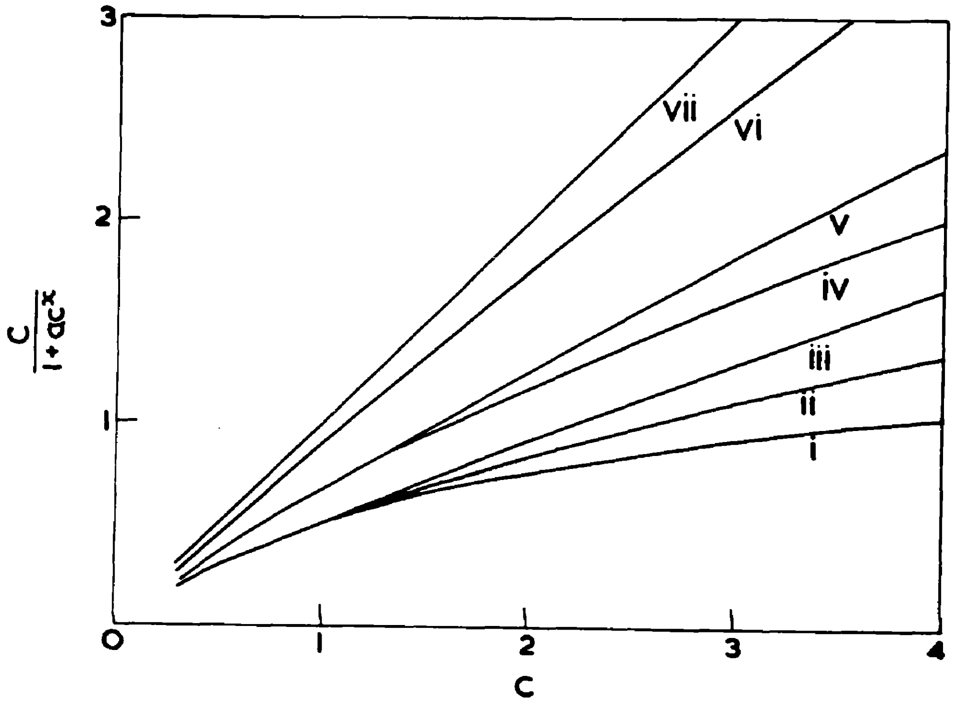


Fig.II.17 Plot of the function $\frac{c}{1 + ac^x}$ (proportional to optical density) against c for various values of a and x. Values of a and x respectively (i) 1.0, 0.75; (ii) 1.0, 0.5; (iii) 1.0, 0.25; (iv) 0.5, 0.5; (v) 0.5, 0.75; (vi) 1.0, 0.5; (vii) a = o.

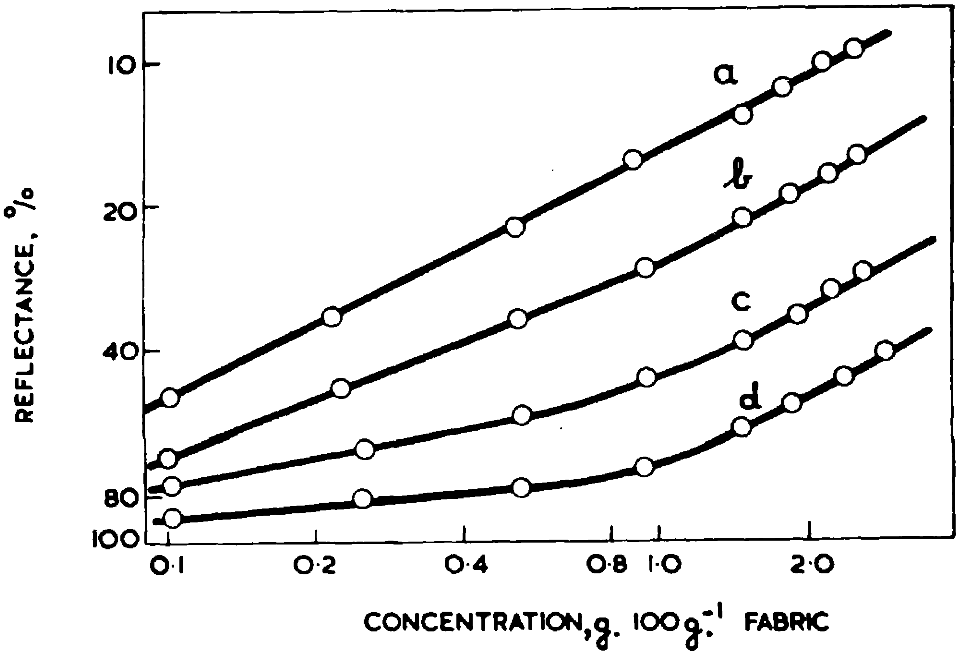


Fig.II.18 Reflectance-concentration curves for viscose rayon fabrics dyed with a direct cotton yellow dye (C.I.13920). Reflectance measured at: (a) 4900A (λmax), (b) 4500A, (c) 4100A, (d) 3900A.

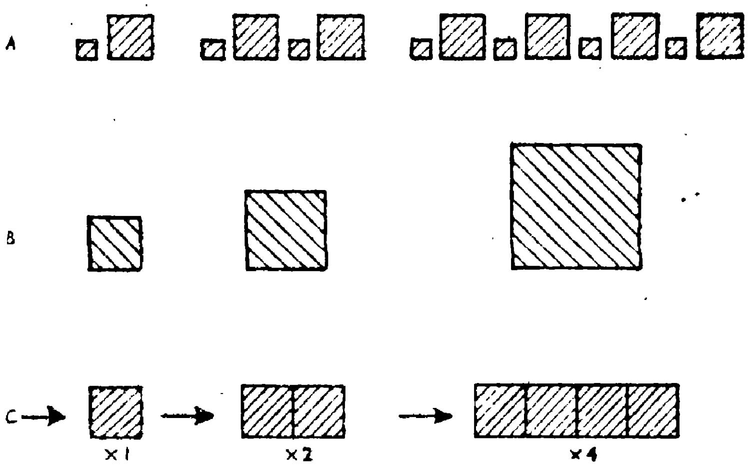


FIG III.1 Ideal Systems of Growth of Dye Particles with Increase in Total Concentration, in Ratio 1 : 2 : 4

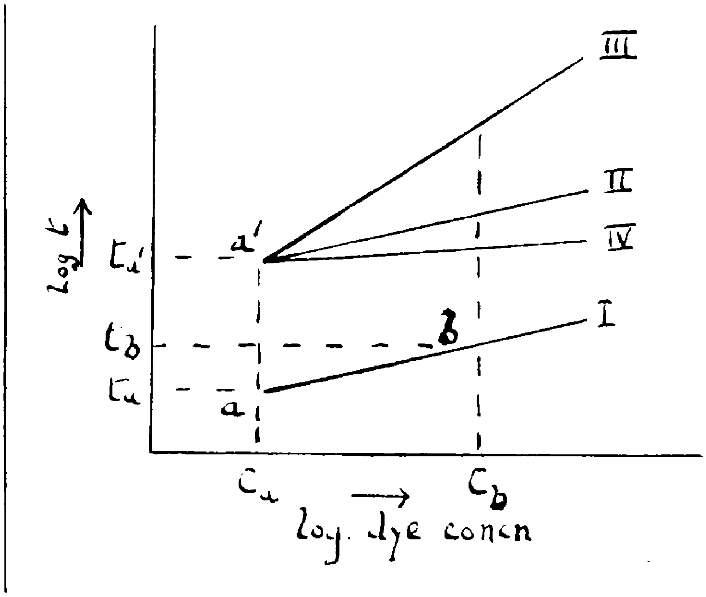


FIG. III.1B. CF CURVES

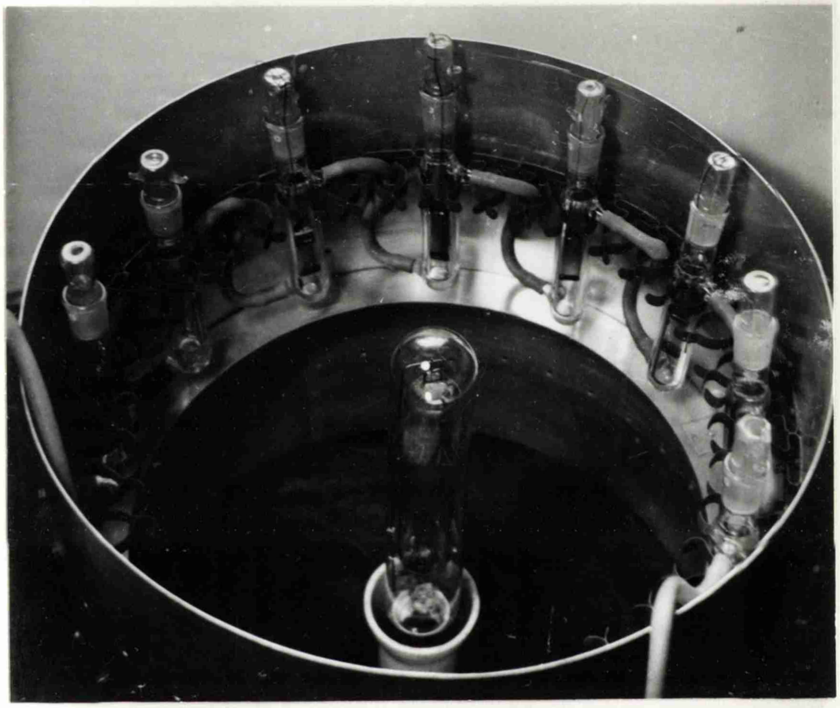


Fig.III.2 Setup of irradiation apparatus.

The coloured films, attached to glass slides cut to fit the spectrophotometer optical cell housing, are suspended by threads in the jacketted tubes equidistant from the arc. Cooling water may be circulated through the jackets, as shown. Solid calcium chloride or water may be placed at the bottom of each tube to give low or high humidity conditions. If temperature or humidity control is not required, the slides are rested on the ledge (shown) around the inside of the cylindrical aluminium shield.

A 400w. mercury vapour lamp is shown: when a source of continuous radiation is required a xenon arc lamp is used.

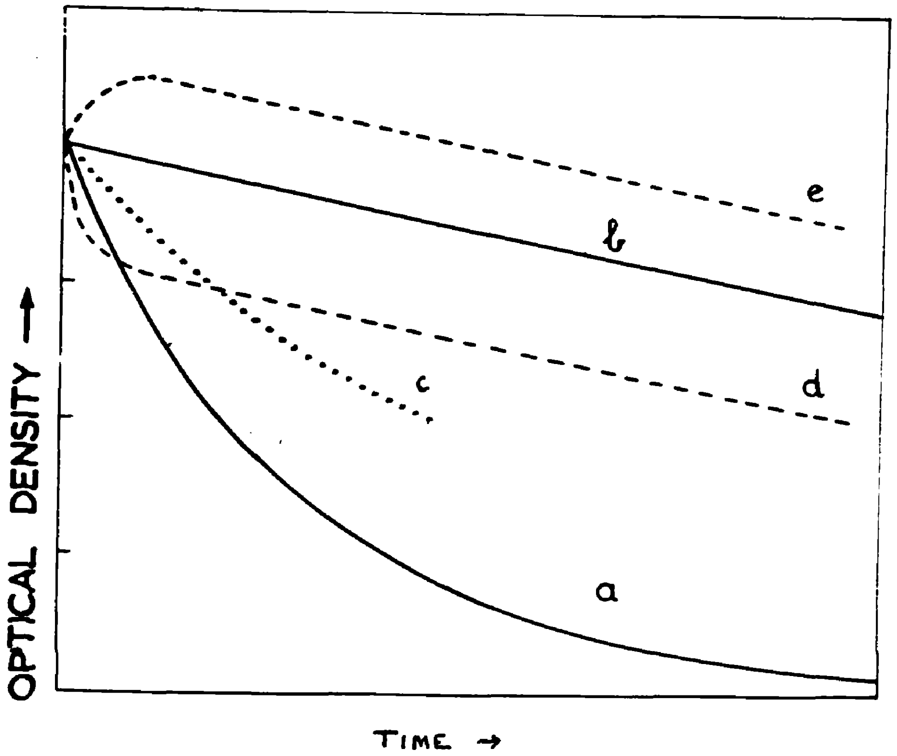


Fig.III.3 Types of fading rate curve given by dyes and pigments.

a. First-order curve-dye in molecular dispersion.

b. Zero-order curve - dye or pigment in large particles.

c. Second-order curve - (dye in molecular dispersion, substrate dry (?)).

d. First-order, followed by zero order curve - dye partly in molecular dispersion and partly in large particles.

e. Zero-order curve with maximum - dye or pigment in large particles: partly disaggregating in heat of illuminant.

Note. In some cases the first part of the falling section of the curve may be of first or second-order type.

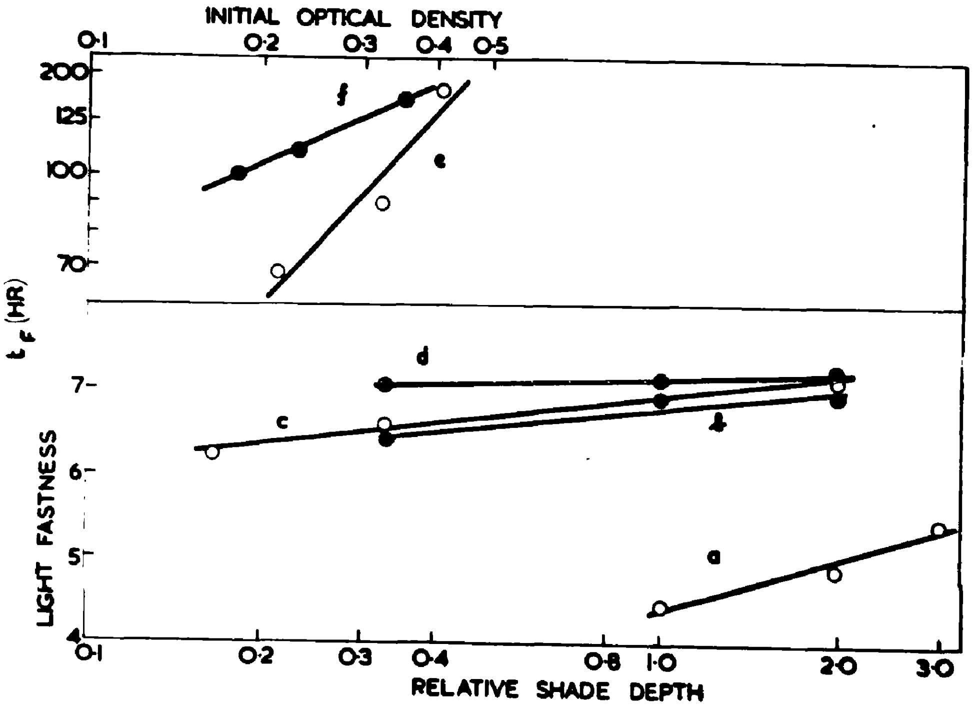


Fig.III.4 CF and CFG curves for pigments and dyeings.

a. Azoic dyes applied by normal method.

b. Azoic dyes applied as resin-bonded pigments.

Data for a. and b. supplied by the same manufacturer.

c. Vat dyes applied by normal method.

d. Vat and phthalocyanine dyes applied as resin-bonded pigments.

Data for c. and d. supplied by the same manufacturer.

Microfix Blue RN (Ciba) applied to gelatin films.

e. By vatting and dyeing on hardened gelatin.

f. By incorporation in gelatin solution as a pigment, with binder, and baking. (Gelatin solution was used because it was found impracticable to obtain even colouration by using a Cellophane film).

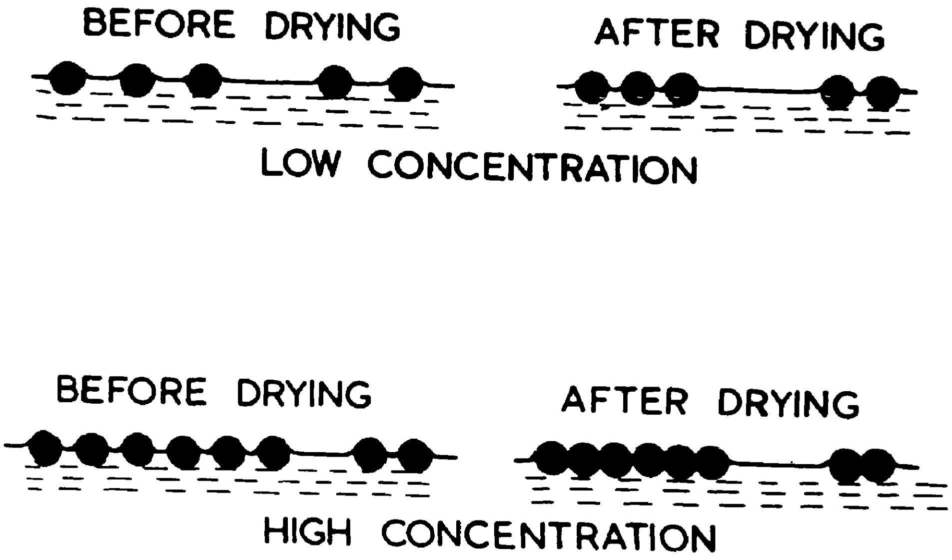


Fig.III.5 Diagram showing suggested aggregation, by capillary action, of pigment particles suspended in a viscous fluid during drying. Before the fluid sets solid, particles more readily aggregate in high than in low concentrations. (In real cases aggregation will take place in three dimensions, not in two as shown here).

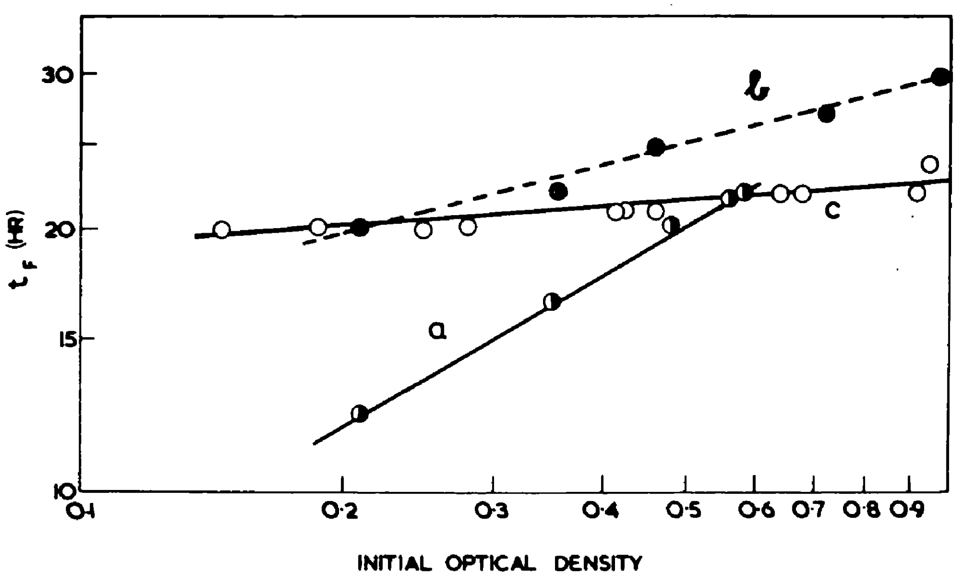


Fig.III.6 Characteristic Fading (CF) curves for the pigment C.I. Azoic Diazo Component 5→C.I. Azoic Coupling Component 5 incorporated in fluid substrates of different setting times.

a. Ethylmethylcellulose solution, dried by heat.

b. Gelatin solution, set and dried by heat.

c. Gelatin solution, first set by freezing, then dried by heat.

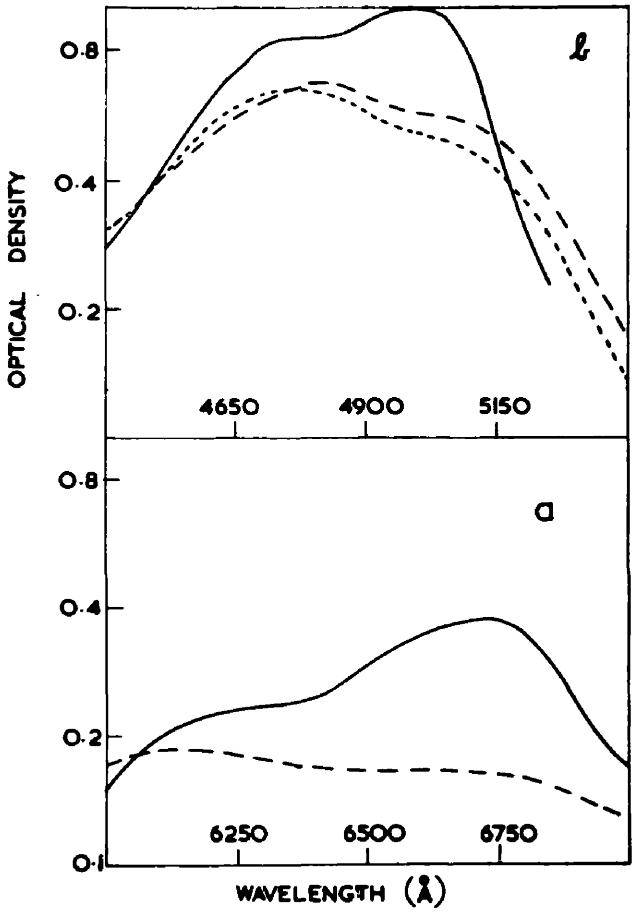


Fig.III.7 Absorption spectra of basic dyes in Cellophane films.
a. Methylene Blue (C.I. Basic Blue 9),
b. Acridine Orange (C.I. Basic Orange 14). Full lines, untreated: broken lines, aftertreated with phosphomolybdic acid: dotted lines, aftertreated with phosphotungstic acid.

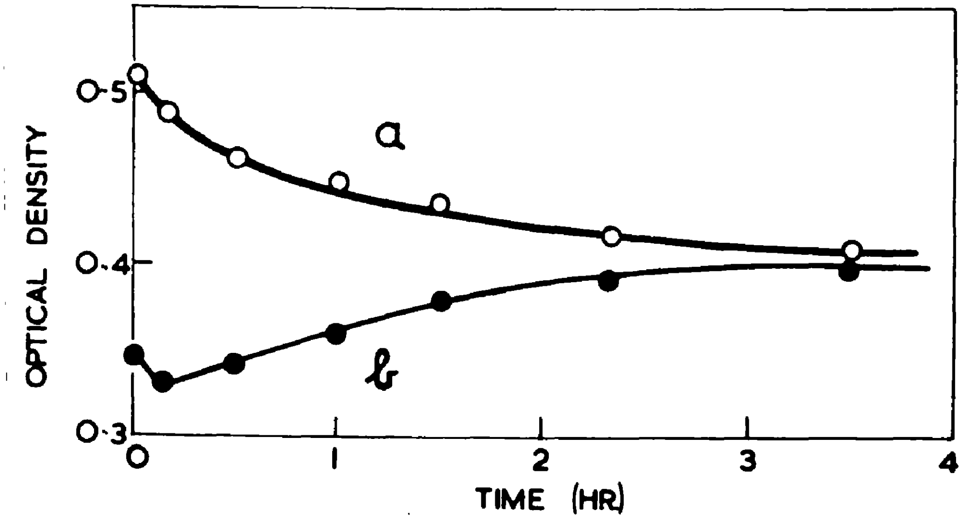


Fig.III.8 Fading rate curves of C.I. Basic Orange 14 on Cellophane film, (a) untreated, (b) aftertreated with phosphomolybdic acid.

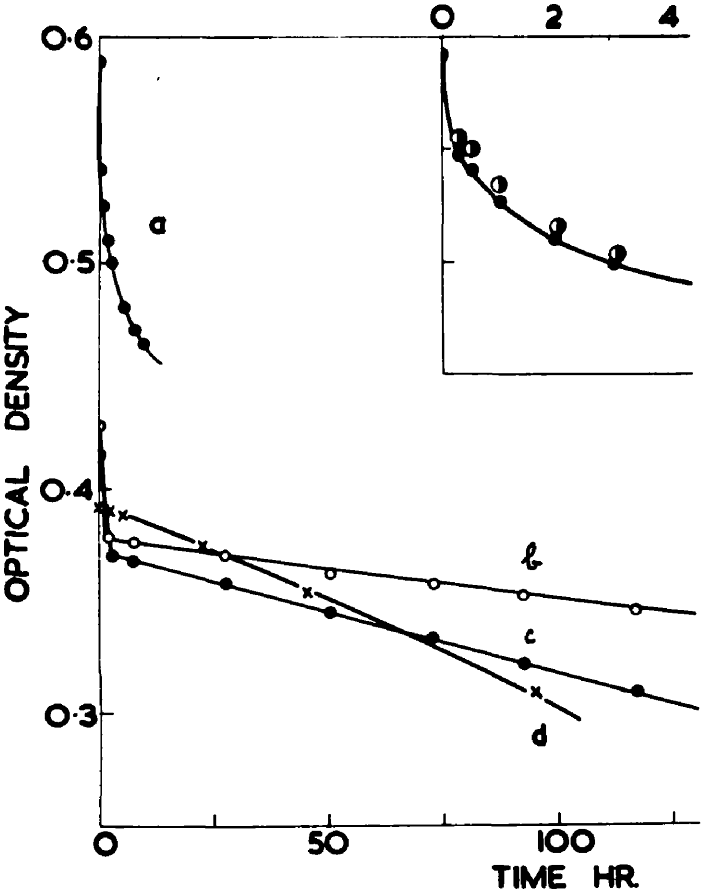


Fig.III.9 Fading rate curves of direct cotton dyes in Cellophane, (a) C.I. Direct Blue 1 at high humidity (insert shows the same curve on an enlarged scale), (b) C.I. Direct Blue 66 (copper complex of Direct Blue 1) at high humidity, (c) as (b), at low humidity, (d) as (b), but dyed film aftertreated at b.p. for 1 hr. with copper sulphate (5% on film weight).

Half-filled circles on curve a (inset) show results in cool atmosphere (10°C.): all others were obtained without cooling (55°C).

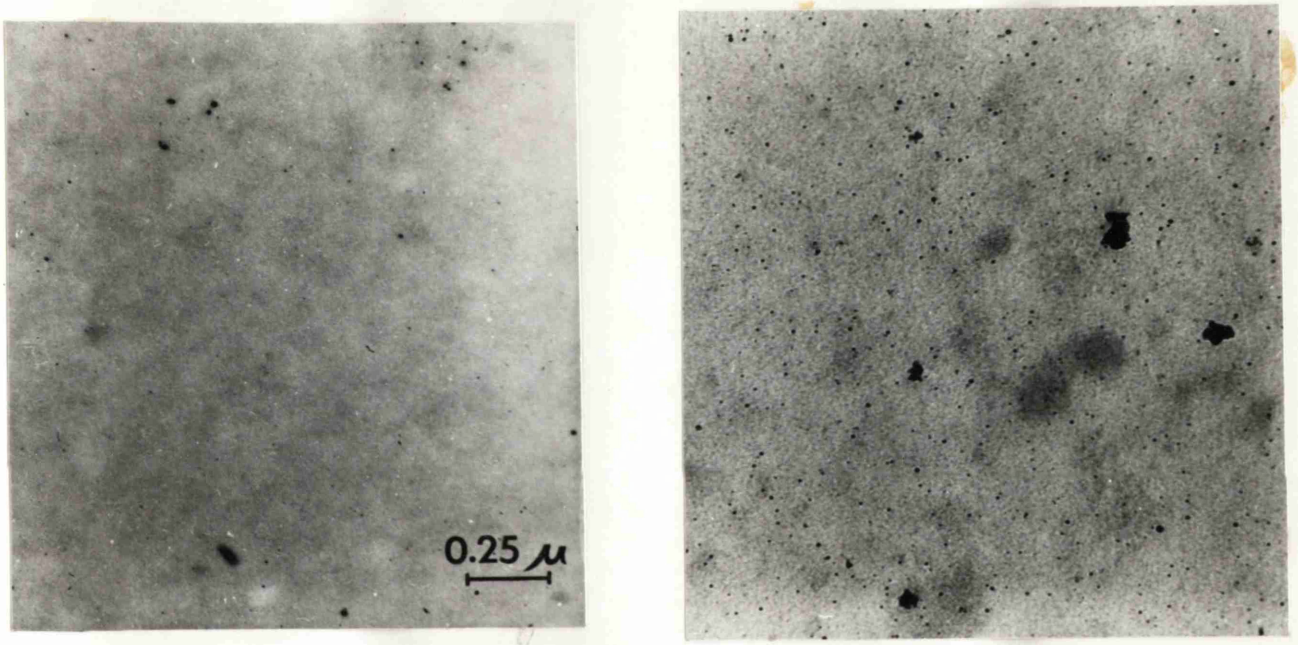


Fig.III.9A. Electron micrographs of dyed ultra-thin viscose film (from Weissbein and Coven).

(i) C.I. Direct Blue 1. No marked aggregation.

(ii) C.I. Direct Blue 66 (copper complex of C.I. Direct Blue 1). Marked aggregation visible.

The small dense spots may be surface dye particles or dirt, the larger shadowy objects in (ii) were shown, by Weissbein and Coven, using uranium shadowing, to be true internal aggregates.

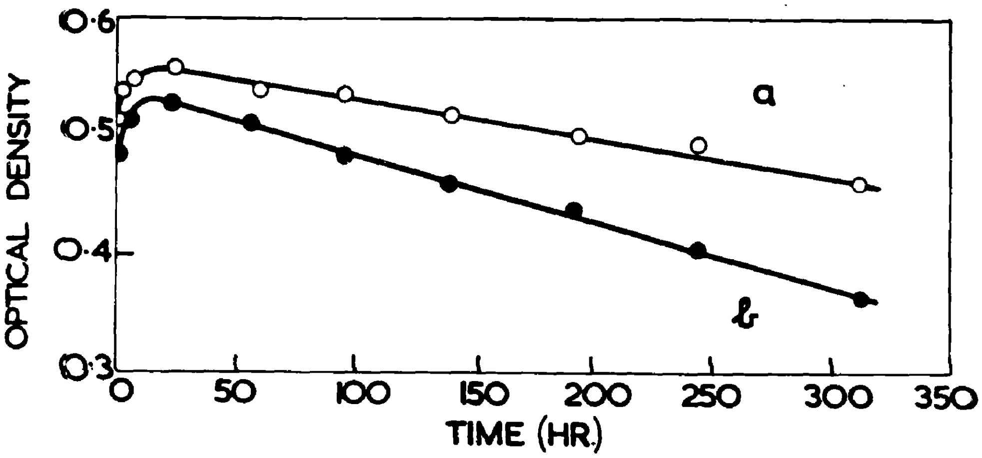


Fig.III.10 Fading rate curves of C.I. Direct Green 26 in Cellophane, (a) at low humidity, (b) at high humidity.

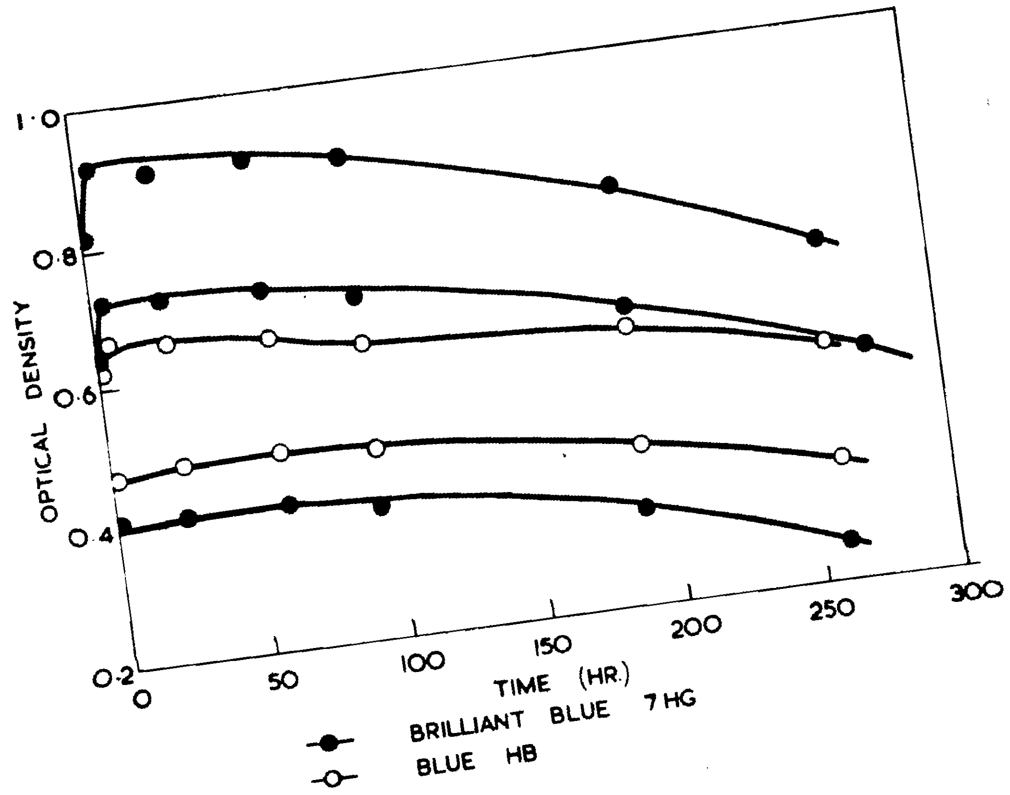


Fig.III.11 Fading rate curves of Procion (I.C.I.) reactive dyes in Cellophane.

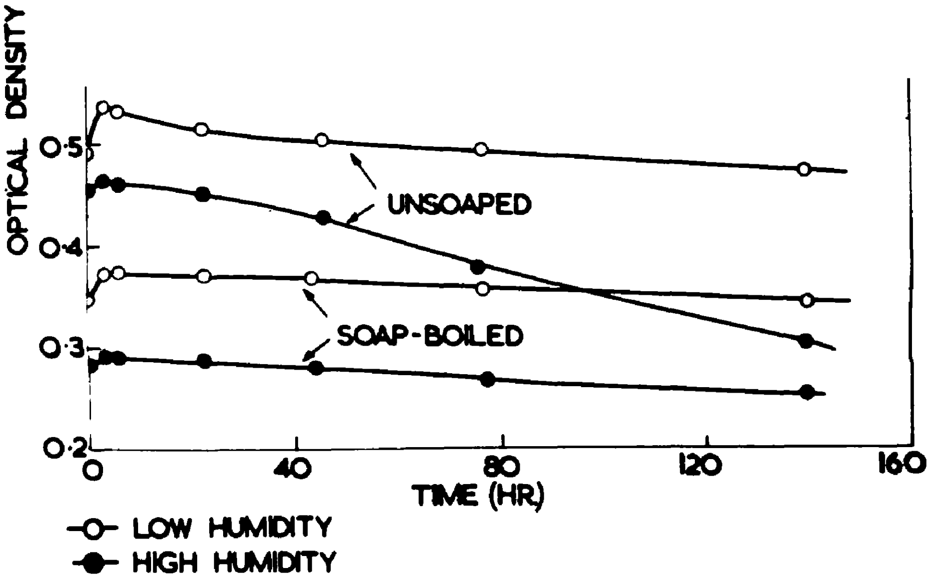


Fig.III.12 Fading rate curves for azoic combinations in Cellophane.

Top: C.I. Azoic Diazo Component 11→C.I. Azoic Coupling Component 4.

Bottom: C.I. Azoic Diazo Component 13→C.I. Azoic Coupling Component 4.

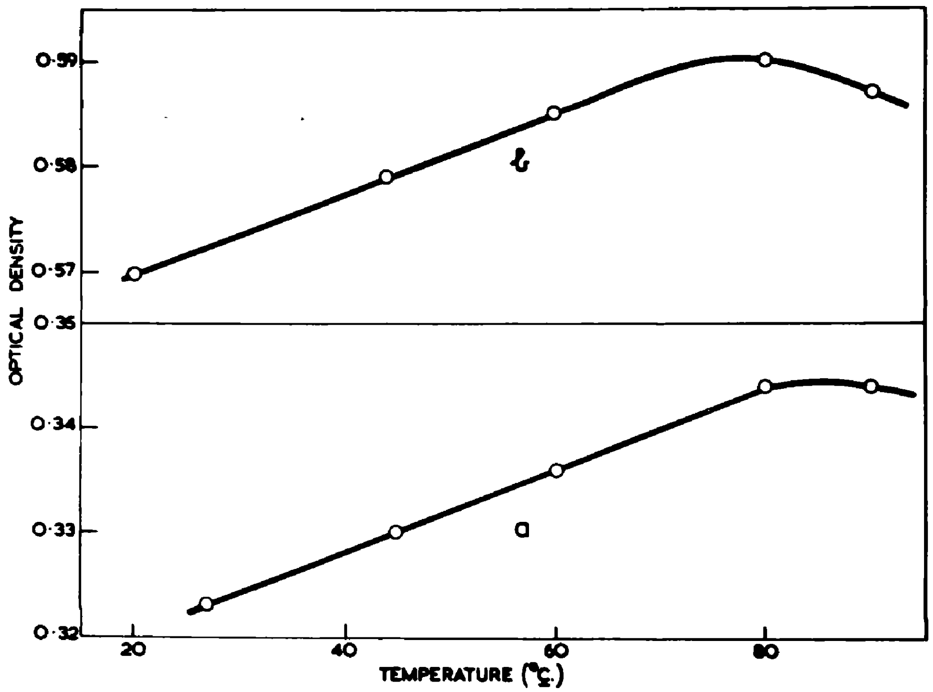


Fig.III.12a Effect of ambient temperature on optical density of aggregated dyes in Cellophane films.

a. C.I. Azoic Diazo Component 13 → C.I. Azoic Coupling Component 4.

b. C.I. Direct Green 26.

Films heated in the dark 20 min. at the given temperature before measurement. Rate measurements showed that the increase in density was in all cases complete in <u>ca</u>.10 min.

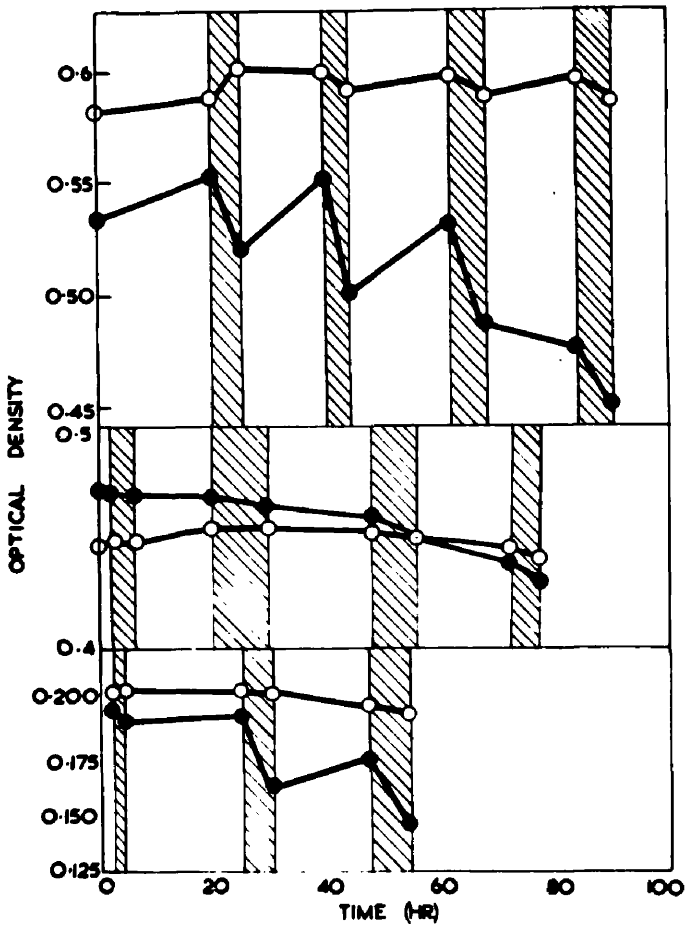


Fig.III.12b Effect on dyed Cellophane fading rates, of alternating irradiation and storage in the dark.

Top: C.I. Direct Green 26 (ca. 55°C.).

Middle: C.I. Direct Green 26 (ca.10°C.).

Bottom: C.I. Azoic Diazo Component 11 → C.I. Azoic Coupling Component 4 (ca. 55°C.).

Hatched areas show times during which the lamp was switched off. Ambient temperatures in parenthesis. Open circles, low humidity; black circles, high humidity.

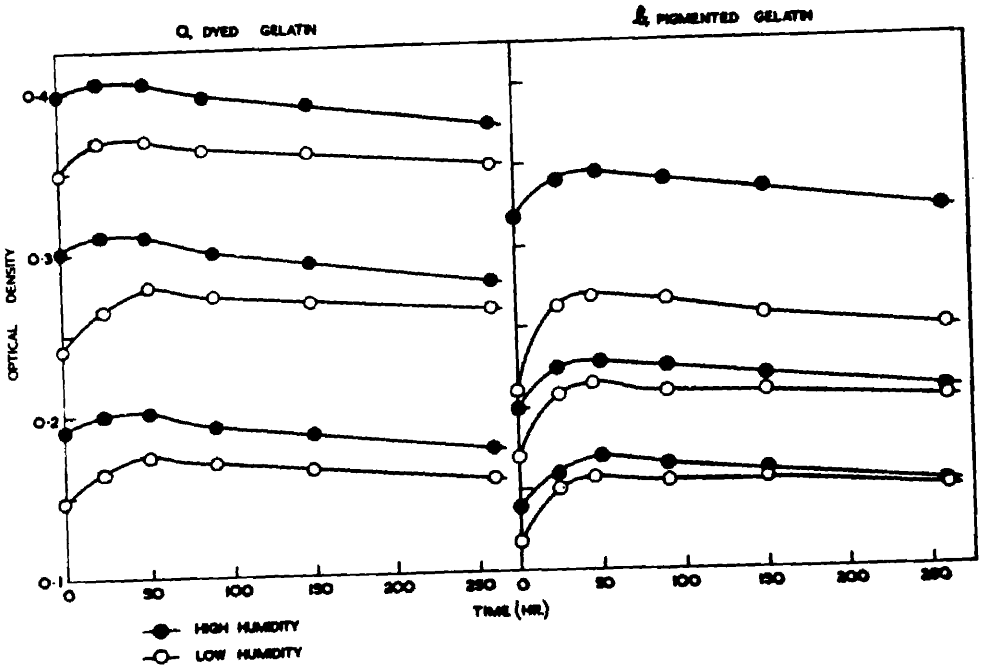


Fig.III.13 Fading rate curves for Microfix Blue - in gelatin, applied by pigmentation or dyeing.

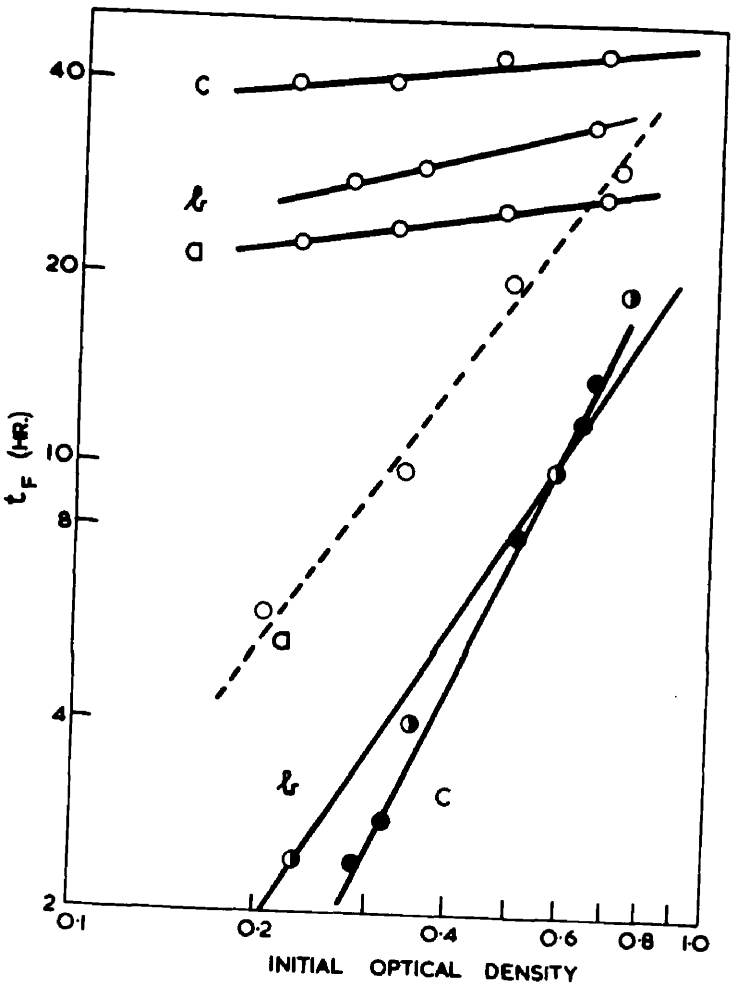


Fig.III.14 CF curves for mordant dyes in gelatin films: (a) untreated, (b) aftertreated with aluminium, (c) aftertreated with chromium.

Top curves: C.I. Mordant Yellow 20.

Bottom curves: C.I. Mordant Red 3 (soluble alizarin).

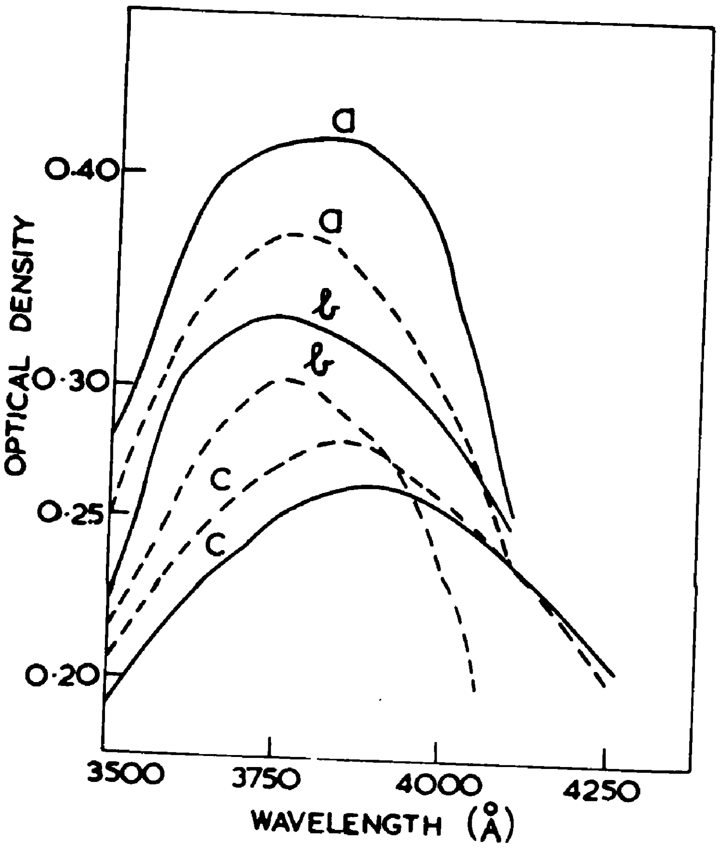


Fig.III.15 Absorption spectra of C.I. Mordant Yellow 20; (a) untreated, (b) aftertreated with aluminium, (c) aftertreated with chromium. Full lines, dye in gelatin films; broken lines, dye in aqueous pyridine extracts (in which aggregation is assumed to be minimised).

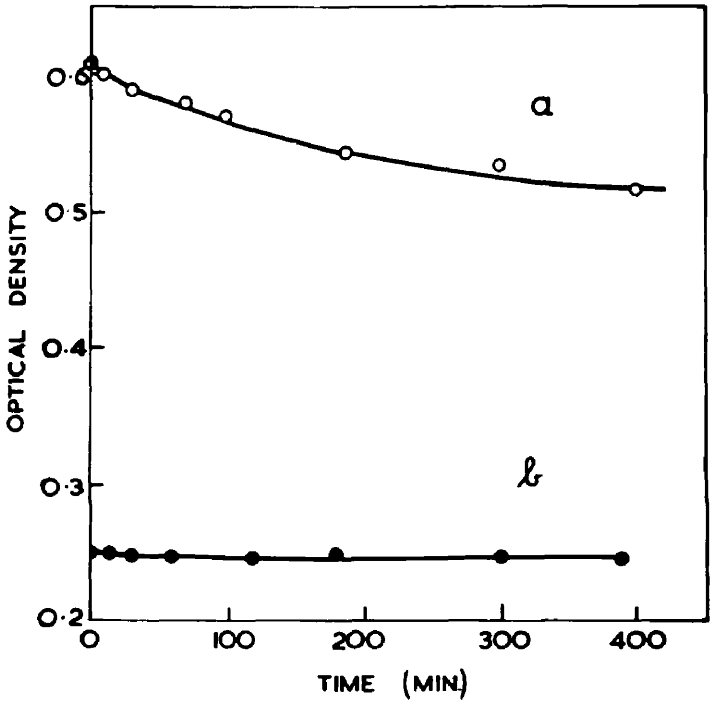


Fig.III.16 Fading rate curves of C.I. Direct Red 173 in Cellophane films, (a) direct, (b) aftercoppered, irradiated at high humidity, and 10°C.

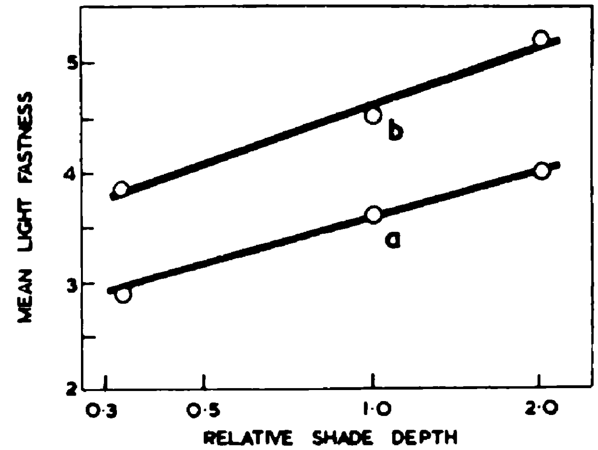
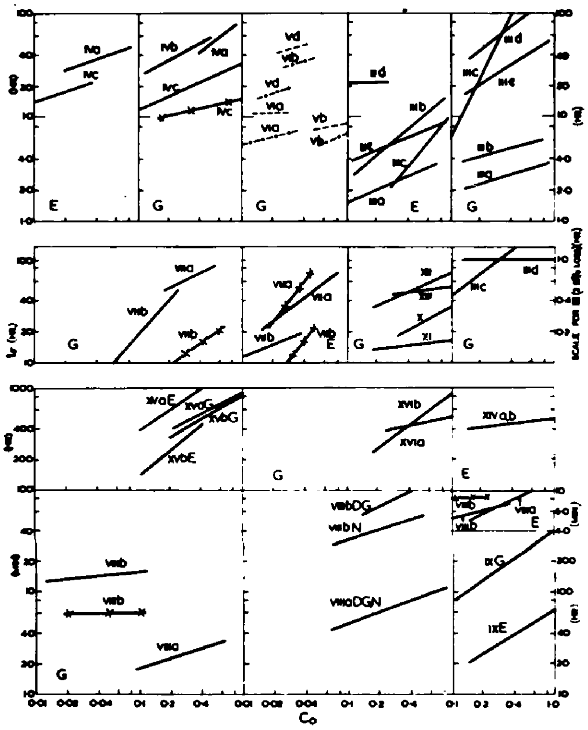
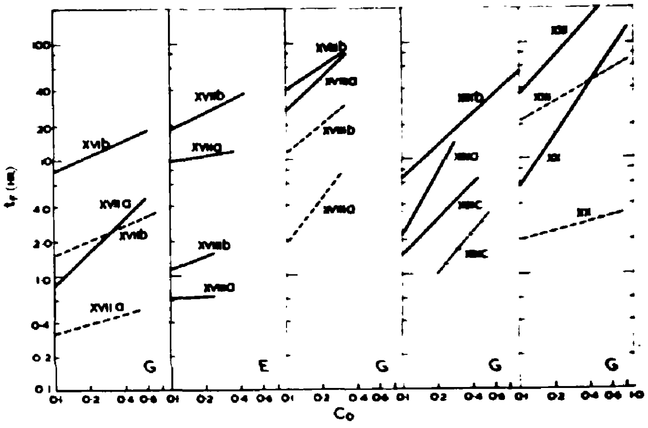


Fig. ~~**6.**~~ III·19a CFG (characteristic fastness grade [12]) curves for (a) "unsymmetrically" and (b) "symmetrically' sulfonated acid dyes on wool. C.I. data: mean values from Table IV. Note: in the *Colour Index* the weakest depths are given as "⅓–½" of the standard. Here they are assumed to be ⅓ of standard depth.



III.17

Fig. ~~2~~. CF curves for azo and anthraquinone dyes in various films. Films: E = ethylmethylcellulose; D = dyed gelatin; G = cast gelatin; N = dyed nylon. xx: CTAB added; –·–·–: low-power m.v. lamp. ----: xenon lamp. All other tests made with 400 w.m.v. lamp; t_r values are for 10% loss of dye, except where shown. All experimental points are omitted, for clarity.



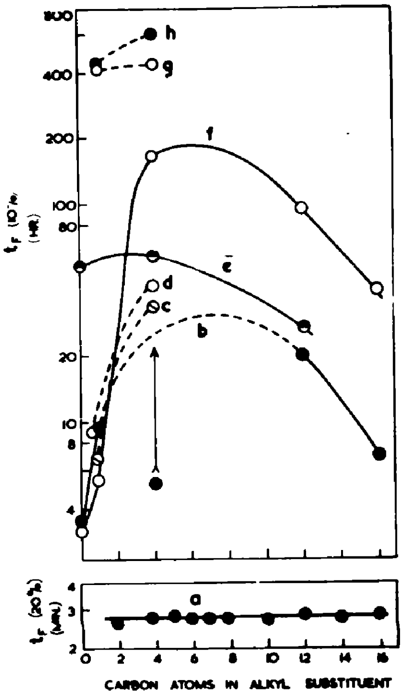
III/18.

Fig. 4: CF curves for azo dyes in ethylmethylcellulose and gelatin. Films: EMC = ethylmethylcellulose; G = gelatin (cast), ---: Curves for 5% loss of dye, ——: Curves for 10% loss of dye, xx: CTAB added. For XVIb, read XVIIb; vertical scale × 10^{-1} for XVIIa, bE.

III.19

Fig. ~~4~~. Relation between length of paraffin chain substituent in dyes and time (t_F) for percentage fade shown: a, nonionic dyes; b–h, sulfonated dyes. Dyes and films. (E = ethylmethylcellulose; G = gelatin). a = I (collodion); b = IIIE; c = VG; d = VIG; e = IVG; f = IIIG; g = XIVE, h = XVIG. t_F values in each series measured at constant C_s values; the shape of these curves will of course vary a little with the particular value of C_s chosen.

→



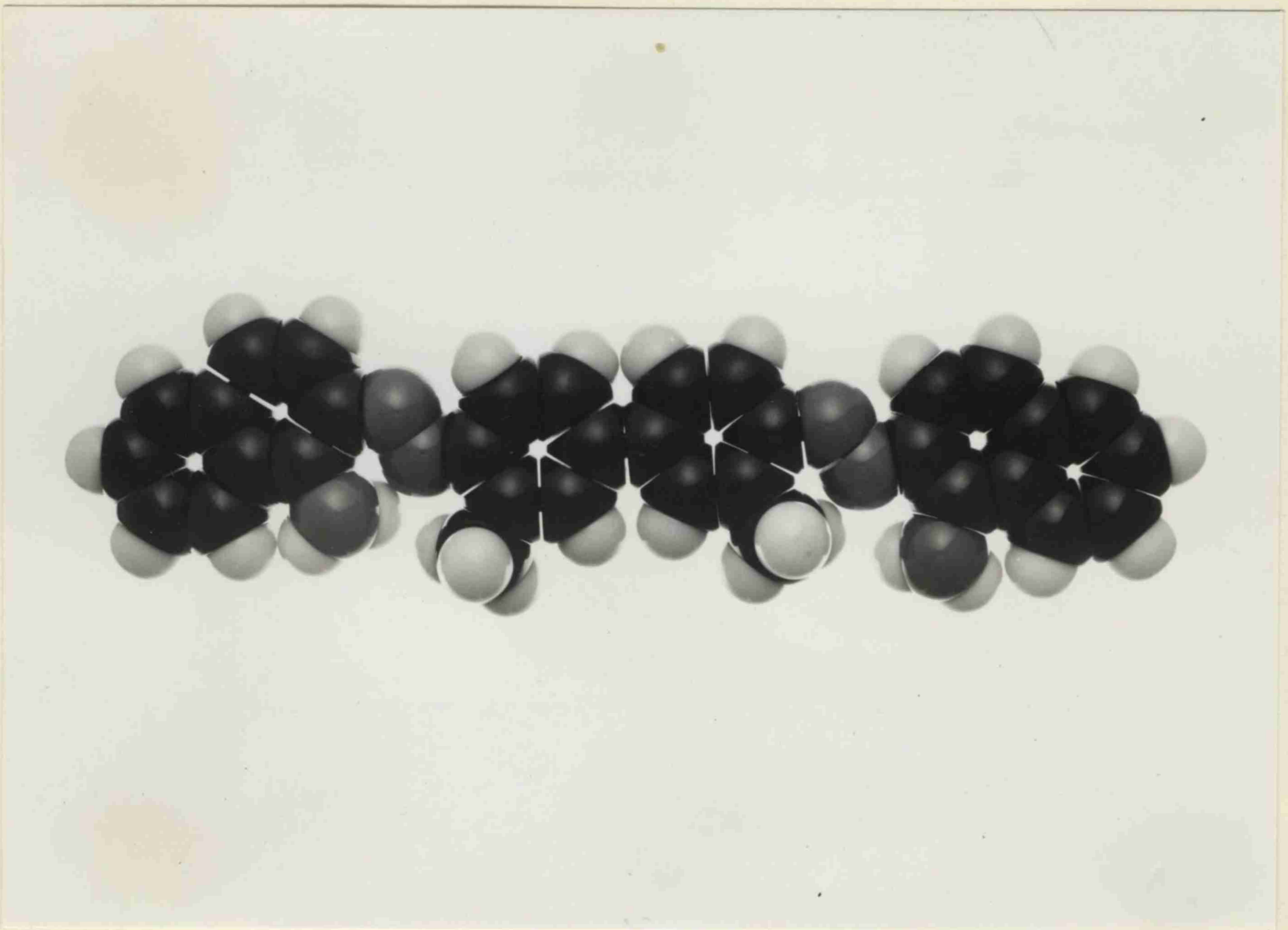


Fig.III.20 Molecular model (without sulphonate groups) of Benzopurpurin 4B (C.I.23500), axial ratio, 3.2; light fastness, grade 1.

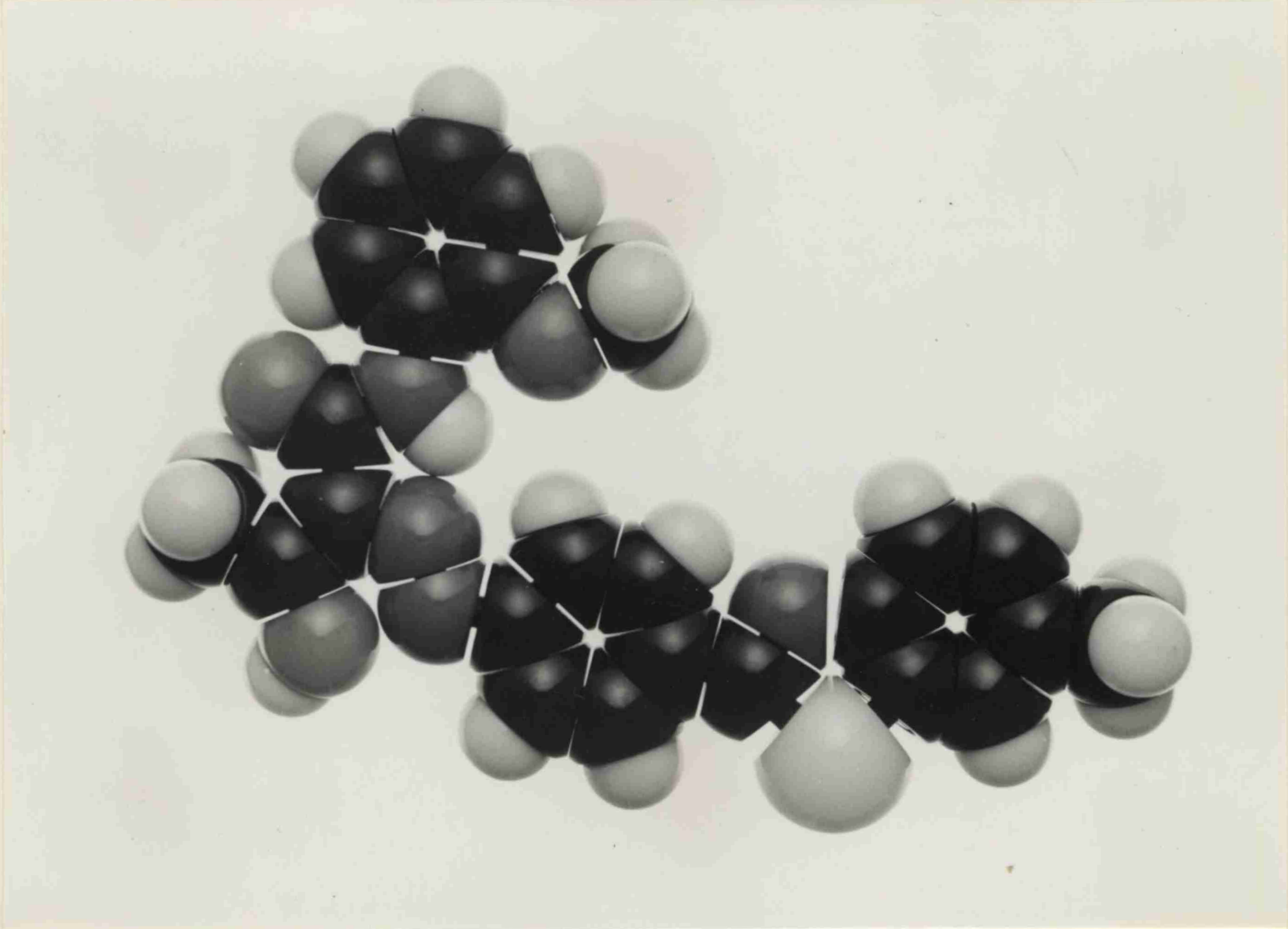
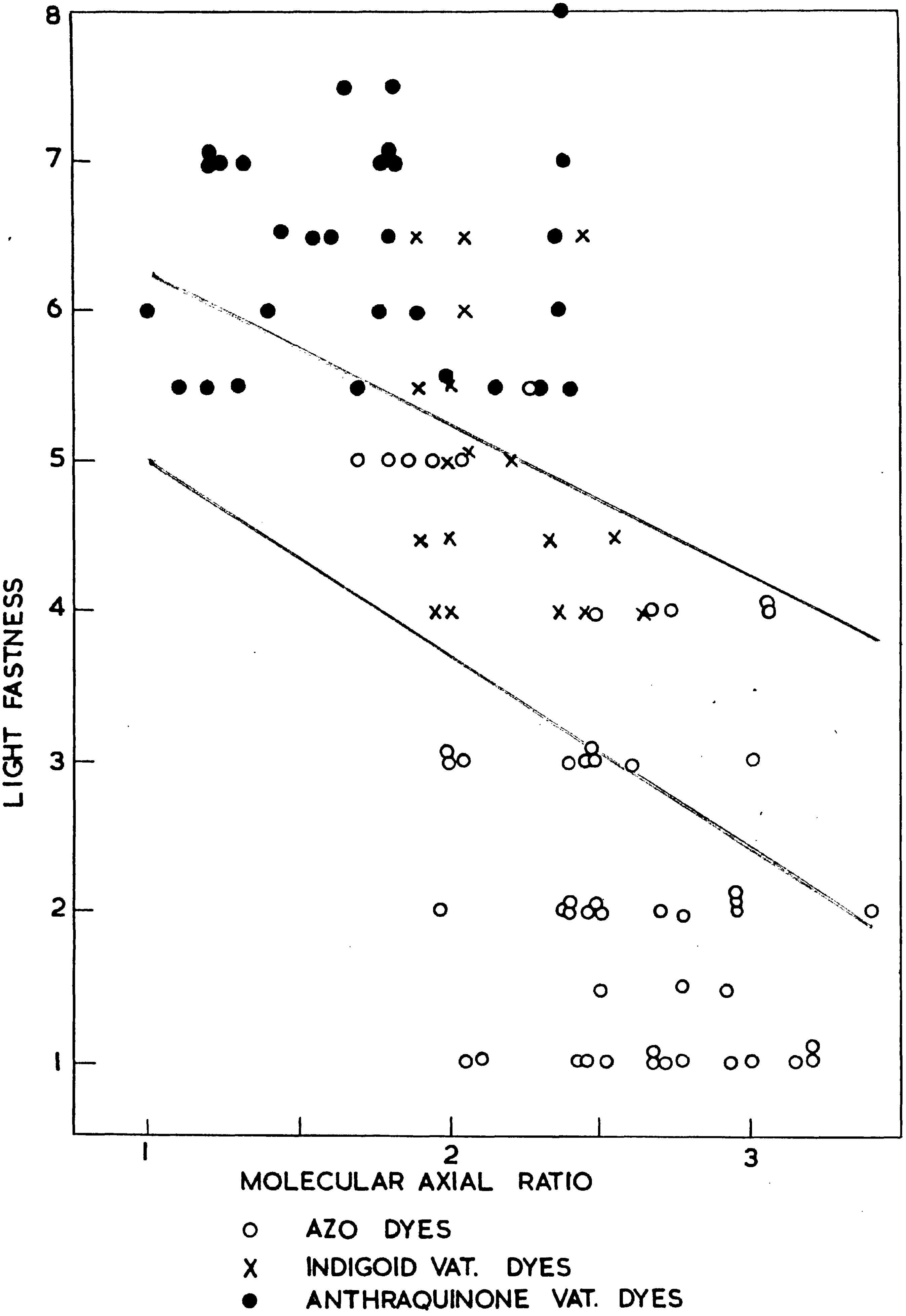


Fig.III.21 Molecular Model (without sulphonate groups) of C.I. Direct Yellow 27 (C.I.13950), axial ratio, 1.6; light fastness, grade 5.

Fig.III.22 Relation between light fastness (standard depth on cotton) and Molecular Axial Ratio of Direct Cotton and Vat Dyes. The least-squares regression lines are shown.


8
7
6
5
4
3
2
1
LIGHT FASTNESS
1
2
3
MOLECULAR AXIAL RATIO
○ AZO DYES
X INDIGOID VAT. DYES
● ANTHRAQUINONE VAT. DYES

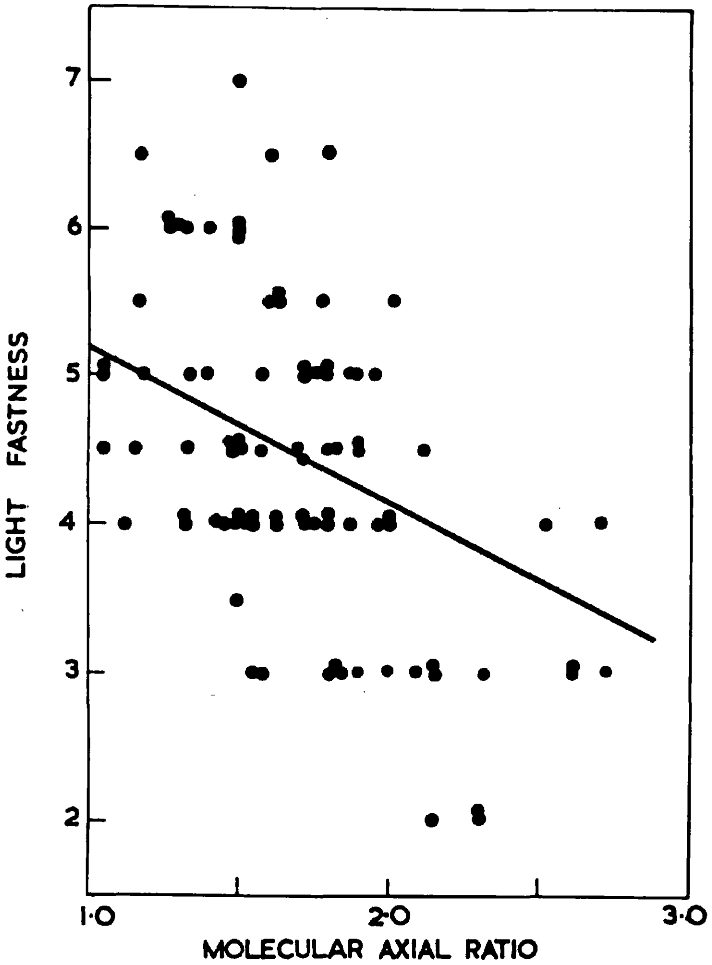
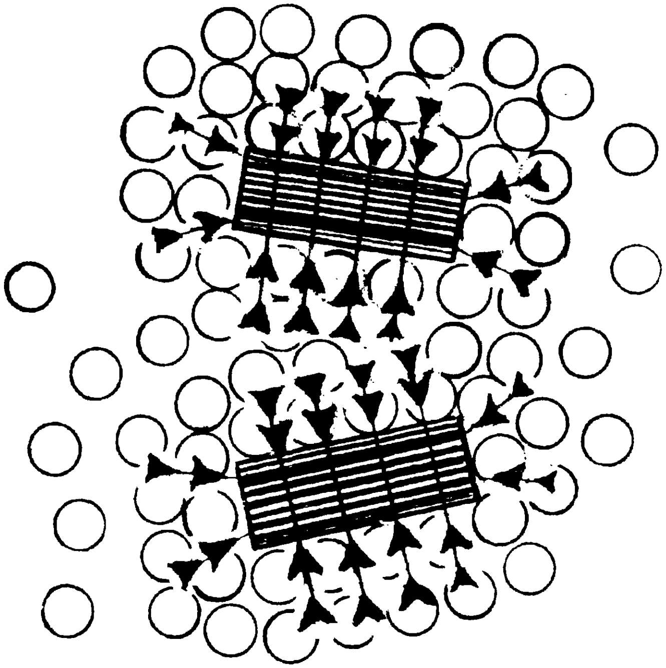
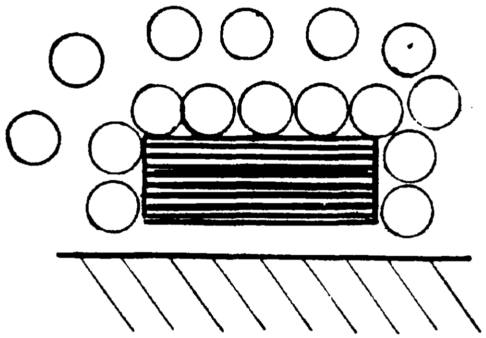


Fig.III.23 Relation between Light Fastness (standard depth on wool) and Molecular Axial Ratio of Monoazo Acid Dyes. The least-squares regression line is shown.

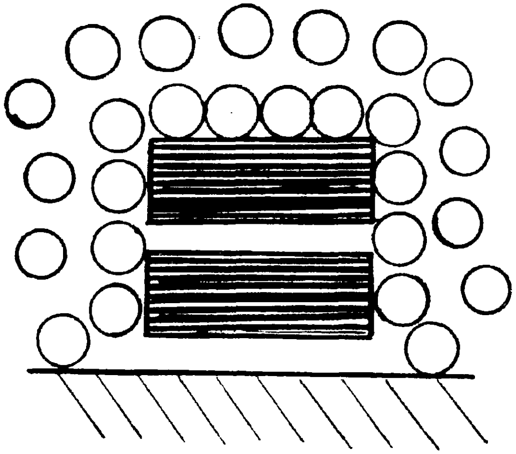
Fig.III.24 Diagram showing how dye molecules may tend to associate when adsorbed at the surface of a solid substrate.
(a) Two dye molecules in dilute aqueous solution are surrounded by layers of solvated water molecules, which are partly held by mutual attraction (shown by arrows) exerted *across* the dye molecule.
(b) A dye molecule adsorbed from solution by a specific attraction at a surface, loses some or all (depending on the nature of the surface) of its layers of solvated water on the side next to the solid. This loss weakens the forces holding the solvated water layers on the outer surface, and therefore a second dye molecule can now more easily associate with the first, as at (c). Thus the substrate acts as a template on which associated dye particles may grow and the form they take will depend more upon the dye-dye force, i.e. upon the geometry of the dye molecule, than upon the nature of the dye-substrate force. This explains the tendency of the regression lines for dyes on cellulose and on wool (Figs2,3) to have the same slope.



a



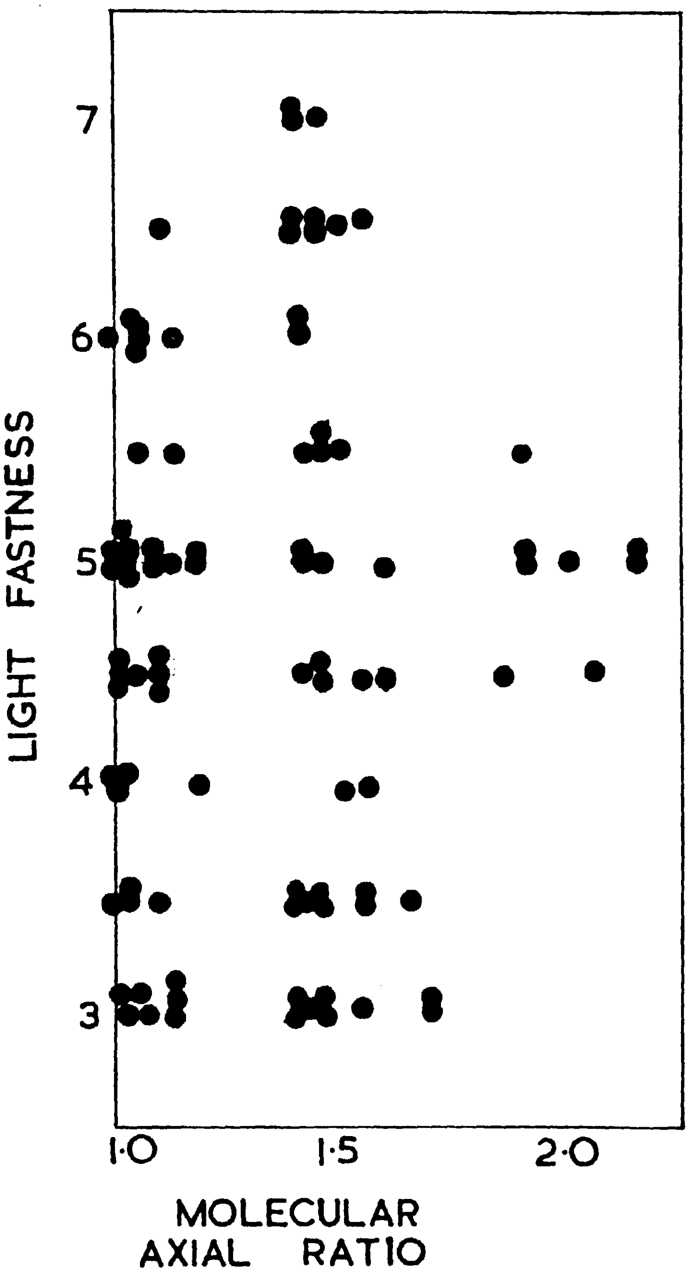
b



c

Fig.III.25 Relation between Light Fastness and Molecular Axial Ratio of Azoic Dyes on Cotton.

Light fastness data from I.C.I. pattern cards. Random selection of eight coupling components, twelve diazo components, all shade depths reduced to equivalent values, based on molecular weights.


7
6
5
4
3
LIGHT FASTNESS
1·0
1·5
2·0
MOLECULAR
AXIAL RATIO

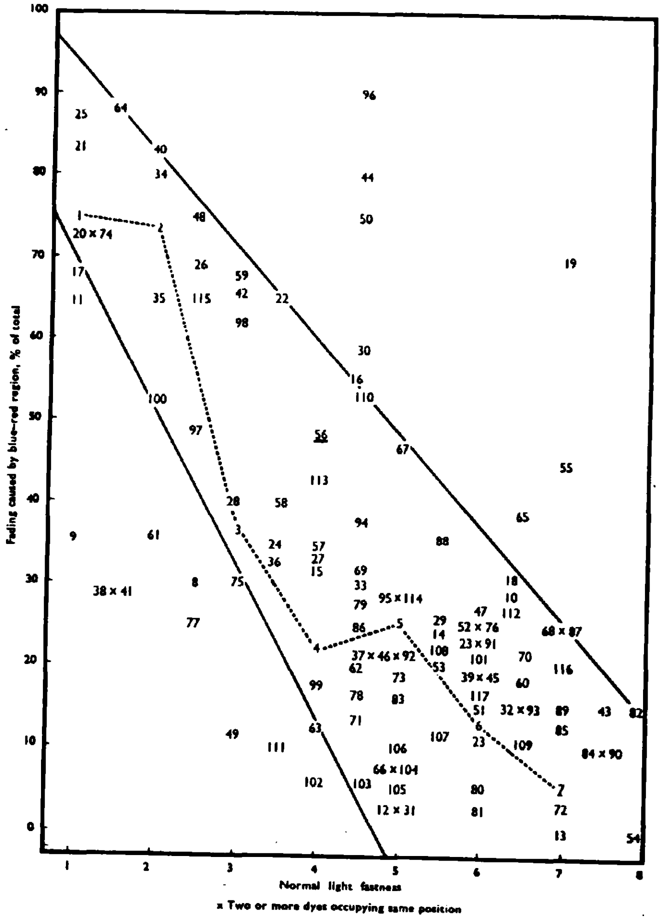
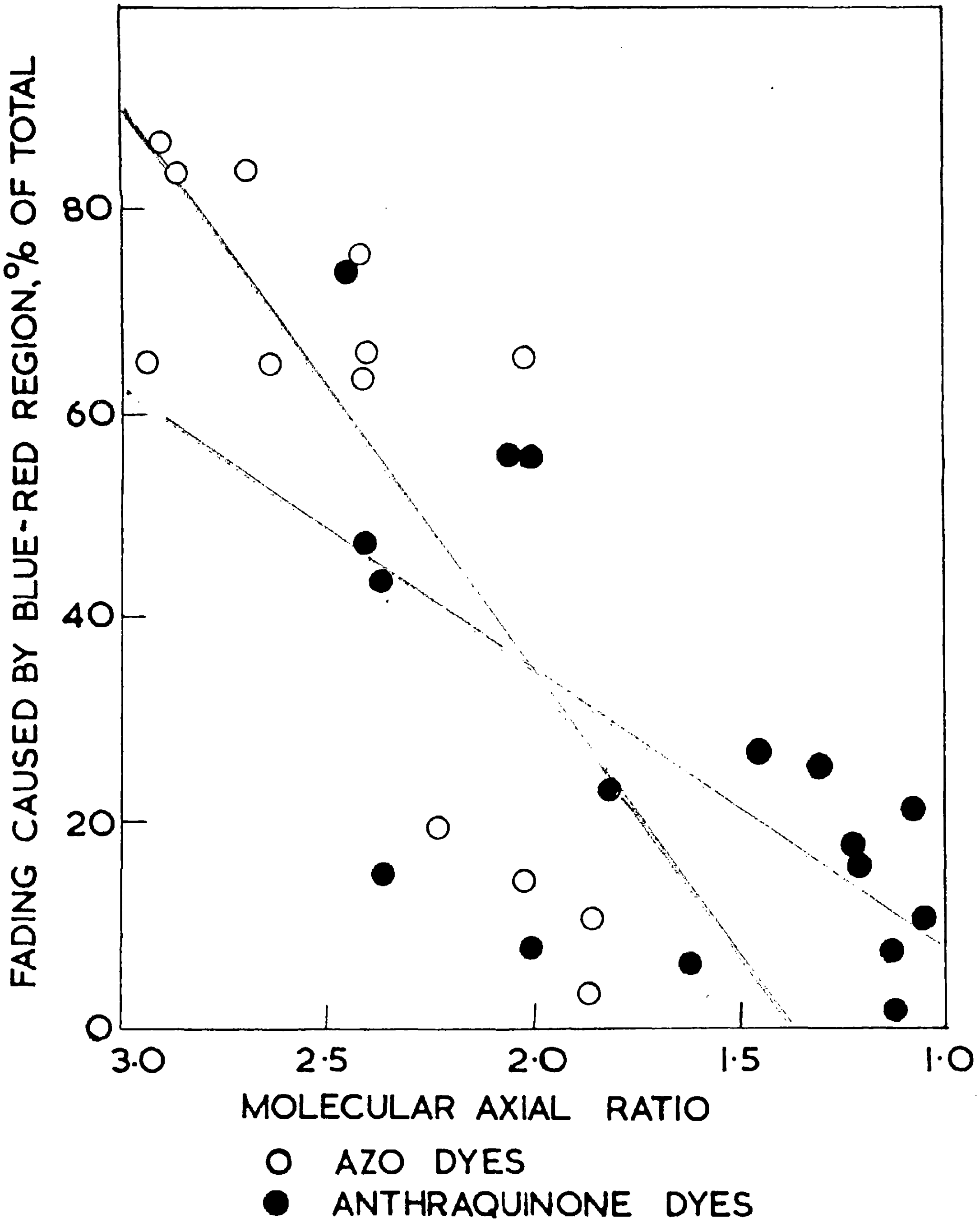


FIG. 5—Effectiveness of the Blue-Red Region as a Function of the Normal Light Fastness

Fig.III.26 Relation between Normal Light Fastness of Dyes and the effectiveness of the Blue-Red Region of the Spectrum in causing Fading. From McLaren, ~~omitting individual points~~, only about 20 out of the total of 117 dyes give points lying outside the shaded band.

Fig.III.27 Relation between Molecular Axial Ratio of Dyes and the Effectiveness of the Blue-Red Region of the Spectrum in causing Fading. (Values for effectiveness taken from McLaren. The least-squares regression lines are shown.


FADING CAUSED BY BLUE-RED REGION, % OF TOTAL
80
60
40
20
0
3·0
2·5
2·0
1·5
1·0
MOLECULAR AXIAL RATIO
○ AZO DYES
● ANTHRAQUINONE DYES