STUDIES IN THE PHOTOCHEMISTRY
OF
DYED PROTEINS AND OTHER RELATED SYSTEMS

by

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Publications

The first part of the work contained in this thesis has been published in the following paper:

> The Influence of the Physical State of Dyes upon their Light Fastness, by G.Baxter, C.H. Giles, (Miss) M.N.McKee, and N.Macaulay, J.S.D.C., 1955, 71, 218-235.

The remainder of the work is being prepared for publication in two papers:

(a) The Influence of the Surface-Activity of Dyes upon their Light-Fastness.

(b) A Study of the Fading Rates of Various Dye-Substrate Systems.

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SUMMARY

The literature on the light fastness of dyes is first reviewed.

In the first part of the present investigation previous work upon the influence of the substrate on the nature of the fading reaction has been followed up; in this, a series of water-insoluble benzene-azo-2-naphthol dyes, substituted in the benzene nucleus <u>meta</u>- and <u>para</u>- to the azo group has been introduced into cast collodion films and faded. The results are discussed, taking account of the sign of the gradient obtained from the curve of relative fading rate <u>versus</u> the Hammett σ- value of the substituent group in the dye. The results agree with those previously reported, and in addition, show much less random error. The main source of error appears to be the non-uniform physical state of the dyes in the substrates.

The influence of the physical state of the dye has next been investigated, with reference to a theoretical model system, developed on the basis of observations made upon the fading of certain water-insoluble dyes in markedly different states of dispersion in solid substrates. The model system has been applied to tests on water-insoluble dyes and allows logical explanation to be given for all observed effects. Its application has been extended to the case of water-

soluble dyes on solid substrates and it would seem from the data obtained that these dyes are also present in the fibre as discrete, sub-microscopic particles or aggregates, the size and nature of which are dependent upon the physical characteristics of the dye:substrate system.

In the final section of the work the influence of the surface activity of dyes upon their light fastness has been studied, alterations in the surface activity being produced by changes in the size and form of the hydrophobic residues and the position of the ionic groups in the dyes. It has been concluded that the position of these groups in the dye molecule can affect the light fastness, by virtue of its influence upon the physical form which the dye assumes when the substrate is dried out. This suggestion is supported by the agreement shown with the predictions of the theoretical model for heterogeneous dye systems. In particular, dissymmetric dye molecules, which are believed to form monolayers most readily, have been observed to give relatively rapid fading.

CONTENTS

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INTRODUCTION

The light fastness of a dye is not an absolute property: it depends further on the medium to which it has been applied. In relation to textiles, it is well known that the same dye may exhibit considerable differences in fastness properties according to the nature of the fibre which is dyed, and various other factors in the surroundings in which dyes are normally employed. These factors include the presence of moisture, air and the impurities therein, the nature and intensity of the illumination, the nature of the substrate, and the physical state of both the dye and the substrate.

The work of the present thesis has been concerned mainly with the influence of the physical state of the dye in the substrate on the light fastness, and, to a lesser extent, with the influence of the substrate on the fading reaction.

The available literature on light fading has been surveyed and is summarised below, emphasising particularly the fading of dyes under practical conditions.

THE MECHANISM OF LIGHT FADING.

The absorption and dissipation of light energy.

Photochemical reactions usually differ from thermal ones in that the energy of activation is wastefully employed, the energy needed for thermal activation rarely being large enough to raise the molecules to electronically excited levels, through which mechanism photochemical activation always proceeds. These latter reactions are initiated by the absorption of light energy in the high intensity regions of the spectrum of the absorbing substance, corresponding to the "permitted" transitions between singlet levels. Bowen has suggested that, in addition, the excited singlet level may pass on to a triplet level which may be chemically more reactive and have a much longer mean life-time than the excited singlet level. He further pointed out that the very low quantum yield of a photoreaction such as that of dye fading (10^{-6}) may quite possibly be due to the low probability of such a "forbidden" transition taking place rather than to the very short life of the excited singlet level. Lewis has also considered the direct transition from singlet ground level to triplet level.

The light energy absorbed by, let us say, a dye-molecule may be re-emitted as resonance or fluorescence radiation;

the electronic energy may be degraded by collisional or other processes into heat energy; or the excited molecule may enter into chemical reaction or may dissociate. Bowen has presented a number of formal schemes to explain these latter "electron transfer" reactions.

The dye molecule D^{x}, either in the excited singlet level or in the triplet level, may react with either reducing agent A and/or oxidising agent B to give the corresponding reduced D^{-} or oxidised D^{+} dye-radical ion, thus:-

$$D^{x} + A \longrightarrow D^{-} + A^{+}$$

$$D^{x} + B \longrightarrow D^{+} + A^{-}$$

The existence of free radicals in the form of dye molecules rather than H atoms or OH radicals has been demonstrated by Hillson and Rideal who detected their presence by the polymerisation of methylmethacrylate present in the dye solution, on illumination and to some extent even in the dark.

A dismutation reaction may occur,

$$D^{x} + D \longrightarrow D^{+} + D^{-}$$

and the ions so formed may react further to give a semiquinone ionisation,

$$D^{-} + H^{+} \longrightarrow DH$$

or, reformation of the dye, either

$$D^- + B \longrightarrow D + B^-$$

$$\text{or} \quad DH + D^+ \longrightarrow 2D + H^+$$

$$\text{or} \quad DH + O_2 \longrightarrow D + H^+ + O_2^-$$

$$\longrightarrow D + HO_2 \longrightarrow H_2O_2$$

$$\text{or} \quad DH + A^+ \longrightarrow D + H^+ + A$$

$$\text{or} \quad D^+ + A \longrightarrow D + A^+$$

Destruction of the dye may take place with the formation of oxidation products,

$$D^+ + O_2 \longrightarrow \text{oxidation products,}$$

and the ions formed other than dye ions may also react with each other to form further stable oxidation products, thus:-

$$\begin{tikzcd}
A^+ + H_2O_2 \arrow[dr] & \\
A^+ + O_2 \arrow[r] & \text{oxidation products.} \\
B^- + O_2 \arrow[ur] &
\end{tikzcd}$$

Two or more of these reactions can take place simultaneously, depending on extraneous conditions such as the nature of the substrate, leading, as in the case of the more complicated dyes, to a complexity of final fading products. The successful separation and identification of these fading products would not, in all probability, elucidate entirely the mechanism of fading, as any attempt to name the unstable intermediates could only be hypothetical.

The evidence of oxidation in light fading.

The evidence of oxidative light fading of dyes on cellulose and related materials is considerable, outweighing the available data wherein fading takes place by reduction. Haller and Ziersch, for example, obtained oxidation products from the fading of insoluble monoazo dyes on cotton, Hibbert obtained isatin from indigo faded on cotton, whilst, more recently, Couper identified by chromatography a variety of oxidation products from the fading of 1:4-bis(methylamino)-anthraquinone on cellulose acetate. It was observed by Harrison that in sunlight or low intensity ultraviolet light the fading of Methylene Blue on cotton was an oxidative reaction and that a number of dyes did not fade in sunlight when exposed in evacuated or nitrogen-filled glass tubes. Gebhard and Lazarev and many other investigators have also shown that fading does not occur in absence of air or oxygen, though this does not necessarily prove that fading is an oxidative process. The observations that oxidising agents act as sensitisers in light fading (presumably on cellulosic substrates), and that reducing agents, or the decomposition products formed by irradiation, act as restrainers, led Mounier to suggest that azo dyes are oxidised during fading. He noted further that the products of oxidation of azo-dyes by hydrogen peroxide or other oxidising agents gave colour reactions with various reagents, similar to those given by the products of azo-dye fading.

Desai and Giles have also pointed out the increased light fastness imparted to azo dyes on cellulose by nitro- and chloro-substituent groups, which also increase their resistance to oxidation. Other workers, e.g. Pinte and Miller, Atherton and Seltzer, and later, Atherton and Peters, also confirmed the beneficial effects of these groups on light fastness, and the adverse effects of electropositive groups, as, for example, methoxy and methyl groups.

It has been reported by Mudrovic that the polymethin dyes such as pynacyanol or pinachrome bleach much more readily in the presence of sensitisers, such as Methylene Blue, than in their absence. The Methylene blue is reduced to the leuco form and according to Mudrovic the pynacyanol is oxidised. Marney records that, after exposing wet patterns to arclight, certain vat blue dyes changed shade in the direction of their oxidation products, the original shades being restored by a weak reducing agent.

The evidence of reduction in light fading.

That cellulose is oxidised to oxycellulose by shortwave ultraviolet light was demonstrated by Harrison. The reaction is accelerated by the presence of certain dyes, e.g. Benzo Violet, Diamine Sky Blue FF (C.I.No.518), and Methylene Blue, even in vacuo, and the dyes are simultaneously faded, apparently by reduction. Indigo (C.I.No.1177) and Crystal Violet (C.I.No.681) were not faded in this way. In other experiments it appeared also that nitro-groups in aromatic compounds suffered reduction in u.v. light in presence of cotton, but that amino-groups were oxidised. Van Nostrand and Stillings later showed that, on exposure to shortwave ultraviolet light, cellulose was considerably degraded both in a nitrogen atmosphere and to a greater extent in an oxygen atmosphere with a consequent drop in the degree of polymerisation and α-cellulose content, and liberation of carbon monoxide and carbon dioxide.

By the Grotthus-Draper law, only light which is absorbed by a substance can cause decomposition. Cellulose shows strong absorption of shortwave u.v. light ($<$ 2000 A)(Kujirai) and it must be this absorption which causes the marked photochemical oxidation of the fibre under the above conditions. Its absorption of longer wave radiations is very weak or nil, so that in sunlight or longwave u.v. radiation little direct photochemical degradation of the fibre, or consequent reduction of the dyes thereon, should occur, and oxidation of dyes should predominate in fading. Indeed, Harrison noticed this when using Methylene Blue. There is, nevertheless, some evidence that reduction can occur even under normal exposure conditions.

Mounier, and Seyewitz and Mounier found that certain nitrohydrocarbons were decolourised when irradiated on cotton, silk or wool. This reaction was found to be sensitised by reducing agents and inhibited by oxidising agents, and it was attributed to reduction to azoxy and hydroxyazo compounds, at least on cotton, from which fading products were isolated, but not definitely characterised. It was suggested that subsequent fading might be due to oxidation of the latter. The reduction was considered to take place at the expense of the fibre itself and of some of the nitro compound. Neuweiler studied the photochemical bleaching of a large number of dyes in the presence of zinc oxide and Eosin, both of which sensitised the reduction of the dyes to an extensive degree. In the presence of "anodic depolarisers" such as cane sugar or glycerine, the dye Victoria Blue becomes reduced to the <u>leuco</u> form on exposure if either zinc oxide or Eosin is present, these last suffering no change. Azo dyes become irreversibly reduced to amines under analogous conditions. Thus photochemical reduction rather than oxidation takes place. Gelatin may take the place of the anodic depolariser.

In their work on the fading of aminoazo dyes on cellulose acetate, Atherton and Seltzer attributed the fading reaction to oxidation, but Atherton and Peters noted that dyes containing any one of three particular substituents, viz., m-NO_2, p-NO_2 or p-$COCH_3$ had anomalously low light fastness which they attributed to these groups being partially reduced to give compounds more fugitive than the originals, as a first step in fading.

Blaisdell obtained aniline and hydrazobenzene as final fading products on irradiation of azobenzene in iso-octane, hydrazobenzene being a likely intermediate product to expect in the reduction of azobenzene to aniline. With 4-amino-4′-nitroazobenzene in isopropyl alcohol the products obtained were aniline, p-phenylenediamine and acetone, the expected products of reduction of the dye and oxidation of the solvent, respectively. Whether reduction takes place first at the nitro-group or at the azo group has not been settled. The reaction is assumed to follow a free radical mechanism, the excited dye in each case reacting with the solvent to give a reduced-dye free radical, which further reacts with the solvent to give the substituted hydrazine, the probable first stable product in the photoreduction of an azo dye to its substituted amine.

In light of wavelength >3400 A (sunlight or mercury vapour light behind glass), which must be quite unabsorbed by pure cellulose, some photolytic degradation of undyed cotton takes place in air or oxygen (Egerton 1947). This has been attributed either to the presence of light absorbing impurities or to an initial thermal oxidation whereby small numbers of aldehyde or carboxylic acid groups are introduced into the cellulose chain. These will absorb radiation at longer wavelengths and so may be photolytically degraded, thereby initiating a chain reaction involving other parts of the molecule. Certain polymers can undergo photolytic degradation in light which they do not normally absorb, by a mechanism of this type (Burgess). Egerton's observation that the extent of degradation of cotton behind glass is negligible in absence of oxygen supports this explanation.

Even if the dye itself is not a photolytic sensitiser some photolytic degradation of dyed cellulosic fibres may occur in normal sunlight, producing reducing substances (Harrison), and thus accounting for the reduction of nitro-groups in aromatic compounds when faded on such substrates.

It does not appear that the fading of dyes by reduction on substrates other than cellulosic, e.g., proteins, has been observed. Potassium dichromate, however, is reduced to chromic salts when irradiated in gelatin , which is itself insolubilised. Biltz and Eggert found that the quantum yield of ammonium chromate converted to an insoluble form by radiation of 4360 A is 0.5 and that for the amount of gelatin rendered non-swelling is 0.3. This means that two molecules of gelatin react with one molecule of insoluble chromic chromate to give a non-swelling adsorption complex. The hydrogen for reduction was assumed to come from the gelatin. These high values, compared with those normally obtained in dye fading, may mean that the mechanism of energy dissipation by the excited chromate ion is much less efficient than that of a dye molecule.

The nature of the fading agent.

Although hydrogen peroxide is known to be produced in some circumstances when dyes are irradiated, little precise information is available upon the nature of the chemical species responsible for the oxidation or reduction of any type of dye in fading. Thus, it is formed on irradiation of aqueous solutions of certain dyes, e.g., Eosin (C.I.No. 768) and Fluorescein (C.I.No.766) in air (Blum and Spealman), and by irradiation of aqueous serum albumin solution at 2536 A. Only in the special case of photolytic sensitisation of cellulose has hydrogen peroxide been identified as a fading agent.

On irradiation of Acriflavine (C.I.No.790), dispersed on dry silica dust in dry oxygen at low pressure, a volatile oxidising agent was formed capable of oxidising <u>leuco</u>-Malachite Green, and which was suggested to be a metastable form of oxygen formed by transfer of energy from the excited dye to oxygen of the air (Egerton). The dye was found not to form hydrogen peroxide on irradiation (Kautsky et al.).

Cellulose is readily tendered by visible and near ultraviolet light in presence of the so-called photolytic sensitisers. The most familiar compounds of this type are certain vat dyes and the tendering action they exert on cellulose and their catalytic effect in fading other accompanying dyes, in presence of light and air, has been the subject of considerable investigation. (Egerton; Scholefield and Patel; Lanigan). The same effect is obtained in presence of zinc oxide or titanium dioxide, which absorb near ultraviolet light, and all these tendering substances, whether dyes or white pigments, form hydrogen peroxide when irradiated in aqueous suspension. The attack on the cellulose fibre itself (above 3400A.) has been shown to be due to hydrogen peroxide and/or activated oxygen, originating probably in this way, and this attack can extend to undyed fibre placed very close to, but not in contact with, the irradiated dyed material (Egerton).

Other dyes, particularly basic and sulphur dyes and the thiazole direct dye Primuline (C.I.No.812) can also act as photolytic sensitisers for cellulose but the azo direct cotton dyes appear to have no sensitising action; in fact they tend to decrease the activity. Insoluble azo dyes show similar inactivity (Ashton, Clibbens and Probert), although Ashton and Probert have recently shown in more extensive tests that insoluble azo dyes on cotton do, in fact, show tendering activity, but of a much lower order than that associated with active vat dyes. In both classes of dye there was observed to be a close statistical correlation between extent of fading and tendering. Both effects are increased by an increase in relative humidity. A complex relation was also observed between degradation by certain vat dyes and relative humidity, suggesting that at least two different factors may be responsible, each affected in a different manner by humidity.

Bamford and Dewar compared the tendering activity of vat dyes on cellulose with their ability to photosensitise the auto-oxidation of tetralin. They concluded that the tendering action is caused by the intermediate formation of hydrogen peroxide, and have suggested that the primary step is the oxidation of the hydroxyl ion by excited dye:-

$$D^x + OH^- \longrightarrow D^- + OH$$

because both tendering and hydrogen peroxide formation had been shown to be promoted by alkali (Egerton). The low quantum yields would be explained by primary recombination of $\underline{D}^-$ and $\underline{OH}$. The hydroxyl radicals might oxidise the cellulose directly, or by first combining to form hydrogen peroxide. In absence of water the initial reaction might be:-

$$D^{x} + \text{Cell-H} \longrightarrow DH + \text{Cell}^{x}$$

(where Cell-H represents Cellulose). Since the dye and cellulose cannot diffuse apart, they can recombine more readily. Tendering could be supposed to be due to:-

$$\text{Cell}^{-} + O_2 \longrightarrow \text{Cell}.O_2^{-}$$

$$\text{Cell}.O_2^{-} + DH \longrightarrow \text{Cell}.O_2H + D^{-}$$

followed by breakdown of the cellulose peroxide. No hydrogen peroxide is detectable under dry conditions (Egerton). This mechanism could account also for the observed tendering of cellulose acetate and nylon which are stable to hydrogen peroxide, and the greater degree of tendering of nylon could be accounted for by the point of attack being hydrogen atoms on carbon atoms adjacent to a carbonyl group. This would break the molecular chain of nylon, but not that of cellulose acetate.

The nature of the fading reaction.

A considerable amount of discussion has been devoted to the actual mechanism by which dyes break down under irradiation, but much of it is speculative and inconclusive, though the consensus of opinion seems to be that some form of activated oxygen or a free radical derived from water or hydrogen peroxide is involved. Hillson and Rideal, who measured the photocurrents produced by illuminating a platinum electrode coated with adsorbed dyes of the azo and triphenyl methane classes and immersed in aqueous solutions, observed that either oxidation or reduction of dye can occur according to the experimental conditions. The two reactions are quite different and may proceed independently of one another. The dye was found to be reduced only when in immediate contact with the electrode, but oxidation could occur even at some distance therefrom, in the bulk of the solution or contained in a film coating on the electrode.

The authors concluded that reduction took place by direct transfer of an electron from the electrode to the excited dye molecule:-

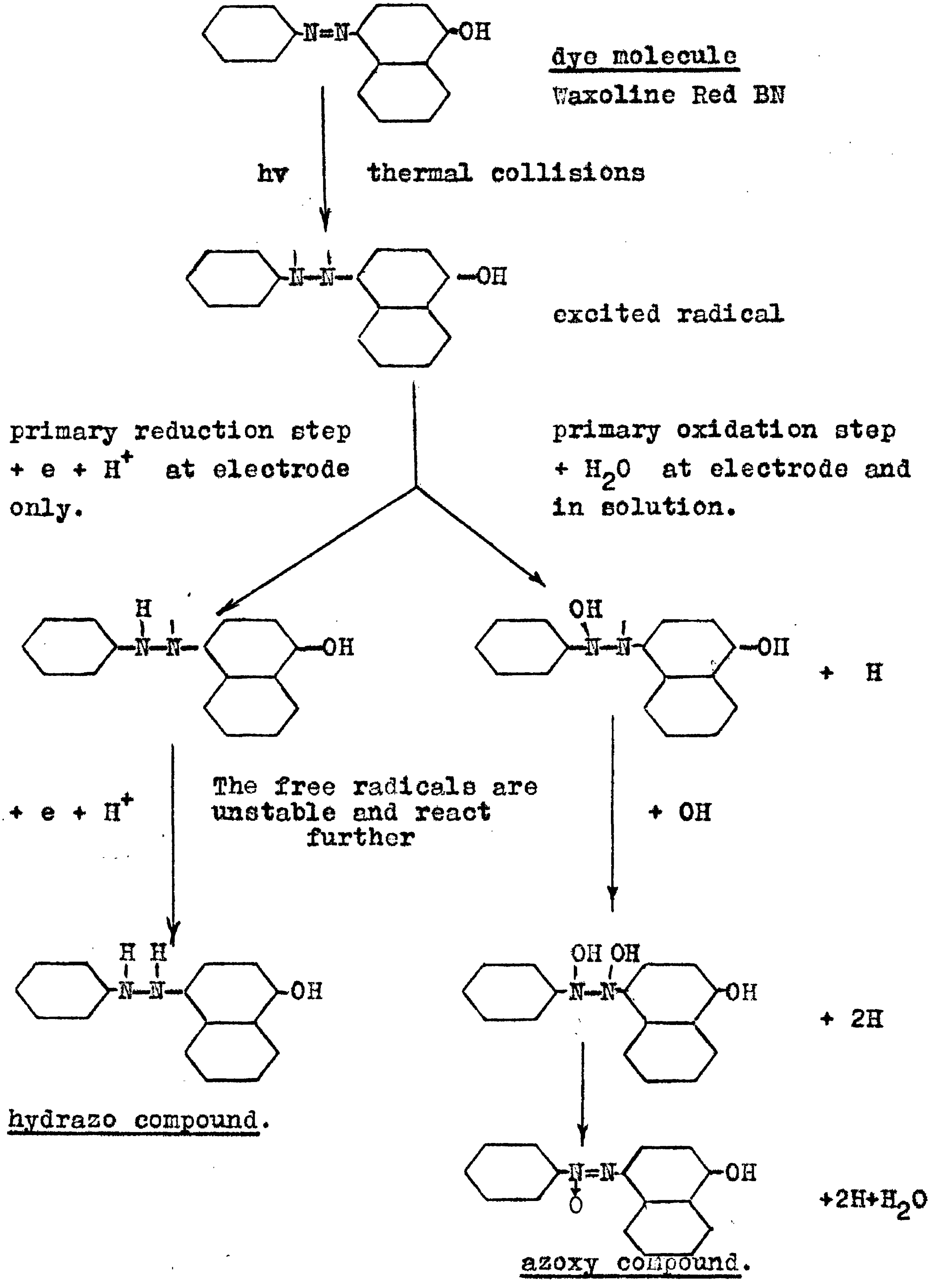
$$D^{x} + H^{+} + e \longrightarrow DH-$$

Oxidation, however, followed a quite different course, the dye reacting with either hydroxyl ions or water molecules in the bulk of the solution:-

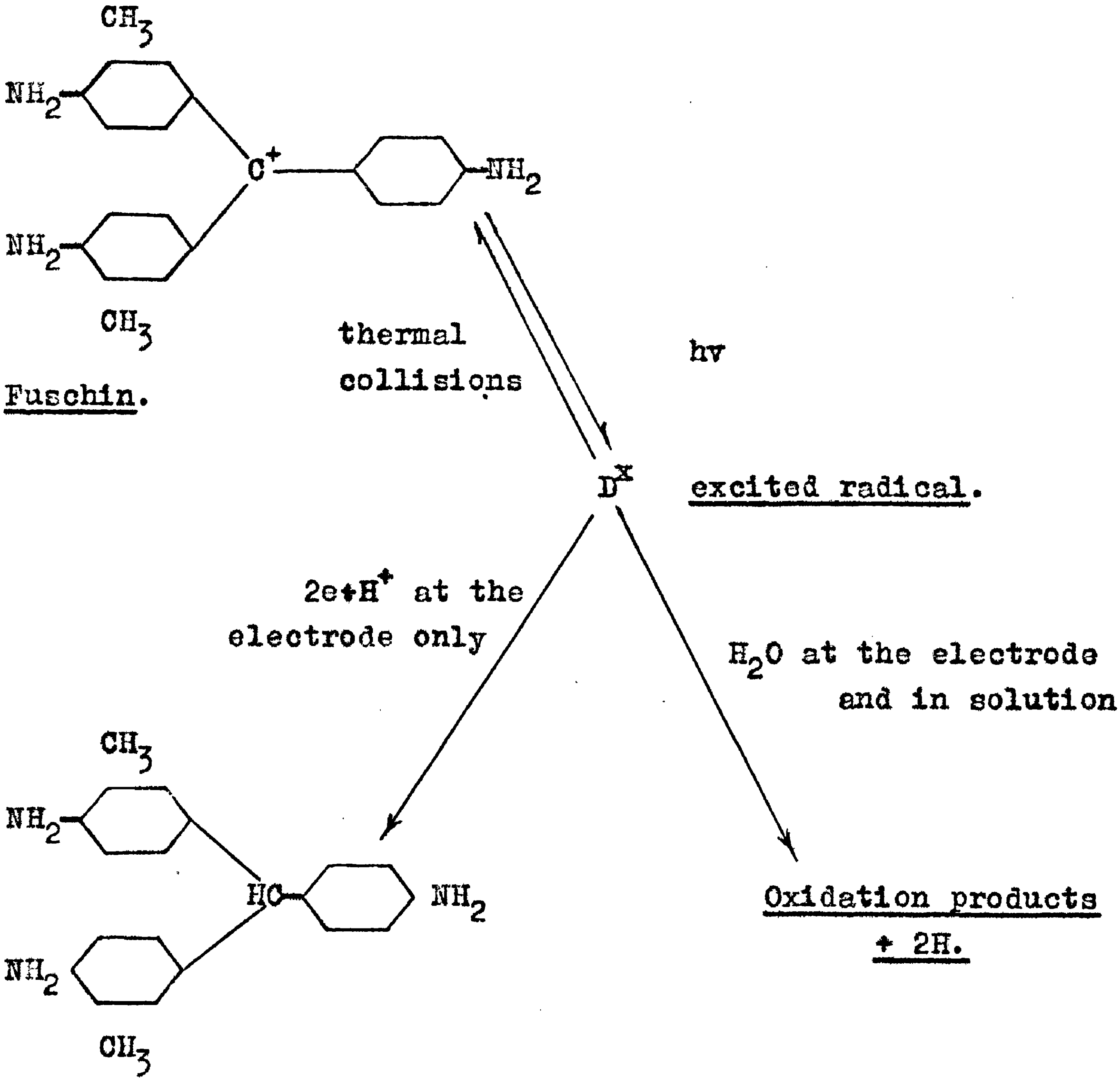
$$D + h\nu \longrightarrow D^{x}$$

$$D^{x} + HOH \longrightarrow DOH- \; + \; H-$$

The mechanism may be expressed diagramatically for a typical azo dye:-


N=N
OH
dye molecule
Waxoline Red BN
hv
thermal collisions
N—N
OH
excited radical
primary reduction step
+ e + H$^+$ at electrode
only.
primary oxidation step
+ H_2O at electrode and
in solution.
H
N—N
OH
OH
N—N
OH
+ H
+ e + H$^+$
The free radicals are
unstable and react
further
+ OH
H H
N—N
OH
hydrazo compound.
OH OH
N—N
OH
+ 2H
N=N
O
OH
+2H+H_2O
azoxy compound.

It was further suggested that triphenylmethane dyes follow a similar scheme except that the oxidation leads to the complete disruption of the molecule.



Fuschin.

Leuco-base.

Under certain conditions photo-oxidation may be masked by photoreduction, e.g., when the rate of reduction is increased by an increase in concentration of hydrogen ions in acid solution, as above.

The authors suggest that a low value for the quantum efficiency of dye fading in solution can be accounted for as follows. In solution in the absence of an electrode, oxidation may take place until a photo-stationary state is established containing a finite number of free hydrogen atoms, and when illumination is interrupted the oxidised dye is reduced by the hydrogen atoms to restore the original equilibrium. This can be prevented and the fading made irreversible only if the hydrogen atoms are removed by a side reaction, the most likely being reaction with oxygen to give HO_2 radicals, which may react further to give H_2O_2. Both these reactions have low efficiency, so that the net rate of formation of oxidised dye is low.

The conditions on a textile fibre are considered by the authors to be very similar to those in aqueous solution and some hydroxyl radicals may be supplied by the fibre molecules themselves, e.g., cellulose fibres which possess a large number of hydroxyl groups. In certain solvents which give hydrogen atoms more readily than hydroxyl radicals, fading may take place by the reductive mechanism (Blaisdell).

These suggestions agree with the indications that fading on cellulosic fibres involves dye oxidation, and also with the known fact that fading is usually accelerated by increase in moisture content of the fibre, moisture being essential to the fading of direct dyes on cotton (Brownlie). The fact that the presence of oxygen has several times been shown to be necessary before fading on fibres can occur is not accounted for, however, unless this promotes a different type of fading when no water except that which is very firmly bound is present in the fibre.

The mechanism of breakdown of the azo group has not yet been determined. Atherton and Seltzer, purely speculatively, suggested the initial formation of an azoxy compound, and Desai and Giles suggested that the hydrazone form of the dye is attacked by hydrolysis to give a quinone and a phenylhydrazine derivative which oxidises further to a diazo compound, thus accounting for the reported detection of diazo compound and quinone after fading (Haller and Ziersch). Rowe and Dangerfield had suggested a similar hydrolytic mechanism to account for the breakdown of some azo dyes in boiling water or acid. Fierz-David et al. have reported that the hydrolysis of the azo dye, sulphanilic acid ⟶ β-naphthol by aqueous acids promotes primary fission at the $>C=N$ link of the hydrazone form, and this can give a quinone and hydrazinosulphonic acid, which later loses ammonia to form the amino-sulphonic acid. But the azo form can also rearrange to give a substituted aminoquinone, which later decomposes into a hydroxyquinone and sulphanilic acid. Burawoy et al. have shown, however, that those groups which generally retard oxidative fading, e.g., NO_2, increase the proportion of hydrazone tautomer of certain dyes in certain solvents. If this is also true of the dyes in their solid state in the fibre, it would mean that the azo and not the hydrazone tautomer is the form most readily attacked.

The quantum efficiency of the light fading of dyes.

It has several times been reported that the quantum efficiency of normal dye fading is very low, but no exact determination of the efficiency at different wavelengths has been published and only isolated notes are available. Some remarkable variations in efficiency have been observed by Collins in a study of the fading of certain colour-developed dyes in gelatin . The quantum efficiency here was at a maximum in the near ultraviolet and fell to almost zero in the centre of the visible region, at which point the energy is ca. 50 kcal. per quantum, which is sufficient to break a bond such as O-O (Burgess), and might therefore be expected to have some effect upon a dye.

A note by Atherton (in the discussion on the paper by Atherton and Seltzer) gives some data based on the relation between the quantal energies at the various wavelengths of maximum light absorption, in the series of seven similar monoazo dyes used in their main investigation, and their initial destruction rates. Although these data are not very conclusive, the author says they may perhaps show that the photoreaction is most rapid in the region 4400-4450 A. That fading increased both with intensity of ultraviolet radiation and with decrease in its wavelength, was demonstrated by Hill in 1927 by exposing a number of dyed woollen patterns to mercury vapour light under several varieties of glass. Blaisdell reports in the discussion on a paper by Morton that cellulose acetate and Terylene films, dyed with a number of disperse type monoazo dyes, and exposed at the focal plane of a spectrograph in mercury vapour illumination, showed greatest fading at the 3030 and 3130 A. lines and inappreciable fading at 4050 and 4350 A. For the yellow and orange dyes the most active wavelengths actually corresponded to a minimum of absorption of the dye-film system. It was reported by Morton that many dyes fade by the action of a comparatively narrow band of wavelengths near the absorption maximum of the dye, and that visible and not ultraviolet light is thus responsible, though his light did not extend to shorter wavelengths than 3650 A. With direct dyes on cotton, aftertreated with Fibrofix, the fading depended primarily on the radiation (3400-3900A.) absorbed by the fixing agent itself.

Recently, McLaren has reported that organic colouring matters are faded by absorbed ultraviolet and visible radiation up to a critical wavelength, above which radiation is non-actinic even if strongly absorbed. He also observed that this wavelength was related to the normal light fastness of the colouring matter, "normal" referring to the substrate for which it was originally developed. The critical wavelength decreases as the resistance to fading increases, being in the red when the light fastness is 1-2 (minimum) and in the blue when it is 6-8 (maximum), there being some exceptions.

Bamford and Dewar measured the quantum yield of a photo-synthesised process of auto-oxidation of tetralin in presence of Cibanone Yellow R at 4500 A. and 4000 A. and found it to be 0.007 and 0.03 respectively. The quantum yield for tendering, using a series of vat dyes, was of the order of 10^{-5}.

Luszczak and Zukriegel used the concentrated-sunlight instrument ("Heliotest") to determine the relative fading rates of some of the blue dyes of the German light fastness standards (nos. 1,3,4,6). They observed that each dye faded mainly in a particular waveband appreciably greater than that of the ultraviolet absorption maximum($\underline{\lambda}$). This band has a fairly definite boundary at 2 $\underline{\lambda}$, separating it from longer wavelengths that are almost devoid of fading action. This phenomenon is explained in the following terms: labile intermediate substances are also formed by radiation which produces fading, but they undergo further changes, in the course of which energy is made available as a smaller number of larger quanta, than that absorbed, probably as ultraviolet luminescence. These quanta then correspond to wavelengths within the ultraviolet absorption band of the dye and produce fading. Supporting evidence is given by the temporary darkening shown by one of the standards on irradiation, and by "fading at a distance" effects.

The influence of the composition of the surrounding atmosphere on light fading.

Rowe and Chamberlain have shown that the "gas fume fading" of acetate rayon dyed with certain blue and violet anthraquinone dyes is due to the combined effects of sulphur dioxide and nitrous fumes (often formed by the combination of nitrogen and oxygen in the neighbourhood of burning gas flames). The products of gas fume fading have been shown by Couper to resemble those of the light fading of the same dye. Gas fume fading is not observed to any marked degree with dyes or fibres other than those mentioned above.

The influence of temperature and humidity on light fading.

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

In this connection Hedges obtained a series of humidity values by placing aqueous solutions of glycerol or certain salts in small boxes containing horizontally fixed dyed patterns behind a Vita-glass window for exposure to a "Hanovia" quartz mercury-vapour lamp. The degrees of fading of a series of patterns exposed under different conditions, after a given period of time, were determined by use of 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, and are of the same order of magnitude as the coefficients for other photochemical reactions, but smaller than for thermal reactions, *ca.* 1.8 to 4.0. Earlier observations by Schwerzam are in agreement with these values.

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

Hedges proposed the formula $F = K,/T(R+c)$, 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 been pointed out, however, by Lead that the moisture content of exposed fabrics cannot directly be determined from the humidity of the surrounding atmosphere since the exposed material is usually at a higher temperature than the atmosphere. This has been confirmed by Nordhammer who found that the temperature of the samples in the Fadeometer fluctuated round 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.

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 (as ordinate), 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 amount may originally be 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 (c.f. Bowen), so that, if the dyed fabrics do absorb the whole of the <u>active</u> radiation, the relationship established by Barker, Hirst and Lambert is normal.

An empirical relationship between fading and the square root of the time of exposure was also observed by these workers. Cunliffe and Lambert examined this relationship in more detail, measuring the colour of dyed patterns before, and at various times during the period of exposure, by the Guild trichromatic colorimeter. As a measure of the 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:-

$$F = a\sqrt{t} + b \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

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

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

where $\underline{c}$ and $\underline{d}$ are constants, applied also to the fading range above about 25% loss. In addition they found empirical equations of other types to hold over a limited range, e.g., a linear relation between $\underline{F}$ and $\underline{\log t}$ for many dyes between ca. 25-80% fading. Since, they argue, photochemical changes always vary in reaction order between the limits of zero (for total absorption of light), where

$$F = kt \qquad \text{.............(iii)}$$

and unity (for partial light absorption), where

$$F = e^{-kt} \qquad \text{.............(iv)}$$

then dye fading should also vary in reaction order between these limits, passing from zero to unity as dye disappears. With most dyes they did find equation (iii) to hold in the early stages of fading, and in later stages the exponential law was found to apply, as predicted. The $\sqrt{t}$ relationship (eqn. i) for medium values of t was shown to be a consequence of the exponential law.

Cunliffe and Lambert also demonstrated a linear relation between fading and initial dye concentration. This is:-

$$F = -f \log C_0 + g \qquad \text{.............(v)}$$

where $\underline{f}$ and $\underline{g}$ are constants, the slope $\underline{f}$ of the curve varying from one dye to another.

They combined their empirical equations in one general expression showing the relation between original dye concentration, time of exposure and extent of fade:-

$$F_t = 100 \left[1 - e^{-t(a \log C_0 + b)} \right] \quad \ldots\ldots\ldots\ldots(vi)$$

Somner studied the same subject and noticed an empirical linear relation between amount of fading and square root of exposure time. We are not aware that since then any further interest has been taken in this type of relationship, or that any relationship between concentration and light fastness grading of a fabric has previously been determined.

Eaton, Giles and Gordon have found that a linear relation exists between light fastness grade number and logarithm of dye concentration on the fibre. 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 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 the time required (t_F) to produce a given percentage loss of any dye and the logarithm of its initial concentration (C_0), i.e.,

$$\log t_F = a' \log C_0 + b' \quad \ldots\ldots\ldots\ldots\ldots (vii)$$

where a' and b' are constants, and this is consistent with equations (ii) and (v) of Cunliffe and Lambert, providing that their equation (ii) holds down to quite low degrees of fading.

Statistical treatment of fastness data : the kinetics of fading.

Eaton, Giles and Gordon have examined several thousand light fastness gradings published in the trade literature of various manufacturers, three grading figures being published for each dye, representing fastness in pale, medium and heavy shade depths, of given values. When the data for each dye/fibre system are averaged, a linear relation appears between (mean) $\log C_0$ (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 (Eaton).

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. Moreover, the magnitude of the slope can be shown (Gordon) to be a measure of the apparent reaction order of fading, as follows.

The derivation is based on the assumption that the dye disappears in the fading reaction according to the mass law equation:

$$-\frac{dA}{dt} = ka^{r} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(viii)}$$

where r is a constant representing the reaction order and k is the reaction constant, which may contain concentration terms of other species and must also be a function of the surface area of dye, and A is the (total) dye concentration present at time t. By integration from $t = 0$, $A = A_0$, to a time t_F when a fraction α of the dye has disappeared, we obtain:

$$\frac{1-(1-\alpha)^{1-r}}{(1-r)A_0^{\,r-1}} = kt_F \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ix)}$$

By taking logarithms, we obtain:

$$\log t_F = (1-r)\log A_0 + (r-1)\Big[\log(1-\alpha)\Big] - \log(1-r) - \log k$$

since α, r and k are all constants, this is a linear expression of the form:

$$\log t_F = a''\log A_0 + b''$$

where the slope a'' of the curve determines the reaction order r.

The chemical structure of dyes and light fading.

The more general effects of structural changes on the chemical reactivity of azo dyes will be considered since these dyes have been used experimentally in the major part of this work.

The basic unit of azo dyes, azobenzene, appears to be relatively more stable to certain conditions of oxidation than more complex derivatives of its class. Thus Seyewitz and Chaix obtained oxidation products by treating certain azo dyes with hypochlorite in hydrochloric acid at 0-5°C., while azobenzene remained unaffected by the reagents used. It would appear however, that the fastness is reduced by increasing the number of units in the dye, to give the corresponding benzidene disazo compound, possibly due to the fact that the second azo group presents an additional point of attack for active reagents. This may be further enhanced by the partial double bond character of the linkage between the benzene nuclei. There is some indication that when the 2:2′-positions in benzidene dyes are occupied by bulky substituents, making the dye molecule non-planar, the fastness is less reduced. In this case the inter-nuclei linkage will have less double bond character. The lowering of the light fastness of certain dyes of the azo, polymethin and triphenylmethane classes is however considered by Kiprianov and Ushenko to be due to the distortion of the planar molecule by substituent groups.

The influence of ortho-substituents.

Substituent groups *ortho*- to the azo-group, if they can act as hydrogen bond donors, e.g., amino or hydroxy groups, appear to improve light fastness on both protein or non-protein substrates (Atherton and Peters, Kienle *et al*.). This is attributed by Atherton and Peters to the protection afforded to the azo group by the chelate ring in which it thus becomes involved. Thus, amongst sulphonated dyes, the *ortho*-hydroxyazo compound Orange II (C.I.No.151) is noticeably faster than its *para*-hydroxyazo isomer, Orange I (C.I.No.150) (Desai and Giles). The difference appears also to hold for a range of sulphonated azo dyes derived from *α*- and *ß*-naphthol, respectively, on wool (Boguslovsky and Sadov), and it extends to unsulphonated *ortho*- and *para*-aminoazo dyes of the benzeneazonaphthalene series on cellulose acetate (Atherton and Peters).

Atherton and Peters also noticed that a methoxy group improves light fastness in the *ortho*-position but lowers it when *meta*- or *para*-, and attributed the *ortho*-position effect to steric protection of the azo group. It has been suggested that the protective action of the *ortho*-methoxy group noticed by Atherton and Peters might be due to chelation involving a CH.....N bond.

Badger and Lewis, who found a linear relation between the rate constants for oxidation (with perbenzoic acid) of *m*- and *p*-substituted azobenzenes, and the Hammett _ -value for the various substituents, noticed that the effect of two such substituents is additive. It has, therefore, been attempted to interpret the influence of *o*-substituents in *o:m*- or *o:p*-disubstituted benzeneazonaphthalene insoluble dyes of the Brenthol class (on cotton) from the I.C.I. data, by averaging a number of fastness figures for the dyes from disubstituted bases (data from very few monosubstituted bases are available), on the assumption that the influence of *m*- or *p*-groups would be additive with that of *o*-groups (Giles). From the results, however, the assumption does not appear to be justified, but some interesting, though rather fragmentary, conclusions emerge. The *o*-Cl and *o*-NO_2 groups, as expected, increase fastness, the *o*-CH_3 and *o*-OCH_3 groups do so too, if there is NO_2 *meta*- to them (i.e. at position 4), but the effect of these *o*-groups and of *o*-Cl is reduced or even reversed if another Cl is present *ortho*- or *para*- to them.

The available evidence appears consistent with the hypothesis that a substituent *ortho*- to the azo-group increases or reduces the light fastness, on any substrate, according to its electrophilic nature, except when it is capable of chelation with the azo-group, when it always exerts a protective effect against light fading.

The influence of meta- and para-substituents.

Kienle *et al.* and Pinte and Miller have established the influence upon fading of substituents *m*- and *p*- to the azo group in benzeneazonaphthalene dyes. The effect of *m*- and *p*-substituents will depend on whether or not they exert a protective effect on the azo group, which must be the point of attack in fading. Thus the above authors have shown that electronegative groups, e.g., NO_2, decrease the fading rate on non-proteins and increase it on protein fibres. Electropositive groups such as OCH_3 behave in the opposite sense.

It has been found that, in general, the logarithms of the relative rate of fading of a series of *m*- and *p*-substituted azo dyes form a linear plot with the σ-values, as determined by Hammett, the sign of the gradient of the line obtained varying according to the substrate in which the dye is contained.

Previous work.

Desai and Giles, in this laboratory, have shown that oxidation of azo dyes in aqueous media, with ceric sulphate, potassium dichromate, or hydrogen peroxide, disrupts the azo group and leads to the formation of a diazo compound and a quinone, which further decompose to give, respectively, a phenol and nitrogen (in acid media) and phthalic acid. This reaction appears to be common to many types of oxidising agent, like effects having been previously observed by workers using, for example, hypochlorite, lead dioxide and nitric acid (Seyewitz and Chaix; Lauth; Rowe and Levin; Schmidt). It is suggested that the initial step in such chemical oxidations is one of hydrolytic attack on the —C=N— bond of the hydrazone tautomer of the dye, which is shown to fit the facts reasonably well by a study of the relative ease of oxidation of several phenylazo dyes of both soluble and insoluble types, with different substituents in the benzene ring.

Chipalkatti et al. extended the observations of previous workers (Kienle, Stearns and van der Meulen; Atherton and Peters; Atherton and Seltzer; Kienle et al.; Atherton et al.) to determine whether any systematic variation of fastness between different substrates could be detected with a view to elucidating its fundamental cause.

Several series of simple phenylazonaphthalene dyes, both water-soluble and water-insoluble, were applied to a variety of substrates, and the relative fading rates of the dyes in each series on each substrate were compared with the

Hammett $\underline{\sigma}$ - values of meta- and para-substituents in the benzene nucleus.

It was concluded that the substrates used fall into two classes, according to the sense in which they influence the relative fading rates, viz., proteins, i.e., (a) wool, silk and gelatin ; and (b) all other materials, including cellulose, cellulose esters and ethers, and nylon. It was suggested that protein substrates may perhaps take part chemically in the fading reaction, probably by reduction of the dye, whereas the other class of substrates, the non-proteins, may not; the fading reaction may then be oxidative in absence of protein. Further, it is shown that the fading reaction on proteins does not appear to involve either the peptide linkages or the hydrocarbon portions of the protein molecules, but the suggestion was made that the tyrosine or histidine sidechains may be involved. Later, Cumming et al. continued this work, confirming that oxidation occurs when dyes are faded on non-proteins and reduction on proteins, and showed that this seems to be a general rule applying to all types of dye and not only the azo series. The actual constituent of the protein responsible for reduction was shown to be, probably, histidine. Some rather inconclusive evidence was also obtained suggesting that tryptophane may also be involved in the reduction.

The differences in the light fastness of any dye on different substrates of the same class are stated to be attributable largely to differences in its state of dispersion determined by the physical nature of the substrates.

EXPERIMENTAL

The preparation and purification of azo dyes.

For a section of the work described later, a series of para-alkylbenzeneazonaphthalene-2-hydroxy-3:6-disulphonic acid dyes was prepared. The unsubstituted dye, and the para-methyl and para-butyl dyes were prepared in the usual manner (Fierz-David and Blangey). The method was modified as follows, however, in the preparation of the para-dodecyl and para-cetyl dyes, the amine hydrochlorides being insoluble.

A solution of 5.2g. of para-dodecylaniline in acetone was added rapidly, with vigorous stirring, to 2.5 c.c. of (conc.) hydrochloric acid in 100 c.c. of water. A finely divided suspension of the amine hydrochloride was thus obtained. A further 2 c.c. of (conc.) hydrochloric acid were added to the suspension and 20 c.c. of N. sodium nitrite solution were added dropwise until most of the material had dissolved. The mixture was then filtered to remove any undissolved hydrochloride and the resultant clear solution was coupled with 6.1g. of naphthalene-2-hydroxy-3:6-disulphonic acid dissolved in 60 c.c. of N. sodium hydroxide solution. The dye, which precipitated on coupling, was filtered and washed with acetone and benzene to wash out unreacted amine or other organic impurities. The dye was purified further by recrystallisation from water by addition of ethanol.

The para-cetyl homologue of the above dye was prepared and purified in a similar fashion.

The more soluble dyes of the same series, viz., the para-butyl, the para-methyl and the unsubstituted dyes, could not be satisfactorily recrystallised, and were purified by passage through cationic and anionic exchange resins in series, followed by exact neutralisation with sodium bicarbonate of the free dye acid formed.

The dye purities were estimated, both by titanous chloride and by the oxidation method of analysis (Arshid), and were found to be of the order of 95%.

Many of the dyes nsed in this work were of normal commercial quality, some having been purified by recrystallisation or by salting out either with sodium chloride or by the sodium acetate method. The purity values of such dyes were rather lower (ca. 90%) and they probably contained sodium chloride.

The illuminant for light fastness determination.

An artificial light source is necessary for light fastness determinations 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. It has frequently been observed, however, that light fading evaluation by artificial light may give results different from those of daylight tests, and recently Gasser and Zukriegel have described an apparatus to accelerate daylight testing. In this apparatus, the "Heliotest", the light from the sun is collected by lenses and concentrated on the patterns under test, giving a 25-fold increase in intensity of the sun's emission. The results are claimed to be highly consistent with those obtained by the normal method of exposure. The carbon arc has probably been used more than any other artificial illuminant for fading studies, the three principal types of arc being the enclosed flame arc, the low intensity arc, and the high intensity arc.

In the present work, a General Electric "Osira" high pressure mercury vapour lamp of power 400w. was used, with the appropriate choke in series, but without a condenser. The lamp was chosen for its relatively constant emission over long periods, low running costs, and because it requires virtually no attention. The lamp was held in a porcelain lamp-holder screwed to a wooden baseboard and surrounded by a cylindrical sheet aluminium screen (17 in. dia. x 15 in. high), fitted at vapour-stream level with a 3/4 in. wide aluminium shelf, on which the patterns were rested during exposure. 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 (Fig.50). The five major emission lines in the spectrum of the lamp are at 3650 A., 4047 A., 4358 A., 5461 A., and 5780 A.

By embedding copper-eureka thermocouples in gelatin films, as used in fading experiments, the internal temperatures were recorded, both for uncoloured film and for film coloured with a high concentration of an R-acid dye (much higher concentration than any used for fading tests), and compared with the surrounding air temperature. The air temperature within the screen was found to be constant for continuous running at 56°C. whereas the surface temperature of the films ranged between 65-70°C. for colourless and coloured films respectively. All the temperatures remained steady within ± 1°C. throughout each fading test, apart from the coloured film where a temperature fluctuation of 3° was noted. The gelatin films required about 1 hour from the start to reach the maximum temperature. Since the experimental work involved is based on the comparison of the fading rates of particular dyes and not on absolute measurements, the above experimental conditions were considered satisfactory.

It was pointed out by Lead that the moisture content of exposed fabrics cannot be directly determined from a knowledge of the surrounding atmospheric humidity, because the material reaches a higher temperature than the surrounding atmosphere and its temperature increases with the amount of dye present. This has been confirmed in the case of the films mentioned above. Films left exposed to the lamp for two days had the following moisture contents: gelatin 2.8%, Cellophane 5.6% .

The visual and spectrophotometric 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 standards no. 1-6 , each fading at about half the rate of the one lower in the scale. Standards nos.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 and the faded specimen, regardless of the character of the change. A visual comparison of the contrast can be made with the contrast represented by the 5 pairs of neutral colour patterns in the Standard Grey Scale, developed by the Society of Dyers and Colourists for evaluating changes of colour in textiles, for both the dyed patterns and the blue standards, leading to a more accurate and reproducible evaluation of light fastness.

It was intended to use these standards as a means of measuring the relative fading rates of a series of dyes on opaque substrates. It was found, however, in a test exposure in the fading lamp, that the standards did not fade in the order specified, nos. 1, 2 and 3 having a preliminary hue change with a definite fade observed first in the case of standard no. 3 rather than 1 or even 2 (Macaulay). This anomalous behaviour was attributed to the differences in light absorption properties of the dyes used in preparation of the standards, and to the effect of line-emission spectrum of the fading lamp. For this reason, fading on opaque substrates was measured merely by the time taken to give a just perceptible fade in the exposure lamp, a just perceptible fade being considered to be equivalent irrespective of shade depth (Weber-Fechner law). Latterly, however, a reflectance attachment for the Unicam S.P.500 spectrophotometer was obtained, enabling the fading to be followed accurately. The degree of fading was determined as the increase in the percentage reflection measured at the wavelength of maximum light absorption of the dye on the substrate under investigation.

A comparison was made of the visual and instrumental determination of fading rates, the data being presented in Fig. 1-3. Visual judgement of fading was made by covering one-half of each pattern by black card, while the other half was irradiated, observing the qualitative extent of fade, as judged by two observers at frequent intervals until a quite distinct loss of dye had occurred, and then recording the time (t_F) at which a just perceptible loss had been noted. The t_F values for reflectance measurements refer to the appropriate reflectance increases corresponding to an actual loss of 5% or 10% of dye, as indicated, the relationship between reflectance and dye content being determined experimentally by pyridine extraction of the dye from the fibre of known reflectance. The curves for the 5% loss are less reproducible than those for 10% loss owing to the difficulty of taking precise measurements of fading rates in the very early stages.

It is evident from Fig. 1-3 that a "just perceptible fade" is equivalent approximately to a 5% loss of dye from the substrate.

In experiments involving transparent substrates the degree of fading was determined as the decrease in optical density measured at the wavelength of maximum absorption of the dye under investigation. By the Lambert-Beer law, for constant thickness of transparent medium, optical density varies with concentration in a linear manner, provided that no changes occur in the light absorption properties of the solute due to alteration in the degree of association and aggregation. A linear relation was, in fact, found in all the cases investigated, justifying the above assumption. All measurements were carried out on the Unicam S.P.500 spectrophotometer, in each case using a "blank" film since it was found that the substrates gave a positive optical density reading due to reflectance from film and glass surfaces and a certain amount of film absorption in the near ultraviolet.

The characteristic absorption curve for each dye in its substrate was determined from wavelengths of 3500 A.- 7000 A. at intervals of 100 A. except at maxima and minima, where the interval was decreased to 50 A. or 25 A. according to the sharpness of the curve. Such curves covering the total range of emission of the fading lamp were required for total absorption comparisons between the dyes.

The calculation of relative fading rate from fading curves.

The determination of fading rate for opaque substrates was carried out as described previously (p.42).

In the case of transparent films, it was found that initial fading in a large number of cases 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 some loss of moisture in the film. 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 concentrations 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 an equivalent fade t_F was taken as the time of exposure, calculated on the mean rate of fading between D_1 and D_2 , required to give a 10% decrease in the value of D_1.

In cases where only slight irregularities occurred at commencement of fading, D_1 was taken as the value obtained by extrapolation to zero time of exposure. Where no irregularities occur, the straightforward measurement of the time of exposure for an equivalent decrease in concentration was made. In any one set of comparisons between fading rates, the same system of calculation was used.

Determination of dye concentration in substrates.

Where transparent dyed films were used in the present work, optical density figures have sufficed as relative concentration values.

In all cases, samples of film of the same dimensions in each series were taken, and their respective optical densities recorded in film form and again in solution in a given volume of a suitable solvent. Where the fading of a series of dyes was being compared, e.g., the dyes differing only in the length of an attached alkyl sidechain, a disaggregating solvent had to be employed to give strictly comparable relative concentration values in the series. In certain cases a comparison was made of the fading of a dye after introduction into films in markedly different states of dispersion, and here also the relative concentrations were expressed as the optical density of the solution of a standard size of film in a suitable solvent.

The amount of dye on opaque substrates was determined by pyridine extraction or dissolution of the dyed fibre, with 80% aqueous sulphuric acid, followed by measurement of the optical density. In this connection, there appears to be a linear relationship between the logarithm of the reflectance and the logarithm of the dye content. Prior to acquiring the reflectance attachment for the Unicam S.P.500 spectrophotometer, the dye concentration was taken as that added to the dyebath and calculated to give the required depth of shade, where the dye had affinity for the substrate. Where complete exhaustion of the dyebath could not be effected, the concentration of dye remaining in the exhaust liquors was determined spectrophotometrically and subtracted from the original quantity present.

Substrates used and methods of coloration.

Gelatin

A 6% aqueous solution (7 c.c.) of gelatin, of pure "inert" photographic quality, was mixed with 1-6 c.c. of 0.001M dye solution and poured on a "subbed" photographic glass plate (4 in. x 2.5 in.) on a screw-levelled platform. When the film had set, it was placed in a steady stream of air from a fan until dry. This procedure ensured the production of films having uniform optical density over their whole area.

In certain cases, a water-insoluble gelatin film was required suitable for dyeing by immersion in a dyebath at 60-80°C. The gelatin alone was cast and dried as before, then the film was immersed in 4% aqueous formaldehyde solution for 15 minutes, after which it was washed with cold water and dried. The resultant film could be dyed satisfactorily as described above, although at the higher temperature (80°C.), the film tended to peel off the glass plate.

Methyl Ethyl Cellulose

A 4% aqueous solution of Cellofas A (I.C.I.) was prepared in the cold by stirring continuously for 24 hr., and then centrifuging at 2,500 r.p.m. for 1 hr. in four 250 c.c. containers, to deposit fibrous material. The supernatant liquor was then used for film casting, 8 c.c. portions being mixed with 1-6 c.c. of 0.001M dye solution and poured on glass plates as for gelatin. The plates were levelled on a sheet of plate glass, placed on a metal surface heated from below by four 130 w. carbon filament lamps. This procedure gave the most uniform films, but even so, inequalities were noticed round the edges, and only the central parts were used.

Collodion

A mixture of 80 c.c. Necol (I.C.I.)(cellulose nitrate) varnish and 20 c.c. acetone was used in the preparation of these films. 8 c.c. of the above mixture of collodion varnish and 1-6 c.c. of 0.001M dye solution in acetone were mixed, spread on a glass plate (4 in. x 2.5 in.), and allowed to dry in air.

Cellophane

Most of the regenerated cellulose films used were normal commercial Cellophane (thickness 0.001 in.). Those used for examining the effect of pore size were dry "PT 600 cellulose film", and the equivalent 600 quality in gel form. The dry film contained a water-soluble plasticiser, but this would be removed in the dyeing process. The aged gel films were stored wet in polythene bags in the dark at room temperature for about six months.

Direct dyes were applied to Cellophane from hot water alone, the different depths of colour being obtained by dyeing rolled strips (10 in. x 1.5 in.) for different periods of time (1-15 min.) at 80-90°C. in 400 c.c. of dye solution (0.75g./litre). The aftertreatments with Fixanol C and Metabol O were made by working the dyed films for 15 min. at 40°C. in a solution of 6g. of reagent per 100 c.c., then rinsing well, and drying at 100°C. Metabol O was first recrystallised from water, with charcoal clarification.

The indigoid vat dyeings were prepared as follows:- 20 c.c. of a 1% suspension of the dye powder was vatted at 60-70°C. for 10 min. after addition of 7 c.c. of 10% aqueous sodium hydroxide and 0.3g. of sodium hydrosulphite. The vat was then diluted to 200 c.c. with warm water containing 1 c.c. of 10% sodium hydroxide and 0.1g. of sodium hydrosulphite and maintained at 50-60°C. Strips of Cellophane (10 in. x 1.5 in.) were immersed for varying periods of time to give a range of depths, then rinsed and air-oxidised. One half of each strip was then boiled for 15 min. in soap solution (1g./litre), rinsed, and oven-dried.

In the preparation of azoic-dyed Cellophane films, sheets of film (6 in. x 4 in.) were worked from periods varying from 1 to 15 min. in a flat dish at room temperature, in a solution containing, per litre, 2g. of the Brenthol component and a total of 1g. of sodium hydroxide, 2g. of sodium chloride, and a little wetting agent (Calsolene Oil HS (I.C.I.)), prepared in the normal manner. They were then removed, well rinsed, first in sodium chloride solution and then in water, and worked for 10 min. in a cold 0.05% solution of the diazotised base (neutralised with sodium acetate after diazotisation). One half of each piece was then boiled for 1 hr. in a solution containing 2.5g. soap flakes and 2.5g. sodium carbonate per litre. Both halves were finally well rinsed in water, oven-dried at 100°C., and mounted for irradiation.

Nylon

Transparent 0.003 in. nylon film, in 2.5 in. x 4 in. strips, was dyed in 400 c.c. of 2-8 x 10^{-6} M dye solution at 60-90°C. for 60 min., a little dilute acetic acid being added in some cases after 30 min. to effect complete exhaustion. The material was then well rinsed, and dried at 100°C.

Vat dyes were applied to nylon as follows:-

Strips of nylon film (4 in. x 3 in.) were first scoured at 40°C. for 15 min. in a 0.5% solution of a non-ionic detergent (Lissapol N (I.C.I.)), and then rinsed. In the dyebath, 0.1g. of the vat dye powder, 14 c.c. of 20% aqueous sodium hydroxide solution, and 200 c.c. of water were heated to 80°C., then 2g. of Formosul G (Br) and 0.2 g.g. of Dispersol VL (I.C.I.) were added, and the temperature raised to 90°C. and kept thereat for 10 min. to ensure complete reduction. The nylon strips were dyed (lightly rolled, in test tubes) for varying periods of time, to obtain different depths of colour, then rinsed, air-oxidised, soaped at 60°C. for 15 min. in a soap solution (10g./litre), and rinsed again. One half of each strip was then treated at 50°C. for 5 min. in 500 c.c. of a 1.5% solution of cinnamic acid in 25% aqueous solution of acetone, next rinsed in hot water, soaped at 60°C. for 15 min. in a solution containing 10g. of soap and 0.5g. sodium hydroxide per litre, and rinsed. Finally, all the strips were oven-dried at 100°C.

All these films were clipped to a rectangular spacer of glass rod during dyeing to ensure levelness.

Silk

One-gram portions of boiled-off silk fabric were dyed to near exhaustion in 0.2% depths from 100-vol. baths containing 1% sulphuric acid, on the weight of fibre, and then rinsed and dried.

The silk fabric had the following specifications: weave, plain; warp and weft, 80 den. 35-40 fil.; set 112 x 112; 1.5 oz./sq.yd.

Wool

One-gram patterns of scoured worsted flannel were dyed by the method used for silk.

Viscose Rayon

The viscose rayon materials used for the results in Fig. 27 and 31 comprised three fabrics identical in structure (weave, plain; warp and weft, 1/18s (cotton count); set, 60 x 54) but made from Fibro (Courtaulds) staple fibre of different physical characteristics, as follows:-

(a) Standard Fibro (1.5 denier, 1 7/16 in. staple).

(b) Strong Fibro (1.25 denier, 1 7/8 in. staple), stated to be a Tenasco (Courtaulds) type of material, having a small crystallite size and thus a rather refined structure.

(c) Low-swelling Fibro (1.5 denier, 1 7/16 in. staple), made from the same spinning as (a) but distinguished by having been recrystallised by a physical aftertreatment.

The imbibition values were - (a) 87% (b) 86% (c) 55% . These figures refer to moisture retention in a standardised test used by the manufacturers, and may be taken as a qualitative measure of the relative internal pore volume of the fibres.

The materials used for the results in Fig.25,26,28,29, 30 and 32 were taffeta fabrics made from continuous-filament yarns and all were identical in structure (weave, plain; warp and weft, 30 denier; set, 104 x 104; 0.8-0.9 oz./ sq.yd.; ordinary viscose rayon and Tenasco, 12 filaments per yarn; Durafil (Courtaulds), 100 filaments per yarn).

The respective imbibition values were 118, 94 and 69%.

All these fabrics were supplied commercially clean and scoured, and were used without further pretreatment.

The viscose rayon fabrics were dyed§ in 1.5g. portions for 45 min. at 85-90°C. in 40-volume baths containing 0.25-6.0% dye (referred to weight of fabric), 20% Glauber's salt, and a few drops of wetting agent (Dispersol VL), then well rinsed, and oven-dried. The amount of dye on each of the samples was measured by dissolution of the fibre in 80% aqueous sulphuric acid or by extraction of the dye from the fibre with 50% aqueous pyridine.

Anodised Aluminium

Pieces (6 in. x 4 in.) of aluminium foil (0.002 in. thick, 99.99% purity) were anodised for 1 hr. in either (a) 20% (wt./vol.) sulphuric acid at 25°C. and 12v. or

---

§ Microscopic examination of fibre cross-sections showed dye penetration to be complete.

(b) 3% aqueous chromic acid at 40°C. and 45v., the electrolyte being continuously agitated. The foil was then well rinsed, dried at 130-140°C. for 1 hr., and stored in a desiccator until ready for use. The actual weight of film present was determined by weighing the anodised material before and after dissolving the film in chromic acid-phosphoric acid solution. Discs 1 in. in diameter, to fit the spectrophotometer reflectance attachment, were cut from the finished sheets, and dyed in 10 c.c. portions of dye solutions of concentrations 0.0125-0.10g./litre for 10 min. on a boiling water bath. They were then rinsed and oven-dried.

Owing to the difficulty of anodising the two sides uniformly, the depth of dyeing was not the same on the two sides. For this reason also, it is not practicable to correlate the data for the total amount of dye adsorbed by each disc (calculated from absorptiometric measurements of the exhaust liquors) with the individual reflectance measurements for the two sides. Consequently the ordinates of Fig.33 refer to a 10% increase of reflectance values, and the abscissae to the initial reflectance readings for each individual disc side. The actual initial percentages of (commercial) dye present (referred to the total weight of film on both sides of each disc) are given below:-

Coomassie Brilliant Blue G 250		Coomassie Violet 2RS	
H_2SO_4 film.	H_2CrO_4 film.	H_2SO_4 film.	H_2CrO_4 film.
0.44	0.23	0.18	0.025
0.58	0.60	0.42	0.13
0.98	0.85	0.66	0.18
1.8	1.5	-	0.21

The self coloration of silk.

A series of para-substituted aniline derivatives were diazotised in the usual manner after which the diazo solutions were neutralised (to Congo Red) by addition of sodium acetate solution. Wetted samples of silk were then introduced to a series of tubes containing a range of concentrations of diazo solution. The silk patterns were stirred for 10-15 min. and left overnight in the refrigerator for completion of coupling, after which they were rinsed thoroughly with cold water and dried. In all cases the coloration was most uneven and unsuitable for fading measurements and, as no satisfactory colorations could be obtained in further attempts, the work was abandoned.

The amines used were sulphanilic acid, p-anisidine and p-nitroaniline.

The preparation of merocyanine and azo dye dispersions.

A water-insoluble merocyanine dye was treated as follows:-

(a) Ground to a fine dispersion in water alone, then added in measured proportions to 6% aqueous gelatin solution, or 4% aqueous Cellofas A (I.C.I.) (methyl ethyl cellulose) solution, with good agitation, before setting and drying.

(b) Added in measured proportions from 0.03% solution in acetone to 6% aqueous gelatin, or 4% aqueous Cellofas A solution, with good agitation, before setting and drying.

(c) As (b), but in place of gelatin or Cellofas A solution, a mixture of 80 c.c. Necol (cellulose nitrate) varnish and 20 c.c. acetone was used.

The films prepared from the merocyanine dispersion had the coarsest particles, those prepared as under (b) were slightly turbid, but no particles were visible, even at 250 X magnification, and the collodion films were completely transparent, and no particles could be seen under the microscope.

The azo dye (p-anisidine ⟶ β-naphthol) was treated by methods (b) and (c).

The mounting of coloured substrates for fading.

For the fading of opaque substrates, judged visually, 5 cm. x 1 cm. strips were stapled to card with a hinged black card flap covering one-half of the surface. When the fading was followed spectrophotometrically, the opaque substrate was cut in 1 in. circles suitable for insertion in the reflectance attachment. The pieces were clamped between glass for irradiation, the back being shielded from the light.

The transparent films were cut in 50 mm. x 11 mm. strips suitable for direct insertion in the cell-carrier of the spectrophotometer. In the case of films cast and dried on glass plate, the film surface was covered with a second, equal-sized portion of similar glass, and the ends were bound together with tape to prevent peeling. The transparent nylon and cellophane films were clamped between two strips of similar glass of the above mentioned dimensions and bound together with tape. For experiments using filtered light, the cover glass was the filter itself, which was placed towards the lamp, the back of the film being shielded from reflected light by black card.

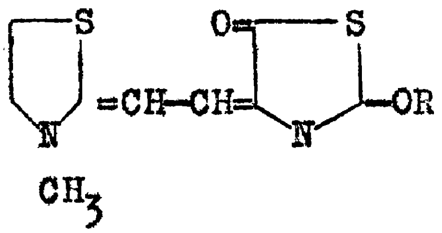
The measurement of oxidation and reduction rates.

The dye and the reagent solution, chosen for its suitable reaction rate, were mixed in a stoppered tube at room temperature, and the optical density measured at intervals. The oxidation and reduction rate measurements were made on a photoelectric ("E.E.L.") test-tube absorptiometer. The choice of reagents and conditions is rather severely limited by the necessity of using dye solutions of suitable strength for direct colorimetric measurement, and reagents which react therewith at a measureable speed; in a number of cases the reaction was not measureable; it either occurred instantaneously or not at all, and in order to obtain a complete series of tests a variety of reagents at a number of widely different concentrations was used. The rate for each pair (or series) of dyes, however, was measured with each chosen reagent under identical conditions at the same time.

Pyridine, ethyl alcohol or acetone were used in certain cases in the above tests to prevent or reduce the formation of dye-aggregates which would give anomalous reaction rates.

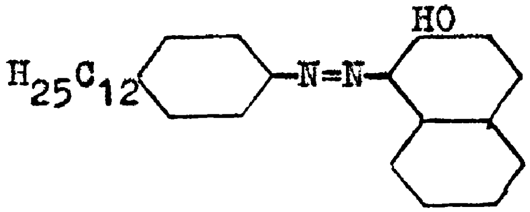
Dyes used in surface-activity section.

Dye-series



I

a, R = C_8H_{17}; b, R = $C_{16}H_{33}$



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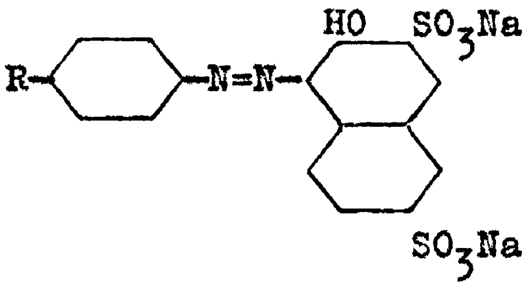
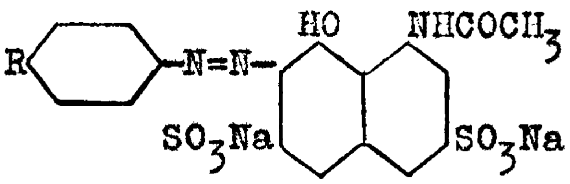


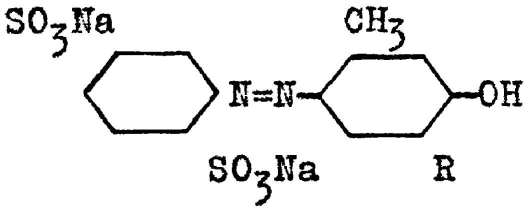
III

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



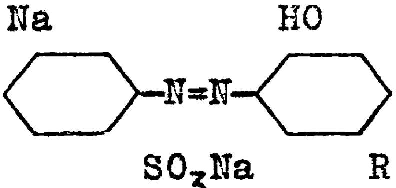
IV

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



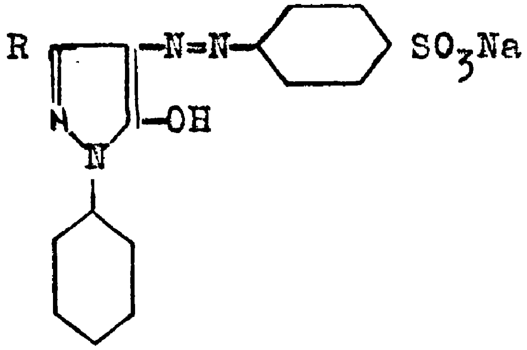
V

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



VI

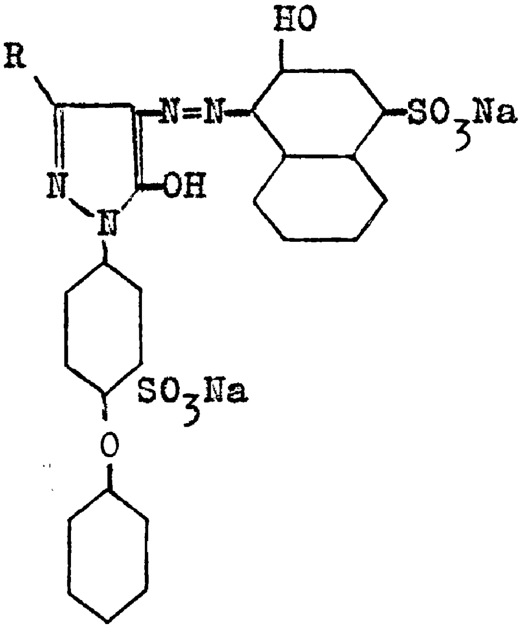
a, R= $-CH_3$; b, R= $-C(CH_3)_3$; c, R= $-C(CH_3)_2CH_2C(CH_3)_3$



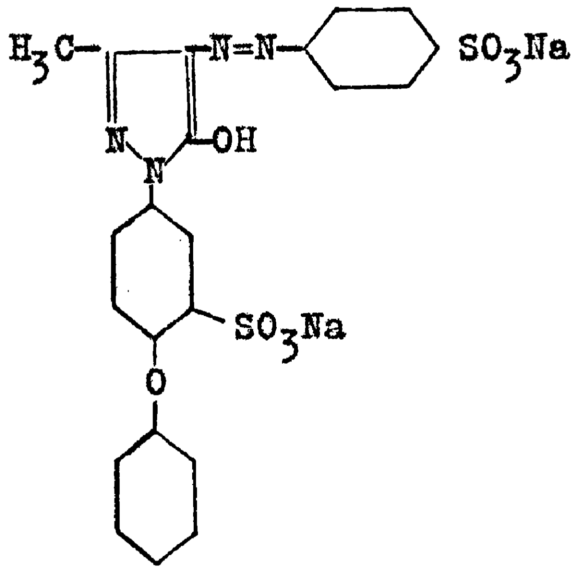
VII

a, R= $-CH_3$; b, R=$C_{17}H_{35}$

VIII



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



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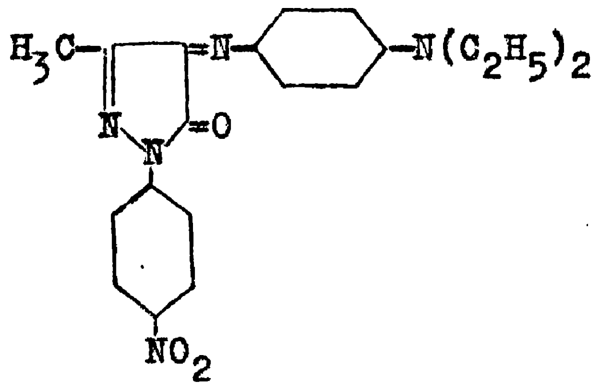
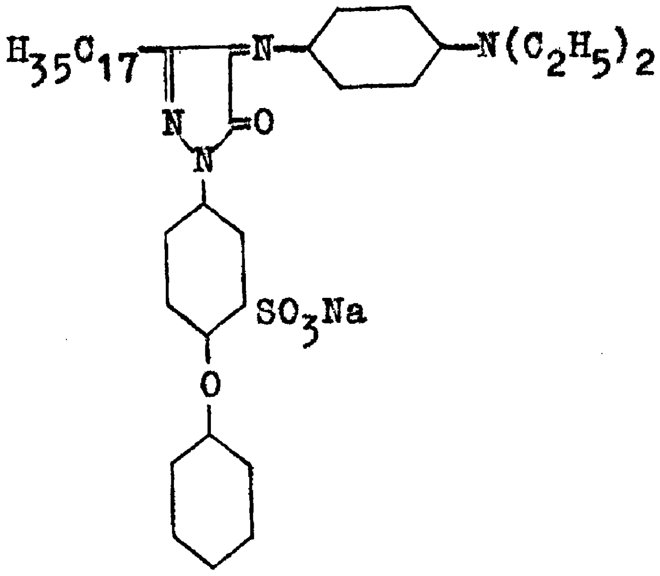


X



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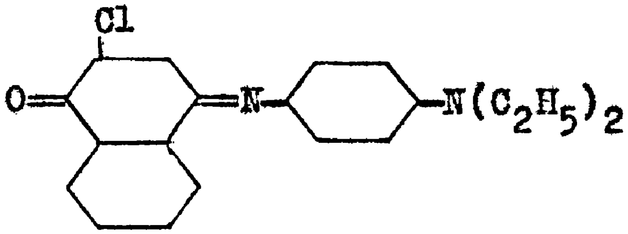

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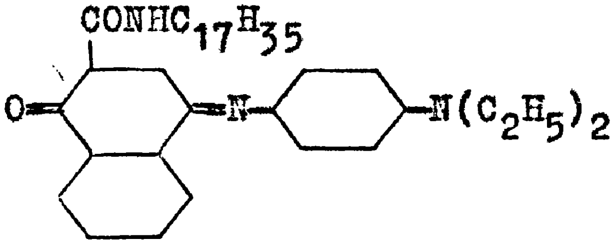

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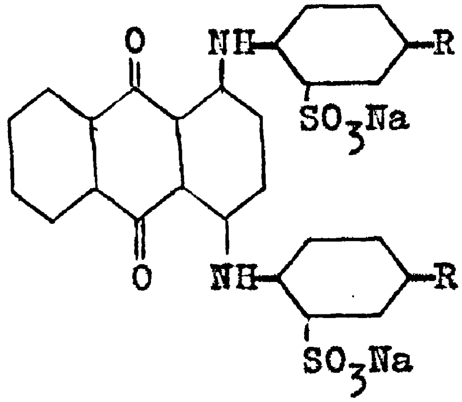
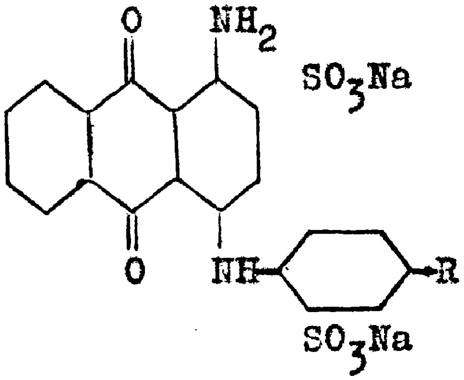


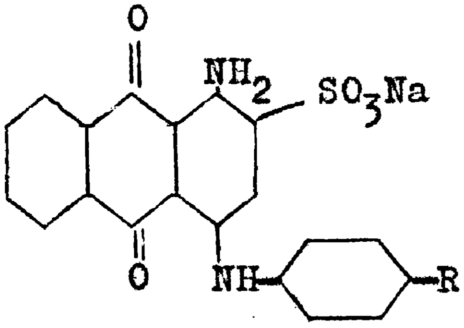
XIV

a, $R= -CH_3$;   b, $R= -C_4H_9$



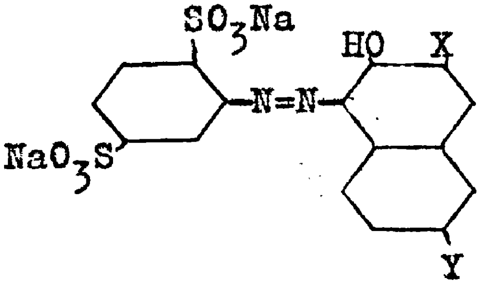
XV

a, $R= -H$;   b, $R= C_{12}H_{25}$



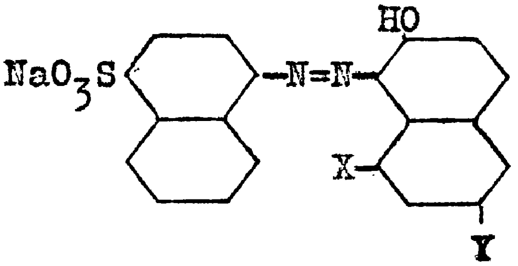
XVI

a, R= $-CH_3$; b, R= $-C_4H_9$



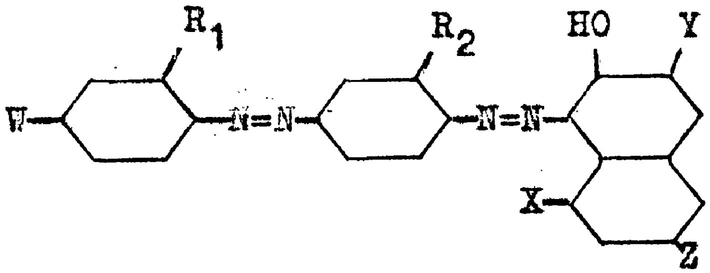
XVII

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



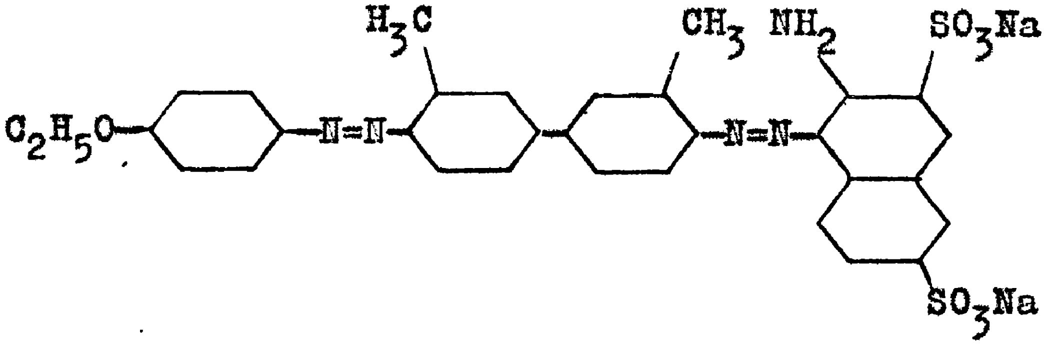
XVIII

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

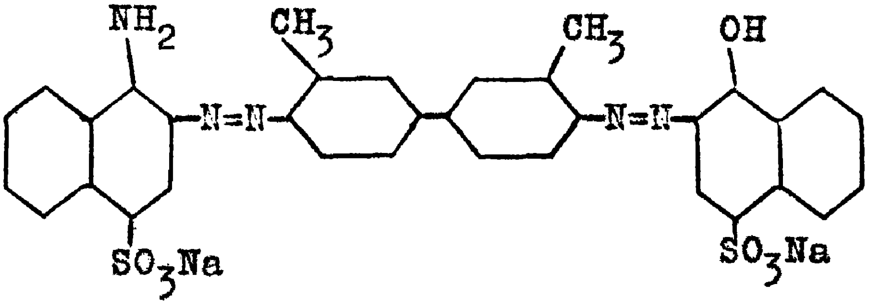


XIX

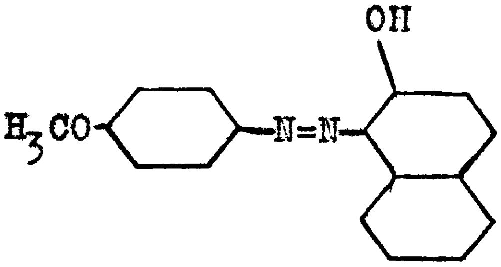
a, W= $-SO_3Na$, X=$-SO_3Na$, Y= $-H$, Z= $-H$, R_1= $-CH_3$, R_2= $-CH_3$;
b, W= $-H$, X= $-H$, Y= $-SO_3Na$, Z= $-SO_3Na$, R_1= $-CH_3$, R_2= $-CH_3$;
c, W= $-H$, X= $-H$, Y= $-SO_3Na$, Z= $-SO_3Na$, R_1= $-H$, R_2= $-H$.


H3C
CH3
NH2
SO3Na
C2H5O
N=N
N=N
SO3Na

XX


NH2
CH3
CH3
OH
N=N
N=N
SO3Na
SO3Na

XXI


OH
H3CO
N=N

XXII

RESULTS AND DISCUSSION

The influence of substrate upon fading.

This work was carried out in continuation of that of Chipalkatti *et al*. upon the influence of the substrate on the nature of the fading reaction. Several series of phenylazonaphthalene dyes, both water-soluble and water-insoluble, were faded on a variety of substrates and the relative fading rates were plotted against the Hammett σ-values for the respective substituent groups in the *m*- or *p*-position in the benzene nucleus. Linear plots were obtained. By extending the work of Kienle *et al*. and Atherton *et al*., Chipalkatti *et al*. had found that the slope of such plots is positive only on protein substrates; on all other substrates, including nylon, it is negative. They concluded that the fading mechanism differed fundamentally on the two classes of substrate, and suggested that on proteins the substrate takes part in the fading reaction, whereas, on other substrates, fading involves only dye and water, and/or oxygen, the substrate behaving as an inert surface.

It had already been observed that the individual points in the plots just mentioned tend to be rather widely scattered about the regression lines (calculated by the least-squares method)(Fig.5-7). In the case of opaque substrates it was thought that the principal source of error was the difficulty of judging the extent of fading by eye, but even results spectrophotometrically determined are not entirely free from random errors (Fig.8). As will be shown later, the light fastness of most dyes is considerably influenced by their state of physical dispersion in the substrate, and much of the random error not accounted for by difficulties of measurement might perhaps be attributable to this cause, originating probably in small variations in the conditions of drying. Further, it had been observed that some water-insoluble dyes appeared to be more uniformly dispersed in films of collodion than in other substrates. Accordingly series of water-insoluble substituted benzene-azo- 2 -naphthol dyes were cast in collodion and examined for fading. The relative fading rates conformed to the order of fading as expected for non-protein substrates, but much improved freedom from random error was also observed (Fig.9).

The principal sources of error in the general method would therefore seem to lie in the non-uniform physical state of the dyes in the substrates, and, in the case of the visually tested materials, in the difficulty of judging the extent of fading.

The physical state of dyes in substrates.

Since the fading reaction involves oxygen and/or water vapour, then it must be influenced by the size and nature of the air-dye interface: the smaller the surface area exposed, the less rapid will be the fading. Bean and Rowe showed that soap-boiling or steaming, which caused microscopically visible crystal growth of insoluble azo dyes on cellulose fibres, therefore reducing the surface area, at the same time improved the light fastness. The very low light fastness of vat dyes on nylon, compared with their fastness on cellulose, has likewise been attributed 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 (Bowker, White, discussing paper by Smith; Douglas). Examining the effect of soaping on vat dyeings on "Cellophane", Sumner, Vickerstaff and Waters obtained no significant increase in light fastness. 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. The surface area of the dye is not shown by the electron photo-micrographs to be decreased by the crystallisation process as it undoubtedly is in the case of the azo dye systems examined by Bean and Rowe. It may be that the transformation of the original amorphous, compact particles of vat dye into long, filamentous crystals may even increase the surface area.

That water-soluble dyes are molecularly attached to fibres is probably true when the solvent (water) is present, but when the fabric is dried out, as it always must be before use, it contains only an equilibrium amount of adsorbed water. The adsorbed water is likely to be some 2-20% of the weight of fibre, and the dye must obviously be largely deposited from solution, although a proportion of the water may continue to solvate the dye. The form assumed by the dye when the water is largely removed will obviously influence the light fastness. The dye may perhaps aggregate. In certain cases the crystals or aggregates so formed may be relatively small: the present results suggest that they may be well below optical microscopic size. Preston and Morton have recorded the behaviour of (air-dry) dyed cellulose fibres observed under the microscope, in polarised light. Morton concluded, by observations on solid dyes and streaming dye solutions, that direct dye molecules are attached lengthwise, i.e. with their long axes parallel to the cellulose molecular chains, and that in the solid powder or crystals they are arranged with their long axes across the length of the crystal.

Astbury and Dawson detected evidence of dye crystallites in samples of dry wool fibre dyed with a few acid dyes (Solway Blues) by X-ray examination. In other cases no such evidence was obtained, but the possibility of amorphous aggregates being present in these cases may not be ruled out. Speakman and Smith also noticed the presence of free particles of solid dye, large enough to be readily visible under the microscope, in wool dyed at 60.5°C. with Solway Blue SEN in presence of sulphonated castor oil. No particles appeared in fibres dyed at 97°C. Royer and Maresh reported similar observations.

Fading reaction orders.

In the normal dye-substrate system only these molecules in direct contact with the atmosphere can take part in the fading reaction, air and/or water, as already stated, being essential participants in the reaction. The reaction order of fading may, therefore, be determined by the absorption of the active radiation by the dye present in the interface, and will not necessarily decrease with increase in the total dye concentration, as would be the case in an "ideal" system. The order may remain constant, additional dye going to increase the dye-particle size without very much affecting the size of the interface, and it may be called the "apparent reaction order". This is a characteristic parameter of the dye-substrate system, but it bears no necessary relation to the order determined by studying the rate-of-fading curve for a single concentration of dye on a substrate. The latter may be referred to as the "real reaction order" and is likely to commence at a value somewhat below unity, and steadily fall towards zero as fading progresses, the smaller dye particles disappearing first, with a resultant steady decrease in surface/weight ratio, until only the largest particles are left, which have a reaction order approaching zero. In the case of a dye fading in a true molecular dispersion under uniform irradiation, a third order may be defined, the "ideal reaction order".

The three reaction orders thus defined have the same numerical value, i.e. unity, where the dye is spread as a true monolayer in the substrate and only a small proportion of the active incident radiation is absorbed. The real reaction order then remains constant throughout irradiation, because no change in average particle size can take place.

The work discussed in the following sections is designed to demonstrate how the features of the CF curve may give information upon the physical state of the dye. To preserve the continuity of the discussion, some of the work included is that of the author's former colleague, Dr. N. Macaulay (see "Acknowledgements").

Characteristic fading curves.

In the present work the results are demonstrated as characteristic fading (CF) curves in which the ordinate is the logarithm of the time t_F in which a given small percentage (10% usually) of the initial quantity of dye is lost by fading, and the abscissa is the logarithm of the initial concentration C_0 of dye in the substrate.

For a dye behaving as an ideal photochemical system, i.e. as a monolayer spread over the internal surface of the substrate or as a molecular dispersion, the CF curve will have a slope of zero. With a view to demonstrating further how the features of the CF curve may give information upon the physical state of the dye in the substrate, certain water-insoluble dyes were faded in markedly different states of dispersion, or aggregation, in transparent films.

(a) The fading of dispersions of merocyanine and azo dyes.

A merocyanine dye (Ia) and an azo dye (XXII), each in a series of markedly different states of dispersion, were faded in transparent films prepared as described previously (page 57).

In all the films of series (a) and (b) (page 57) particles were easily visible under the microscope(Fig.11A.B), but none could be seen in the collodion films of series (c).

The CF curves for the merocyanine dispersions in gelatin have virtually a zero slope (Fig.10), whilst those in methyl ethyl cellulose have a slight positive slope, as also has the azo dye dispersion in methyl ethyl cellulose. There is probably some differential migration of particles during the drying of these latter films. The curves for the azo dye-collodion films have a more pronounced slope than any of the above systems. Further, the rate of fading increases, i.e. the y-axis intercept of the CF curve falls, with increase of surface/weight ratio of dye (as judged visually under the microscope).

In systems of this nature, with a wide range of particle-sizes in the substrate, the fastness measured by the present method is obviously largely determined by the rate of fading of the smaller particles, which are probably invisible in the illustration (e.g. Fig.11A). The largest would fade at a much slower rate than that observed. It is noticed, for example, that fading is much more rapid in the earlier stages of the irradiation than later.

(b) The fading of soaped and unsoaped azoic dyes.

Regenerated cellulose films (Cellophane) dyed with typical azoic combinations were faded in the unsoaped state and after soap-boiling. The soap-boiling was sufficient to cause the growth of particles in the film which were visible under the microscope, no particles being visible before this treatment (Fig.12 A,B). The expected increase in light fastness with the soap-boiling is obtained in each case (Fig.13 and 14), the fastness for any given depth of dyeing being in fact approximately doubled by this process. Even on allowing a film to soak in cold water overnight, a slight change in the CF curve is observed (Fig.14). The changes in the slopes of the curves are only slight in all cases.

Theoretical model of the light fading of a dye deposited on a solid substrate.

As mentioned previously (page 68), the fading rate is probably determined by the extent of the air-dye interface, i.e. the surface/weight ratio of the dye. On the basis of observations made in this and previous work, a theoretical model system will be developed, representing all dye-fibre systems, whether the dye is soluble in water or not.

The dye is considered to be present in the substrate as a series of discrete particles (see Fig.15) 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 changes with increase in concentration will now be discussed with respect to three types of idealised systems.

(a) Uniform Particle-Size Distribution System.

This system (Fig.15 A) 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 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 reaction thus has an "apparent" first order and the CF curve is a horizontal line (Fig.16 a).

As observed previously, the merocyanine and azo dye dispersions give CF curves with slopes nearly or quite zero, confirming the predictions of the above system.

(b) Constant Particle-Concentration System.

The dye particle may expand symmetrically as more dye is added, thus retaining the same shape (Fig.15 B). 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 theoretical slope of the CF curve can be calculated.

The amounts lost from each of a series of cubes, e.g. of initial weights 2, 4, 5 and 8 units, when 10% has been lost from a cube of unit weight, are thus respectively 7.95, 6.3, 5.85 and 5.0% of the total, and the corresponding times for 10% loss (t_F) can then be determined from the first-order relation. This enables the CF curve to be plotted.

(c) Unsymmetrical Particle-Growth System.

In this system (Fig.15 C) 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.

To calculate the theoretical slope of the CF curve, a graphical method is used to determine t_F for a 10% fade; assuming, say, 0.1 unit loss in 1 hour from unit weight, the first-order relation is used to determine the times required for 0.2, 0.3, etc. unit, these then being the corresponding t_F values for initial weights of 2, 3, etc. units.

If a system is found to have a linear CF curve with positive slope, it follows that aggregated particles are probably present. Further, if it is supposed that some treatment is applied to a dye-fibre system which causes no chemical change, but which promotes physical aggregation of dye particles, the surface/weight ratio of the dye will be reduced and the light fastness raised at all concentrations. The CF curve of the system $p_1 q_1$ (Fig.16) is therefore raised, but its slope may decrease, increase or remain constant, giving, say, curves p_2q_2, p_2q_4, p_2q_3 respectively.

If the dye particles in the upper concentration ranges are already approaching a size limit determined by their own crystal habit or by restraints imposed by the structure of the substrate, the higher the concentration the fewer the number of particles there are which grow. This results in a decrease in slope of the CF curve.

Where the dye becomes aggregated more readily at the higher concentrations, its particles being closer together, an increase in slope of CF curve results. The slope of the CF curve remains constant where the dye shows a uniform tendency to aggregate at all concentrations. Any treatment causing purely physical disaggregation will have the reverse effects on the CF curves.

The case of a CF curve with a negative slope has not been encountered in any system examined. A negative slope would of course mean that the dye aggregates more at low than at high concentrations.

It is possible to envisage conditions which would lead to a CF curve of slope greater than the highest calculated on the above theory. Such a slope would imply that the air-dye interface actually decreased with increase in dye concentration. This could perhaps occur if very large dye aggregates formed, forcing apart the substrate molecules which lie around them, so far that in other regions containing no dye these molecules are drawn together. Thus the substrate pores, even those not containing dye, would be reduced in size and access of air, etc thus retarded.

Indirect tests of the theoretical model systems.

This section comprises indirect tests on water-insoluble dyes, but it is extended to determine whether the theoretical model can be applied to water-soluble dyes.

Water-Insoluble Dyes.

Anthraquinonoid vat dyes on nylon.

Nylon film dyed with two vat dyes before and after treatment with a swelling agent (cinnamic acid), gave CF curves which were higher in the treated film, due, perhaps, to the more ready growth of large dye particles when the fibre is swollen (Fig.17).

Indigoid vat dyes on cellulose.

In view of the observations of Sumner, Vickerstaff and Waters (page 68), two indigoid vat dyes were applied to Cellophane film, and the dyeings were examined both untreated and after soaping. Indigoid dyes of relatively low fastness were chosen because of the exceedingly lengthy exposures which would have been required with vat dyes of normal high fastness on cellulose. The CF curves appear to demonstrate an increase in surface/weight ratio after soaping (Fig.18 and 19). This is in good agreement with the results of Sumner *et al*. as discussed on page 68 above.

Lakes of basic dyes with complex acids.

No conclusive explanation has been given for the considerable improvement in light fastness exhibited by basic dyes when irradiated in the form of lakes with certain complex inorganic acids, e.g. molybdophosphoric acid, although this improvement has long been known. The CF curves for Victoria Blue BO (Fig.20) are consistent with the lake being more aggregated (at least at higher concentrations) than the untreated dye. The alternative suggestion that the improved fastness is due to a chemical change in the dye molecules is difficult to justify, because only the nature of the gegenion of the dye cation is changed, and not the chromophoric system.

Water-Soluble Dyes.

Previously reported work (see page 69) seems to indicate that there is a distinct possibility that water-soluble dyes are present as aggregated particles in air-dry substrates. The presence of aggregates is investigated in the present work by examination of the slopes of the CF curves of water-soluble dyes and comparison of their light fastness on substrates of different porosity but of the same chemical nature. In this connection, three such substrates have been used, viz., films and fibres of regenerated cellulose, and anodised aluminium. It is to be expected that, if the dyes aggregate, an increase in pore size may promote the formation of larger particles with a consequent increase in light fastness. If the dye is present in the substrate as a monolayer however, an increased porosity of substrate would cause no increase in light fastness for a given concentration of dye.

Direct cotton dyes on regenerated cellulose films of different porosity.

The two types of "Cellophane" regenerated cellulose films used were normal dried film and gel film of higher porosity, which had not been dried after coagulation. The respective pore sizes were stated to be of the order of 20 A and 30 A (British Cellophane Ltd.). The light fastness of both Chlorazol Sky Blue FF (I.C.I.) (C.I. 518) and Chlorazol Rose B (I.C.I.) is considerably higher at all concentrations on the gel film than on the normal dry material (Fig.21 and 22). Further, all the curves have a positive slope.

It may be implied from these observations that the dye is present at least partly in the form of aggregates, and also that the maximum size of these aggregates is determined by the porosity of the substrate. The fact that the gel film contracts when dried after dyeing does not appear to prevent the dye aggregates in it from growing larger than they do in the normal film, so that aggregate formation must precede this contraction. It may be that aggregation occurs during the adsorption process itself (direct cotton dyes have a pronounced colloidal nature)[xx], and if so the larger pore size gel film would be expected to contain more dye molecules per pore than the normal dry film, so that, when dried out, the pore sizes then being the same on both materials, more dye molecules per pore will be contained in the "gel" material.

It was observed that the "gel" film slowly reverts to the normal state on keeping, presumably by a process of slow crystallisation of the cellulose. Dyeings on material which had been stored for several weeks, in the wet state, had no significantly higher light fastness than those on normal film. (Fig. 23 and 24).

Direct cotton dyes on viscose rayon of different degrees of crystallinity.

The two series of viscose rayon staple-fibre fabrics used in this work were similar in construction, but were prepared from filaments of different degrees of crystallinity.

As mentioned previously (page 47), a linear relationship was observed between the logarithm of the dye content of the fabric and the logarithm of the reflectance (Fig.25-28). As a result, any given percentage gain of reflectance will

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[xx] Modern theory suggests that the dyes form monolayers only (Morton) but all the reported experimental facts could just as readily be explained by the formation of multilayers (Giles, private communication).

represent a constant loss of dye at any concentration, and in the present work reflectance gains corresponding in each case to 10% loss of dye content have been used in determining t_F values. Further, it was found (see Fig.28) that the relationship between concentration and reflectance altered only very little when two fabrics were irradiated until considerably faded, so that the use of reflectance values in this way is considered to be fully justified.

As anticipated, the results demonstrate higher fastness for each dye on ordinary viscose rayon than on the more crystalline Durafil (Fig.29-32). A Tenasco-type fibre gave an intermediate fastness in one case as expected (Fig.31), but in another (Fig.30) it resembled ordinary viscose rayon.

In these tests the dyeings of lower fastness were obtained on the Durafil fibres with a much finer filament than those of the normal viscose rayon. The fastness differences persist, however, even when all the fibres varieties have almost the same filament size (Fig.31), so that they cannot be attributed to any effect of differences in external surface areas of the fibres.

Acid wool dyes on the anodic film on aluminium.

The anodic films consist essentially of $\underline{\gamma}$-alumina (Al_2O_3), that prepared in chromic acid being substantially pure, whereas the sulphuric acid film contains up to 13%

aluminium sulphate, which, it is assumed, will not affect the present results. The sulphuric acid film, however, is much more porous, as is demonstrated by the dyeing times recorded for two mordant dyes which were obtained under identical conditions of agitation, etc.

Rates of Dyeing of Anodic Films on Aluminium

Temp. (^{o}C.)	Film and Dyeing Times	
	H_2SO_4 film	H_2CrO_4 film
	$t_{0.5}$	$t_{0.5}$
	Alizarin Red IP (I.C.I.)(C.I. 1027)	
40	10.0	34.0
60	5.2	11.0
75	2.4	-
80	-	9.0
	Solway Blue BNS (I.C.I.)(C.I. 1054)	
20	-	16.0
40	4.5	12.0
60	2.5	8.0

$t_{0.5}$ = Time (hr.) of half-dyeing.

The CF curves (Fig.33) show rather a wide scatter of points, due to experimental difficulties, but there is no doubt that both acid dyes used show higher fastness on the more porous film.

This work is confirmed by data in a list of seventeen commercial dyes in "full" shades (I.C.I.), each dye having a higher fastness grading on sulphuric acid film than on chromic acid film, the mean fastness grades being about 7 and 5 respectively.

Examination of possible disaggregating treatments.

The application of a cationic fixing agent and of a crease-resisting treatment respectively, are known to reduce the light fastness of many direct dyes on cellulose. The two processes were examined here to consider the possibility of some physical effects being involved. The crease-resisting treatment may reduce the fastness through some chemical reaction between the dye, fibre and, e.g. formaldehyde, but in the case of the fixing agent, the possibility that chemical reaction is responsible for the reduction of fastness seems remote. The first-named treatment may cause a blockage of the fibre pores with resin, with a resultant reduction in the size of any aggregates present. The fixing agent may interfere with the crystallisation of the dye, the larger cation disturbing the crystal lattice structure. Further, some cationic agents are surface-active and thus may act as dispersing agents.

The change in the CF curve of Durazol Red 2B (I.C.I.) on viscose rayon after crease-resisting treatment (Fig.34) is consistent with a reduction in aggregate size as suggested above. Two typical direct cotton dyes showed reduction in light fastness after treatment with cationic agents (Fig.35 and 36) and the change in their CF curves and in the corresponding light absorption curves (Fig.37 and 38) are quite consistent with the reduction being due to disaggregation effects.

<u>Alternative explanation of slopes of CF curves</u>.

In the present work the positive slope of the CF curves has been interpreted as being an indication of the presence of discrete particles or aggregates of dye in the substrate, the proportion of larger particles increasing with the total dye concentration. It is necessary, however, to consider alternative explanations for the nature of these curves, assuming in each case that no aggregated material is present, all adsorbed dye being present as monolayer.

The positive slopes of the CF curves might be considered to be due to a screening effect by virtue of which the molecularly dispersed dye molecules become more tightly packed together with increasing concentration. In this way they would become less accessible to irradiation and an increased light fastness would result. In this case, however, the CF curves would not be linear, but would be nearly horizontal at very low concentrations and then would steadily rise. In fact, curves of this type have been observed (Fig.10 and 49), but only in collodion where it is possible that the dye is in a form of solid solution.

The only other alternative explanation of the positive slopes would seem to be that as the pores of the substrate become more nearly filled with dye, light and/or air and moisture are less able to reach the dye, even though it may be present as a monolayer. If this were the case, then the light fastness of a dye at a given concentration would obviously fall with increase in pore size of the substrate, whereas actually it increases (cf. Fig.21,22,29-33). Further, if this hypothesis were correct, the CF curves should always have positive slope, and in a homologous series of dyes the slopes should be either the same, or increase with length of alkyl chain, when the molecule becomes more bulky. This however, as will be shown below, is by no means the case.

It would seem that the first-mentioned interpretation of the positive slope of the CF curves is the most acceptable, being in good agreement with almost all experimental data.

The validity of the theoretical model.

The slopes of almost all the CF curves so far obtained lie within the theoretical limits of 0 and +1.4, implying that with increase in concentration the total dye surface increases more rapidly than does the photochemically active surface. This may be explained if the faces of the dye crystal are not all equally reactive, and/or the crystals grow so that they block the pores of the substrate and only the dye surfaces at the "open" ends of the pores are in contact with air and water vapour.

The validity of the model system is further demonstrated in that dye dispersions known to have uniform size distribution give CF curves of zero slope or nearly so; and that such curves cut the y-axis higher as the average particle-size increases, whether the particle-size distribution is uniform or not (Fig.13 and 14).

Fig.39 and 40 show two typical groups of fading-rate curves, for sets of transparent films and viscose rayon fabrics respectively.

The relationship between the light-fading and the surface-activity of dyes.

Many dyeing processes involve insolubilisation of the dye, and aggregated particles, often submicroscopic, are then formed. If the dye remains in a water-soluble form throughout, however, it is not yet clear how aggregates originate. They may, of course, build up by multilayer formation while the dye is being adsorbed from the aqueous solution; but even if the dye is adsorbed only as a monolayer, the complex equilibria involving dye, water and substrate will be disturbed in the subsequent drying process, possibly causing some degree of aggregation. Whichever of these processes occur, or if both occur together, the physical state of the dye in the dry substrate, and thus its fading characteristics, should be markedly affected by the degree of its surface activity.

The next section of this work was therefore designed to examine the influence of the surface-activity of dyes produced by alterations in the size and form of their hydrophobic residues, and the position of their ionic groups, upon their light fastness, on the basis of the theoretical model system as defined in the previous section.

The dyes used (see page 60) were selected in series of two or more, of the same fundamental constitution, but differing in the relative size and/or position of the hydrophilic and hydrophobic portions of their molecules, and thus in surface-activity. In certain cases a surface-active cationic agent (cetyltrimethyl ammonium bromide) was added to the dye to enhance its ability to spread as a monolayer.

As mentioned previously (page 36) dye fading appears usually to take place by reduction if the substrate is a protein, and by oxidation if it is one of a variety of other materials, including cellulose and its derivatives. Gelatin and methyl ethyl cellulose ("Cellofas A", I.C.I.) were used here as typical protein and non-protein substrates respectively.

Linear relationships have already been shown to exist between the rates of fading, and of oxidation and reduction in solution, of a series of azo dyes at a given concentration and the Hammett $\underline{\sigma}$-values of the substituents (Chipalkatti et al.). This shows that the rate-determining step in fading is probably the chemical reaction causing breakdown of the chromophoric centre, viz., the azo-group.

The relative fading rates of any series of dyes should bear a direct relationship to their rates of reduction (for fading on proteins) or oxidation (for fading on non-proteins) provided they do not differ much in either light absorption characteristics or physical form in the substrate. In the present work, the dyes compared have very similar light absorptions (e.g. Fig.42), so that no differences in the relative amounts of effective fading radiation absorbed need be considered. Moreover, the attachment of an alkyl chain to the aromatic nucleus would not be expected to influence greatly the intrinsic reactivity of the dye-molecule, so that any marked changes in fading-rate produced by changes in an attached alkyl chain must be ascribed to physical effects. Any such effects would be expected to differ in sense if the dyes are wholly present as monolayers or as heterogeneous systems.

The influence of the surface-activity of dyes upon light fastness.

The addition of an alkyl chain to any dye present wholly as a monolayer in a substrate would be expected either to have no effect on fading, or to retard it, by more effectively blocking the pores of the substrate against entry of air and moisture. The blockage would either be a result of the increased molecular size or perhaps also of the enhanced hydrophobic property of the dye, the retardation of fading becoming progressively more noticeable with increase in length of the alkyl chain. Further, if fading were retarded, it would also be expected that the slope of the

CF curve would always progressively increase with size of the attached residue.

If however the dyes are present in the substrate as discrete particles, then the addition of a hydrophobic residue might have certain noticeable effects on fading rate. Small residues might increase the tendency to aggregate, larger ones might decrease it, by increasing the stability of a 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.

It might be anticipated also that the position and number of sulphonate groups in the dye-molecule would influence fading by affecting the size and shape of the aggregated dye in the substrate.

Cameron, working in this laboratory, has made a parallel investigation into the monolayer-forming properties on water of many of the dyes used in this work.

The physical state of dyes and their fading rates.

The effects upon fading rate of changes in the physical state of dyes are now considered with reference to Fig.43. The progress of fading of a dye in a solid substrate will vary according to its physical state of dispersion, provided the illumination and conditions of exposure remain constant.

Fading of any given concentration of dye will follow the first order law (Fig.43 A) when the dye is present as a molecular dispersion, or a monolayer spread over the internal surface of the substrate, only a small proportion of the photochemically active radiation being then absorbed. The fading of a solid solution of certain dyes in collodion and of a highly surface-active water-soluble dye in methyl ethyl cellulose or gelatin demonstrates first-order fading (Fig.44 and 45).

When the dye is present in the substrate wholly as large solid particles, however, zero order fading will take place (Fig.43 B), because only the molecules of dye at the surface of the aggregates are accessible to oxygen and moisture. As these dye molecules are destroyed, the surface of the aggregates breaks up and successive fading of deeper layers occurs. This is illustrated by the rate curve for a solid dye powder mechanically incorporated in a film-forming colloid and dried out (Fig.46).

If the dye is present as a heterogeneous system ranging from dye as a monolayer to aggregated or crystalline dye, then the course of fading will be more complex, and a curve of the general form shown in Fig.43 A,B will result. The

The initial portion of the curve (section A) represents the first-order fading in the monolayer, and section B, the subsequent zero-order fading of the aggregates. Most of the dye-substrate systems in the present work give curves of this latter type (Fig.47), this being considered to be evidence of the heterogeneous physical state of the dyes.

The fading in gelatin of two sulphonated anthraquinone blue dyes of a type similar to those which Astbury and Dawson found to be crystalline in wool show an initial rise in optical density (Fig.48) due, perhaps, to some disaggregation in the heat of the illuminant. The subsequent fall in dye concentration approaches zero order in nature. Barker, Hirst and Lambert (1927) observed that the rate of fading of dyed wool followed a zero-order law.

Where a comparison between the CF curves for two dyes suggests a difference in their state of aggregation, that dye with apparently the higher proportion of monolayer should give fading curves in which the portion A (Fig.43) is more noticeable. Further, the higher the value of the loss of dye for which the t_F values are calculated, the greater is the slope of the CF curve likely to be, because the amount of fading of aggregates is then likely to increase.

DISCUSSION OF RESULTS.

Dye-series I.

A series of tests with water-insoluble merocyanine dyes (Ia,b) in films formed from collodion solutions, show that the fading rate is not influenced by the length of the attached alkyl chain (Fig.49). The fading is remarkably rapid, which fact together with the first-order form of the rate curves (Fig.44) suggests that the dyes are all in the same condition of molecular dispersion in the film.

Dye-series II and III.

Collodion films of dyes II, IIIc and IIId were tested and compared with dye II in films made from aqueous alcoholic methyl ethyl cellulose solution (Fig.51). The two C_{12} dyes (II and IIId) are probably largely monodispersed in collodion, with IIIc less so, whereas dye II in methyl ethyl cellulose is largely present as minute particles or aggregates. The CF curves show that dyes II and IIId fade at very similar rates in collodion, IIIc less rapidly and II in methyl ethyl cellulose less rapidly still. These differences in physical form are reflected further in the shape of the fading rate curves (Fig.41).

Dye-series III.

The fading data of dye-series III (Fig.52-55) show that the curve for IIIc has a much steeper slope on both gelatin and methyl ethyl cellulose than the others in the series. In fact, the slope of the curve for IIIc rises above the theoretical maximum of 1.4. The only explanation which can be offered for this apparently anomalous behaviour is that the extent of the air-dye interface is progressively reduced by the products of the fading reaction adhering to the surface of the dye-aggregates. The other curves, with one exception, (IIId on methyl ethyl cellulose), have positive slopes of less than 1.4, implying a non-uniform particle-size distribution. IIId has a zero slope on methyl ethyl cellulose, together with the highest light fastness of the series on that substrate, which implies that it has a uniform particle-size distribution. Further, it is noticeable that as the percentage loss of dye for which t_F is calculated is reduced from 10% to 5% there is a tendency for the curves to flatten at lower concentrations (Fig.52 and 53, IIIc,d), whilst t_F for a 2.5% loss of dye gives a curve of zero slope for IIId and considerably reduces the slope of that for IIIc (Fig.54). This may indicate that as the value of the loss of dye for which t_F is calculated is decreased, the amount of fading of aggregates is also likely to decrease (see page 94).

Dye-series IV.

Both the gelatin and methyl ethyl cellulose films of dye-series IV show positive slopes of CF curves (Fig.56 and 57), those of the gelatin films being slightly steeper generally. The addition of a surface-active cationic agent to the dyes reduced their light fastness on gelatin, more so perhaps with the C_{12} sidechain dye (IVc). The data for the C_4 sidechain dye(IVb) with the cationic agent are less reliable, there being a tendency for the films to peel off the glass plate on drying, but here also there is a tendency for a reduction in light fastness. The slope of the CF curve for the C_{12} dye also flattens slightly, the cationic agent tending to reduce the dye-aggregation.

Dye-series V and VI.

The positive slopes of the CF curves for the dye-series V and VI are most noticeable (Fig.58-61), although there is a tendency for the curves to flatten with the dyes of lower fastness. The dyes with the hydroxy-group *ortho-* to the azo linkage tend to be faster to light than the *para*-hydroxy dyes, especially on gelatin. It has been noted previously (Atherton and Peters; Kienle *et al.*) that substituent groups *ortho-* to the azo-group, if they can act as hydrogen-bond donors, e.g., amino- or hydroxy-groups, appear to improve light fastness on both protein and non-protein substrates. Atherton and Peters suggested that the azo-group was protected by the chelate ring thus formed. The general effect of increase in sidechain length in series V and VI is either to reduce the light fastness or to have no effect.

Dye-series VII.

Dye VIIb has a CF curve of positive slope on both substrates but the gelatin curve is much the steeper (Fig. 62 and 63). The shorter sidechain dye (VIIa) on gelatin has a flatter curve, whilst on methyl ethyl cellulose it is steeper than that of dye VIIb. On both substrates the dye VIIb has a lower light fastness than VIIa, which is further reduced on gelatin by addition of the cationic agent, the slope also being reduced. On methyl ethyl cellulose the cationic agent has the effect of steepening the CF curve of both dyes with no reduction in light fastness in the case of the shorter sidechain dye.

Dye-series VIII.

Very low light fastness is shown by dyes VIIIa and VIIIb on both substrates (Fig.64 and 65) and the CF curves are flat at low concentrations, the slope increasing with concentration. These two observations suggest that the dyes are present in the substrates as molecular dispersions, or nearly so, and that fading therefore follows the first order law. This is confirmed by the plot of log. concentration (as Optical Density) against fading time (Fig.45). The lowest fastness of the series is shown by the shorter sidechain dye (VIIIa) on gelatin. It may be that this dye is in true molecular dispersion, whereas in the systems showing higher fastness the dyes may be present partly as micelles. The cationic agent reduces the fastness of dye VIIIb on gelatin, but on methyl ethyl cellulose it increases it, as it also does in the case of VIIIa on gelatin. The fastness improvements in the latter two cases are difficult to interpret, but the following explanation is tentatively offered.

The addition of a cationic agent to an anionic dye may either cause it to spread as a monolayer, or to aggregate in the form of mixed micelles, or both. If the dye is already present as aggregates, the production of some additional monolayer material will tend to cause a decrease in light fastness. If, however, the dye is almost wholly present as monolayer already, then the agent may cause an increase in fastness by micelle formation. It may be significant that the dye VIIIb which is improved in light fastness by the cationic agent is also caused to flocculate out of solution (on long standing) in presence of this agent.

In order to examine the effect of dyeing rather than casting, gelatin films were hardened and rendered water-insoluble as described previously (page 48). Films were then dyed with VIIIa and VIIIb at 60°C. with no additions to the dyebath, to facilitate dyeing. Under these conditions VIIIa had the same light fastness as it had when cast in methyl ethyl cellulose films, but VIIIb showed a remarkably improved light fastness (Fig.66) compared with the results for cast gelatin and methyl ethyl cellulose films. Transparent nylon film was then dyed at 90°C. with these two dyes and whilst VIIIa showed the same light fastness as when dyed on hardened gelatin, the fastness of VIIIb was almost halved on nylon. In an investigation upon the colloidal behaviour of dyes in solution, Alexander and Stacey concluded that dyes having sulphonate groups situated at one end of a long non-polar chain may form micelles in which the ionised groupings extend outwards while the hydrophobic portion of the molecule is within the micelle, as in a high molecular weight soap. These micelles are stable in solution to temperatures up to 60°C. This may be the case with dye VIIIb, its molecular structure satisfying the above conditions for micelle-formation. The gelatin and methyl ethyl cellulose solutions are possibly heated to a temperature of the order of 70-80°C. in drying, which, together with the colloidal nature of the film-making materials, may largely break up the micelles, giving a low light fastness.

Dye VIIIb dyed both the hardened gelatin and nylon films very rapidly, having a high affinity for these substrates, possibly by the attachment of micelles of dye, which would be larger the lower the dyebath temperature.

Dye IX.

Dye IX has very steep CF curves on all substrates which, together with the very high fastness compared with the dye series VII and VIII, may indicate a high degree of aggregation (Fig.67).

Dye-series VII, VIII and IX.

The basic structures of VIIa, VIIb and IX are very similar to each other and to series VIII, so that fastness differences could be accounted for by the first-mentioned dyes being aggregated in the substrate. There is, however, a considerable difference in their spectral absorptions. To find out whether this could account for the fading differences the dyes VIIIb and IX were exposed for fading behind Chance colour filters transmitting light of wavelength 4358 A. At this wavelength however the dye which was very much more fast to light (IX) absorbed more radiation from the fading lamp than the more fugitive dye (Fig.68), but here also dye VIIIb was considerably more fugitive. The explanation of the fastness differences would therefore seem to be that the faster-to-light dye is more aggregated than the other. There are also no apparent chemical factors likely to influence the fastness in the above fashion, because the more fugitive dyes have two hydroxy-groups ortho- to the azo-linkage which would tend to improve fastness whereas the faster-to-light dyes have only one.

Dyes X, XI, XII and XIII.

Dyes XI and XII, having C_{17} sidechains, give almost horizontal CF curves, and light fastnesses lower than their corresponding dyes X and XII, of shorter sidechain length (Fig.69). In view of their relatively high light fastness, the low slopes of the CF curves for dyes XI and XIII may indicate a system in which the relative abundance of particles of each size is the same at all concentrations, i.e. a monodisperse system of micelles.

Dye-series XIV, XV and XVI.

Dyes XIVa and XIVb have an identical light fastness, giving a CF curve of very low slope (Fig.70). The slopes of the curves for dyes XVa and XVb are fairly steep and the C_{12} sidechain dye has a lower fastness, much more marked on methyl ethyl cellulose (Fig.71). The dyes XVIa and XVIb have a very similar light fastness but the C_4 substituted dye gives a curve of steeper slope (Fig.72). From these data it would seem that a sidechain of length C_4 is not sufficient to confer any high degree of surface activity upon a dye, although it may increase the tendency to aggregate at higher concentrations.

Dye-series XVII and XVIII.

Dyes XVIIa and XVIIb give a CF curve of positive slope on both substrates (Fig.73 and 74) and the CF curve for 5% loss of dye on gelatin is slightly flatter. On both substrates dye XVIIa has a lower light fastness than XVIIb, more marked in the case of gelatin as substrate. Very steep CF curves are shown by dyes XVIIIa and XVIIIb on gelatin (Fig.75), but dye XVIIIa on methyl ethyl cellulose gives an almost flat curve, that for dye XVIIIb being slightly steeper (Fig.76). The CF curve for 5% loss of dye on gelatin shows a very steep slope also for both dyes. On both substrates the dye XVIIIb is faster, the difference being much more marked on methyl ethyl cellulose. It was observed previously (page 95) that sulphonation makes almost no difference to fading on hydrophobic substrates (see Fig.51, dyes II and IIId). This may confirm that the sulphonate group has an effect on monolayer formation in aqueous media, in view of the differences in fading rates encountered above, and, further, that the effect of that grouping in the molecule on the fading rate is not by direct chemical means.

Dye-series XIX.

The steeper slope of the CF curve for dye XIXa compared with those for the dyes XIXb and XIXc is most striking (Fig.77), the latter two dyes giving curves of almost identical slope, dye XIXb being considerably more fast to light. The superior fastness of dye XIXb may result from some measure of protection of the azo-linkages by the ortho-methyl substituents. The most symmetrical dye XIXa, which also has two methyl substituents ortho- to the azo-linkages, would be expected to show similar light fastness to that of dye XIXb, whereas at low concentrations it is similar to dye XIXc. This may perhaps indicate that the fastness differences between XIXb and XIXc are a result of differences in dye-aggregation only.

Dyes XX and XXI.

The slope of the CF curve for dye XX shows a spectacular drop from 10% to 5% loss of dye, whereas dye XXI, having a sulphonic acid group at either end of the molecule, gives a CF curve for 5% loss of dye which, by comparison, is only slightly lower than the curve for 10% loss (Fig.78). These data may indicate a tendency for monolayer formation in the case of dye XX which has two sulphonate groups at one end of a long, straight molecule, whereas the symmetry of dye XXI making it unsuitable for monolayer formation would promote aggregation in the substrate. Dye XXI is also considerably faster to light than dye XX, the difference being more marked for 5% loss of dye, substantiating the above suggestion.

The light-fading of water-soluble dyes.

Photochemical reactions may be regarded as being anywhere between zero order and unity. As already discussed, in solution, the plot of log. concentration against log. t_F will result in a curve of zero gradient at very low concentrations, increasing to give a gradient of approximately 1.4 at high concentrations, where the fading rate is zero order.

This type of curve will not necessarily apply to the case of a dye dispersed in a fibre substrate, where there is the tendency for the formation of dye-aggregates. The CF curves of most of the dye-substrate systems examined in the present work are linear. This is believed to be a consequence of the presence of aggregated material, only a proportion of the total dye-weight being accessible to the fading agencies, the rate of increase of this proportion relative to increase of total weight of dye being low (see page 77). The curve is thus a virtually linear segment of the whole "ideal" curve, over normal concentration ranges.

Some of the water-soluble dyes give CF curves of very low slope, together with very low light fastness, facts consistent with their being present as a monolayer in the substrate. In most systems, however, the CF curves have a positive slope, implying a non-uniform particle size distribution, the majority of these curves having slopes of less than 1.4. In certain cases, however, a CF curve of low slope is consistent with the relative abundance of dye-particles of each size being the same at all concentrations. This applies where a relatively high light fastness is obtained.

If the percentage loss of dye for which the values of t_F are calculated is reduced from 10% to 5%, the resultant CF curve is often found to have a lower slope than the curve calculated on the basis of 10% loss of dye. As explained earlier (page 94), this may indicate that the amount of fading of aggregates has been decreased.

There would seem to be no systematic influence of chain length on the slope of the CF curve, but chain lengths of the order of C_4 tend to increase the proportion of larger dye-particles at higher concentrations, increasing the slope of the CF curve. That the slope of the CF curve does not progressively increase with size of the attached residue is a further indication of the presence of the dye as discrete particles (see page 91).

It is evident from the results that the tendency for monolayer formation is governed largely by the geometry of the dye molecule. Ideally, monolayer formation would take place with a dye having sulphonate groups situated at one end of a long, non-polar chain. Very rapid fading, an indication of molecular dispersion or monolayer formation, has been obtained, at least in the initial stages of irradiation, with several dyes whose molecular structures satisfy, to some extent at least, the above conditions for monolayer formation. In other cases where it was expected from the geometry of the dye molecule that the dye (e.g. VIIb) would tend to be present as a monolayer in the substrate, no such evidence was obtained (Fig.62 and 63). It would seem from the facts disclosed that the tendency for monolayer formation is also largely dependent upon the balance of certain intermolecular forces when the solvent (water) is removed. These forces include polar attractions and dispersive forces between substrate and dye molecules and, dependent upon which of these forces is predominant, the dye will tend to aggregate or spread as a monolayer on the substrate. The dye VIIb, mentioned above, was found to form a coherent, stable monomolecular film when spread on water (Cameron), as also did the dyes VIIIa and VIIIb which also have remarkably low light fastnesses.

In most dye-series one or other of the intermediate chain lengths decreases the fading rate, which would appear in these cases to pass through a minimum value. This is demonstrated by the curve showing the relationship between the time of fading of dye in a given concentration and the length of an attached alkyl chain (Fig.79), which at first rises with increase in length of chain, and then falls. The maximum changes position with change in the basic dye structures but appears usually to lie between chains of length C_4 and C_{12}, and dyes with C_{16} or C_{17} chains, of high surface activity, appear to show the most rapid fading.

There is little difference in spectral absorption between dyes of the same series with straight alkyl chains of different lengths when they are in solution in aqueous pyridine (Fig.42). It is suggested by Martin and Standing that aggregation of dye in aqueous pyridine is probably prevented by complex formation between the pyridine and the dye. Aqueous ethyl alcohol has been used in this work also (page 59) to prevent the aggregation of dyes in solution. The above authors suggest that disaggregation is due to the effect of alcohol on the dielectric constant of the solution.

When the dyes are cast or dyed in films for fading, however, there are slight differences in spectral absorption between dyes in the same series and also with increase of dye concentration in the film (e.g. Fig.80). The nature of these differences in spectral absorption is consistent with the aggregation of the dyes in the substrate. It has been shown (page 101) that differences in spectral absorption do not account for fastness differences between dyes of similar molecular structure.

Boguslovsky and Sadov have reported a relationship between light fastness on wool and the position of sulphonate groups in the naphthalene nucleus of benzeneazonaphthalene dyes. These groups are reported to have a beneficial effect on the light fastness in various positions in α-naphthol and β-naphthol dyes. It may be suggested that the position of these groups affects the size and shape of the dye-aggregates in the fibre.

In the present work, a dye having sulphonate groups located at one end only of the molecule tends to have a lower light fastness than one in which both ends are sulphonated. This is thought to be due to the promotion of monolayer formation by the favourable dye-symmetry.

The differences in fading rates in the various series of dyes could not in many cases be accounted for merely by differences in chemical reactivity of the individual dye molecules. This is evident from a comparison of the relative oxidation and reduction rates of the various series in solution with their fading rates in methyl ethyl cellulose and gelatin respectively (Table I). Neither can variations in light absorption account for the differences: in most cases the dyes compared have the same spectral absorption. Further, the exposures were made side-by-side under identical conditions, obviating the possibility of any variations in illumination, conditions of the atmosphere during irradiation or in the state of the substrate. That the differences do originate in the physical state of the dyes is demonstrated by the fact that they agree largely with the predictions made above for heterogeneous dye systems.

TABLE 1.

—— Relative Rates of Degradation of Series of Azo Dyes. ——

Dye.	Oxidation. (min.)	Reduction. (min.)		Methyl Ethyl Cellulose. t_F (hours)	Gelatin. t_F (hours)
IIIa	·01a^{2}	·23e^{3} ·16f^{6} 0·3g^{6}		3·2	3·2
IIIb	·01a^{2}	·25e^{3} ·70f^{6} 1·1g^{6}		9·3	5·5
IIIc	·01a^{2}	·43e^{3} ·70f^{6} 1·2g^{6}		5·1	175
IIId	3·0a^{2}	3·0e^{3} 1·0f^{6} 0·8g^{6}		21	95
IIIe	1·6a^{2}	$\not-$e^{3} 0·6f^{6} 0·4g^{6}		7·0	40
IVa	·20a^{1} 0a^{5}	36c^{1} 0·7b^{1} 1·2d^{5}		39	52
IVc	·14a^{1} 0a^{5}	1·3c^{1} 3·5b^{1} 0·9d^{5}		25	27
VIIa	0a^{2}	1·5c^{2}	·45l^{1}	53	83
VIIb	·06a^{2}	$\not-$c^{2}		22	130
VIIIa	0·1h^{1} ·08j^{4}	·03e^{1} ·05k^{6} 0·7g^{6} 5·0d^{4}	·83l^{1}	·15	·05
VIIIb	0·3h^{1} ·12j^{4}	$\not-$e^{1} 32k^{6} 0·5g^{6} 2·0d^{4}		·15	·43
IX			·33l^{1}	42	250
XIVa	2·0a^{1}	1·1b^{1}		450	—
XIVb	4·0a^{1}	1·7b^{1}		450	—
XVa	4·0a^{1}	2·2b^{1}		1250	610
XVb	1·2a^{1}	·27b^{1}		500	565
XVIa	1·8a^{1}	0·6b^{1}		—	470
XVIb	1·0a^{1}	1·8b^{1}		—	520
XVIIa	0·5a^{1}	3·0c^{1} 8·0b^{1}		1·2	2·7
XVIIb	0·6a^{1}	21c^{1} 2·2b^{1}		4·0	17·5
XVIIIa	·17a^{1}	5·0c^{1} ·05b^{1}		·65	130
XVIIIb	·33a^{1}	6·5c^{1} 0b^{1}		2·0	170

Details of oxidation and reduction tests:

1. 0·25cc. dye solution (·001M) + reagent, at room temp.
2. 0·50cc. " " " " " " " .
3. 0·10cc. " " " " " " " .
4. 0·25cc. " " " " + 2cc. Pyridine, at room temp.
5. " " " " " + 4cc. Ethanol, " " " .
6. " " " " " + 4cc. Acetone, " " " .

Reagents:

a. 8cc. (2·2%) NaClO; b. 8cc. (2·5%) $TiCl_3$; c. 8cc. (0·02%) $SnCl_2$; d. 6cc. (0·02%) $SnCl_2$;
e. 8cc. (2·5%) $Na_2S_2O_4$; f. 6cc. (0·2%) $Na_2S_2O_4$; g. 6cc. (2·5%) $TiCl_3$; h. 8cc. (5·0%) $K_2S_2O_8$;
i. 8cc. (5·0%) $Na_2S_2O_4$; j. 6cc. (2·5%) $K_2S_2O_8$; k. 6cc. (5·0%) $Na_2S_2O_4$; l. 8cc. (1·0%) Thiourea Dioxide.

0 Decolorisation too rapid to measure.

$\not-$ " " slow " "

CONCLUSIONS

The conclusions reached in the present investigation may be summarised thus:-

The theoretical model is shown to represent fairly well the nature of dye-particle growth with increase in concentration.

All normal dye-substrate systems in the air-dry state contain some of the dye in the form of discrete aggregates or crystals. The improvement in light fastness exhibited by a water-soluble dye when the porosity of a substrate is increased is attributed to the formation of larger aggregates of dye in the dry substrate.

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

The fading rate of these systems varies with concentration in a manner characteristic of the range of distribution of particle sizes of dye present, within the limits imposed by the theoretical model system.

Dye-substrate systems obeying the normal photochemical laws for ideal systems are comparatively rare and are found only in the case of water-insoluble merocyanine dyes in solid solution in collodion and possibly in certain hydrophilic substrates dyed with highly surface-active dyes. These systems show abnormally rapid fading and a low rate of decrease of fading rate with increase of dye concentration.

A dye molecule having a hydrophobic nucleus with the ionic group or groups located at one end tends to form a monolayer at a water interface (Cameron), and the present results show that the rate of fading is also increased thereby. This general principle appears to apply to all the series of dyes examined in the latter part of this work.

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§§§§§§§§§§§

Suggested further work.

(a) Examination of the light absorption spectrum before and after fading of a dye known to exist in solution, and therefore in cast films, both as the monomer and polymer.

(b) Examination of the fading of dyes shown to aggregate in the previous work, incorporating phenol or urea in the films.

(c) Examination of the light absorption curves of dyed hardened gelatin films when wet and when dry and also with addition of urea to the dyebath.

(d) Re-examination of the fading of the spun-dyed viscose material (Courtaulds Ltd.)

§§§§§§§§§§§

APPENDIX

The Light Fastness of Dyes applied as Pigments.

On the basis of the argument of the main part of this work it would be expected that any colouring matter applied in a range of concentrations as a pigment, where it is not in solution at any part of the process, should give a horizontal CF curve, i.e. the light fastness should not fall with decrease in concentration as it normally does. It is to be expected that high light fastness at low depths of colour will therefore be obtained by use of pigment dispersions rather than by a dyeing process. There are certain factors, however, which may tend to prevent equality of fastness over a range of concentrations of a pigment.

In the first place, adjacent particles may screen each other from the light to an increasing extent as the concentration rises, particularly if they are not evenly spread, as is very likely to be the case, clumps of dye being present. Thus a pigment dispersion may be more effectively aggregated at higher concentrations than at low, although the original particles remain the same size. In the mosaic screen process of colour photography an analogous case will be found in which a screen consisting of a printed reseau of colour rectangles is found to give a finer resolution in the image than one consisting of a random mixture of particles, even though these are individually finer than the rectangles of the reseau; the reason for this is that the particles form many irregular clumps, according to the laws of probability.

Secondly, differential migration of pigment particles may occur during the drying process, particularly in the case of films as used in this work. Thus in Fig.82 the pigments dispersed in methyl ethyl cellulose (Cellofas A, I.C.I.) films give a CF curve with slightly steeper slope than those in gelatin, because the latter sets more rapidly and so hinders migration. Further, two series of azoic-dyed viscose fibres were obtained (by courtesy of Courtaulds Ltd.), one series dyed by the normal method and the other spun-dyed (dye incorporated in the spinning process). The normally dyed material showed to some extent the expected regular increase in fastness with increased concentration (Fig.81). The spun-dyed material gave rather irregular results, due perhaps to practical difficulties in uniform irradiation and in reflectance measurement of the material in the form of unwoven yarn.

Some of the pigment itself was obtained and cast in gelatin and methyl ethyl cellulose films in the usual manner. Further, strips of Cellophane were dyed as described previously (page 50) with the components of the above pigment. The pigment dispersion in methyl ethyl cellulose gave a slightly steeper slope of CF curve than the gelatin films, as observed earlier. The azoic-dyed Cellophane, however, gave an almost flat CF curve and also a higher light fastness than both dispersions. The low slope of the CF curve indicates the growth of dye-particles of uniform size distribution, but it would have been expected that the light fastness would be lower in the case of Cellophane, the particles of pigment being assumed to be smaller.

Pigments used in paints are usually much less fast to light in pale shades than in deep (I.C.I.), and this may be attributed to the influence of other photochemically reactive ingredients (e.g. extenders) in the film, which are necessarily present in relatively increasing quantities with decreasing pigment strength.

It may be concluded, however, that pigment dispersions applied in films or to fibres do tend to give flatter CF or CFt (where fastness ratings are used instead of time for a given percentage fade) curves than dyes. This is shown in Fig.10, and for fibres, the data on Helizarin colours may be cited. It is clear (Fig.83) that the Helizarin pigments do give a much flatter CFt curve than the most comparable set of vat dyes, which are applied from solution. (These latter dyes were selected at random from the pattern card to have the same mean grade in deep shades as the Helizarin colours. They comprise Indanthren Yellow 7GK, 4GF, Orange RRTS, F3R, 4R, Red GG, FFB, Brilliant Pink BBL, Rubine GR, B, Bordeaux B, Turquoise Blue 3GK, Brilliant Green B, FFB, GG, Maroon BR, Grey RRH).

COMPARISON OF VISUAL AND SPECTROPHOTOMETRIC DETERMINATIONS OF FADE.

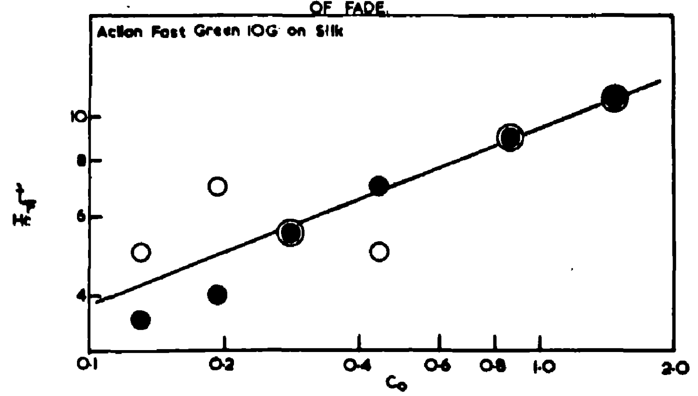


Fig.1

● Visual Detn.
○ Instrumental Detn.

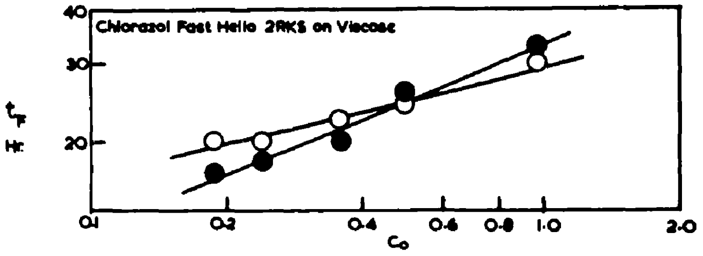


Fig. 2

● Visual Detn.
○ Instrumental Detn.

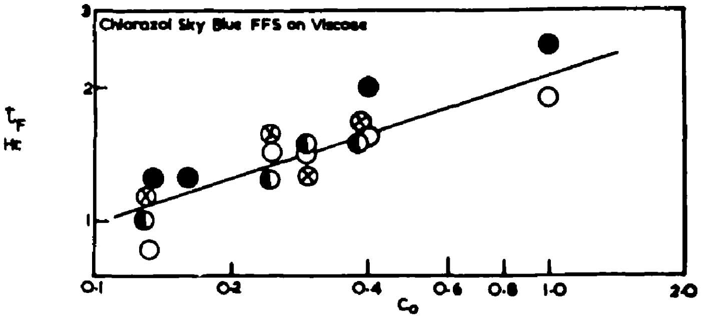


Fig. 3 Visual Detn.● Std. Fibro. ● R. imbib. Fibro.
Instrumental Detn.○ Std. Fibro. ● R.imbib. Fibro.

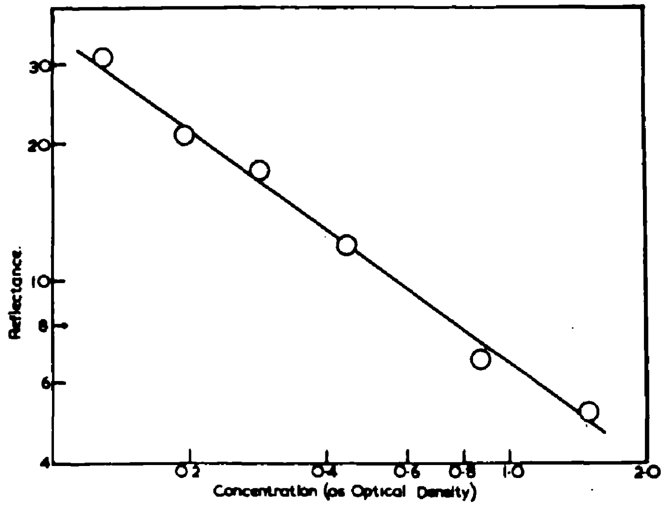


Fig.4 Relationship between Conc. of Aclan Fast Green IOG on Silk and Reflectance

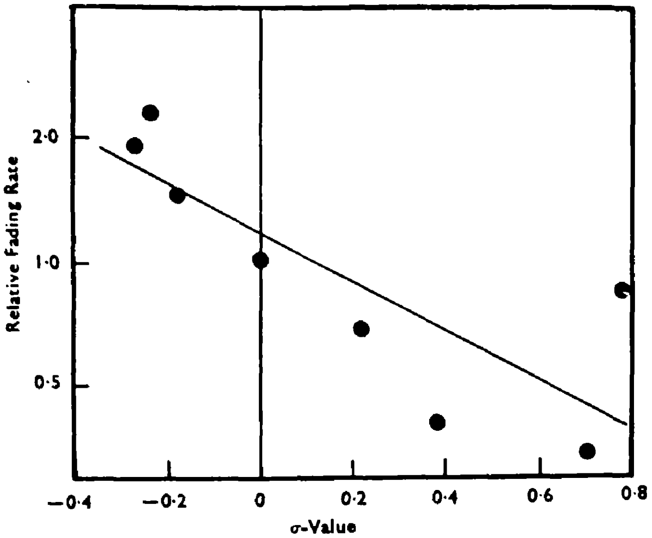


FIG. 5 – Anodised Aluminium

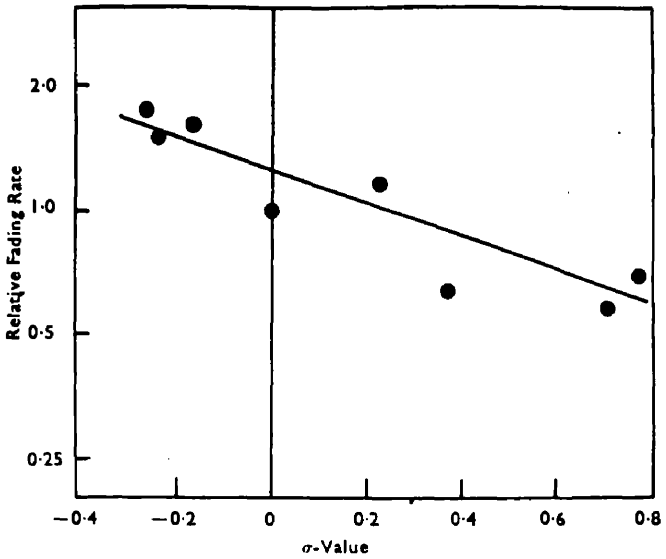


FIG. 6 – Asbestos

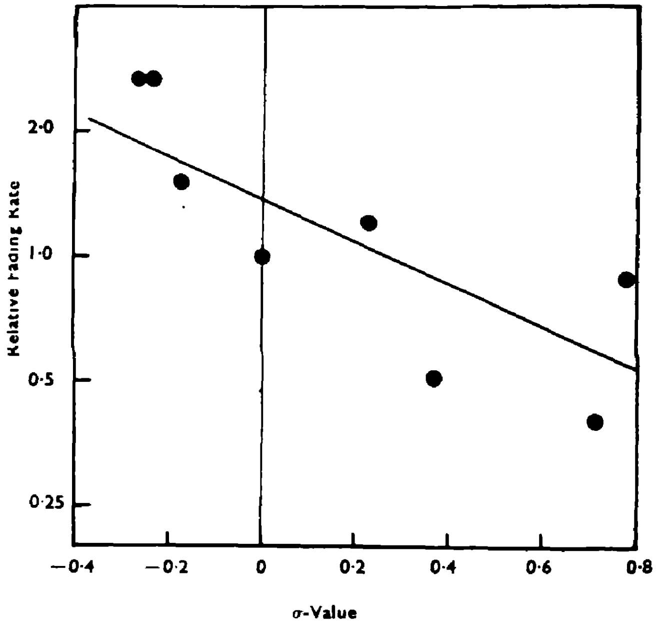


FIG. 7 – Polyglycine

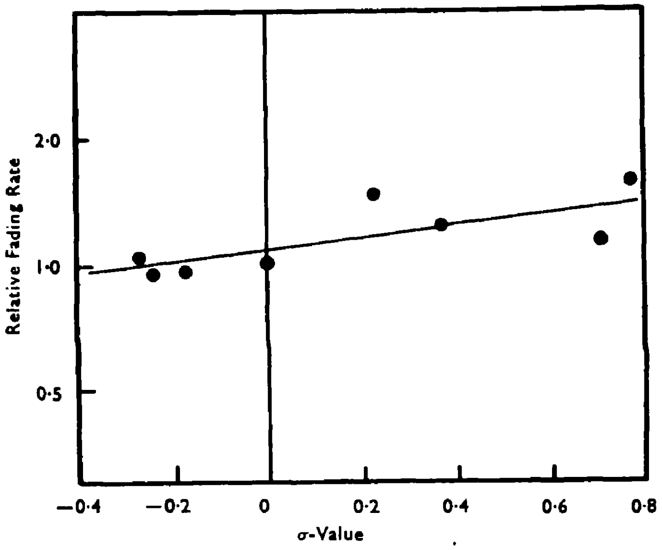


FIG. 8 – Gelatin

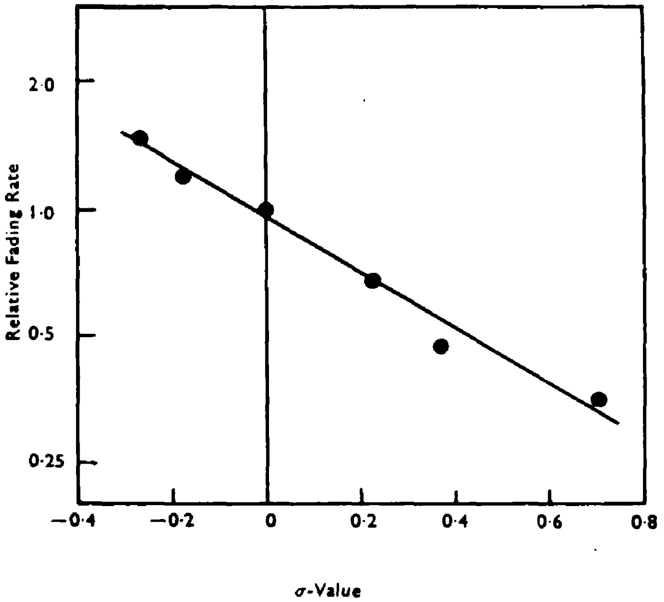


FIG. 9 – Collodion

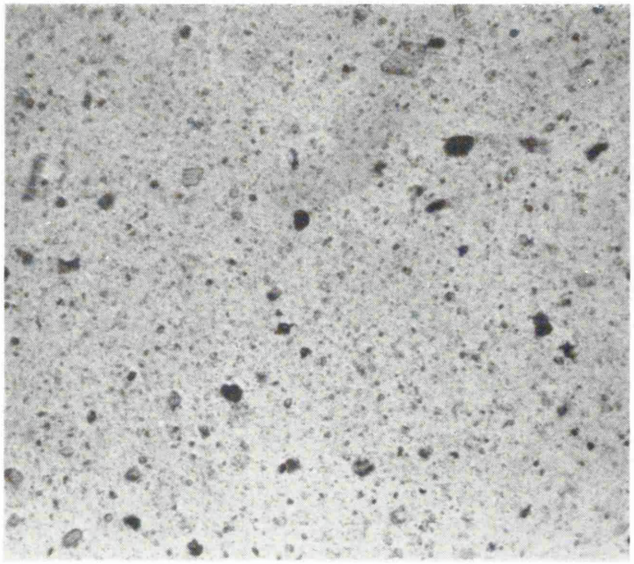


FIG. 11A — Dispersion of *mero*Cyanine Dye in Gelatin (× 500)

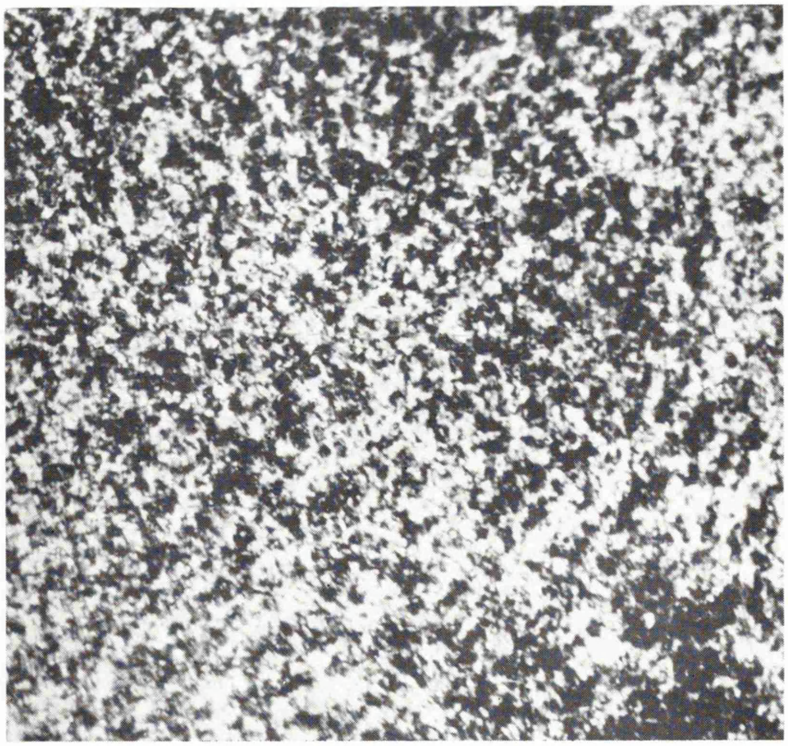


FIG. 11B — Dispersion of Azo Dye (*p*-Anisidine→2-Naphthol) in Methylethylcellulose (× 500)

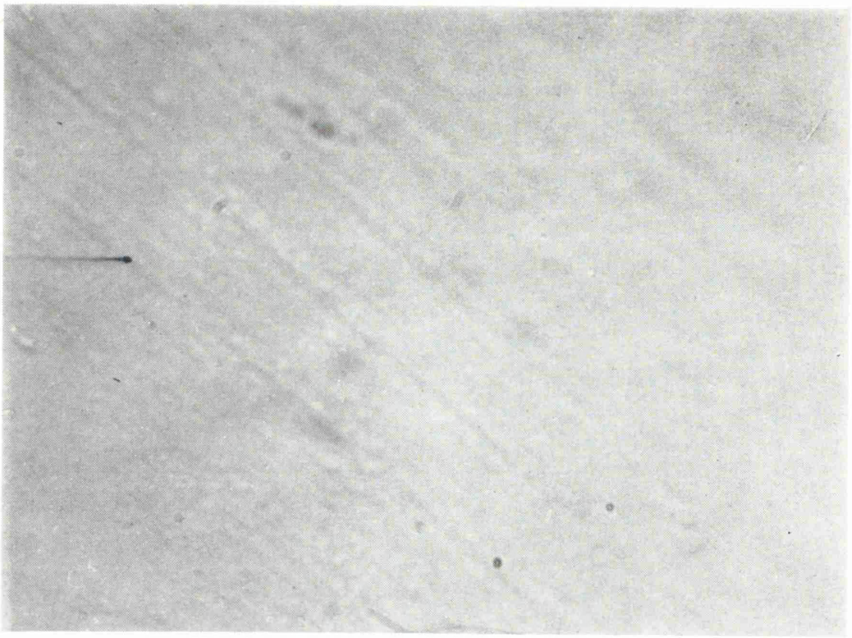


FIG. 12A — Azoic-dyed Cellophane before. Soaping (× 500)

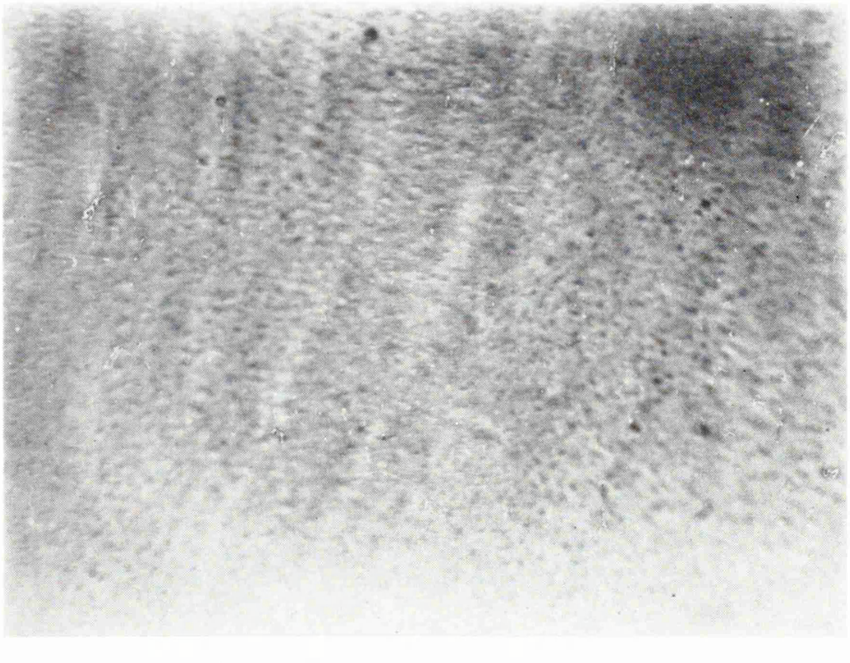
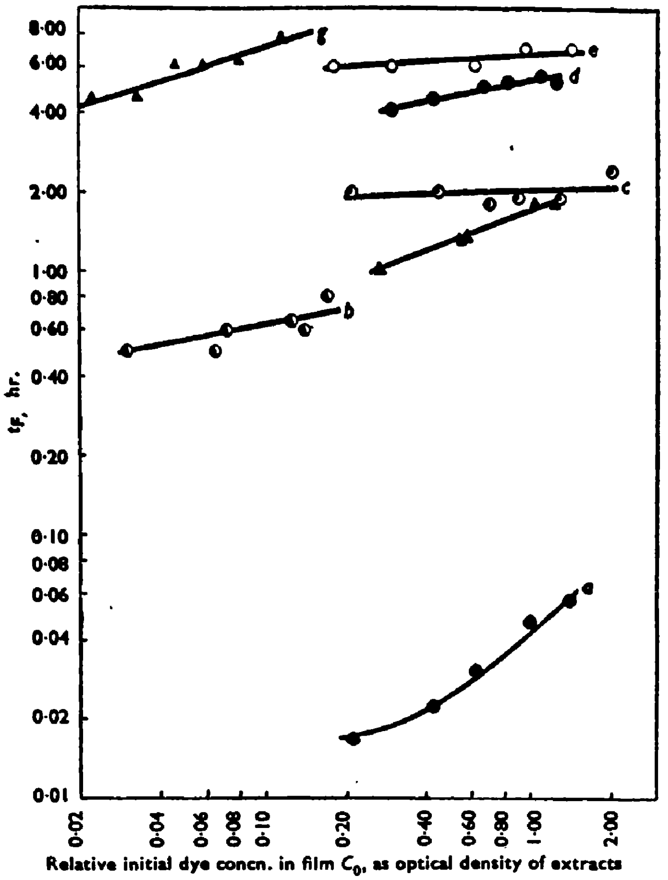
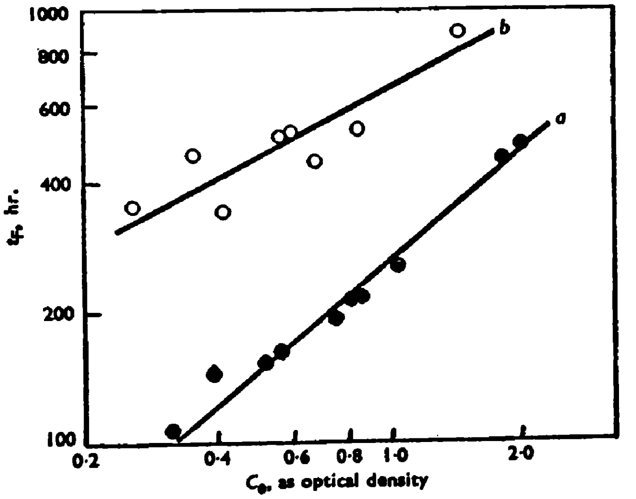


FIG. 12B — Azoic-dyed Cellophane after Soaping (× 500)



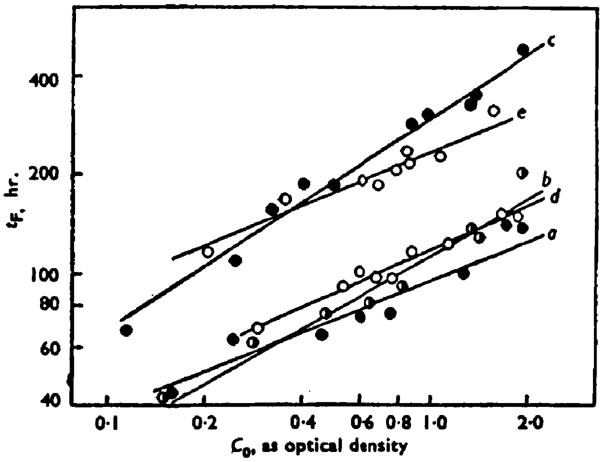
(*a*) *mero*Cyanine dye I in collodion
(*b*) *mero*Cyanine dye I precipitated in methylethylcellulose
(c) *mero*Cyanine dye I precipitated in gelatin
(*d*) *mero*Cyanine dye I dispersed in methylethylcellulose
(e) *mero*Cyanine dye I dispersed in gelatin
(*f*) *p*-Anisidine→2-naphthol in collodion
(*g*) *p*-Anisidine→2-naphthol precipitated in methylethylcellulose

FIG 10 – C_F Curves for Azo and *mero*Cyanine Dyes in Various Films



m-Chloroaniline→α-naphthylamide of 2:3-hydroxynaphthoic acid
(Brentamine Fast Orange GC→Brenthol AN (ICI))
(*a*) Unsoaped (*b*) Soaped

FIG 13 – C_F Curves for Azoic Dye on Cellophane



m-Chloroaniline→α-naphthylamide of 2:3-hydroxynaphthoic acid
(Brentamine Fast Orange GC→Brenthol AN (ICI))
(*a*) Untreated (*b*) Steeped in water overnight (c) Soaped

m-Chloroaniline→anilide of 2:3-hydroxynaphthoic acid
(Brentamine Fast Orange GC→Brenthol AS (ICI))
(*d*) Untreated (*e*) Soaped

FIG. 14 – C_F Curves for Azoic Dyes on Cellophane

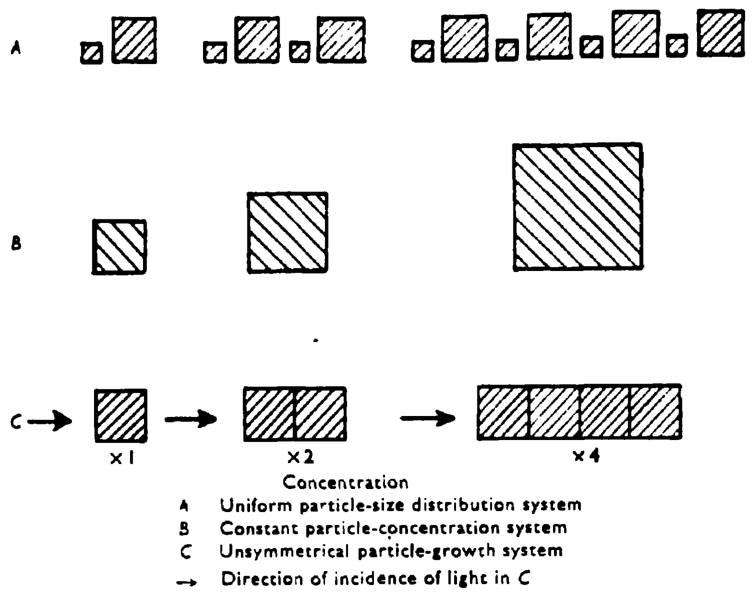
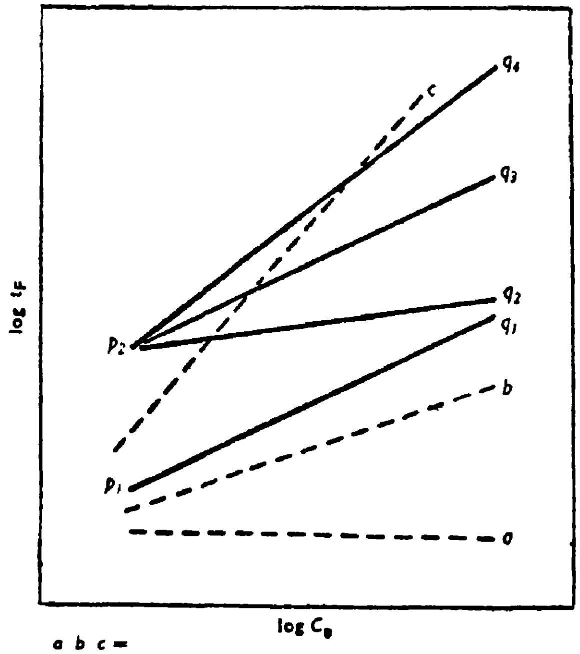


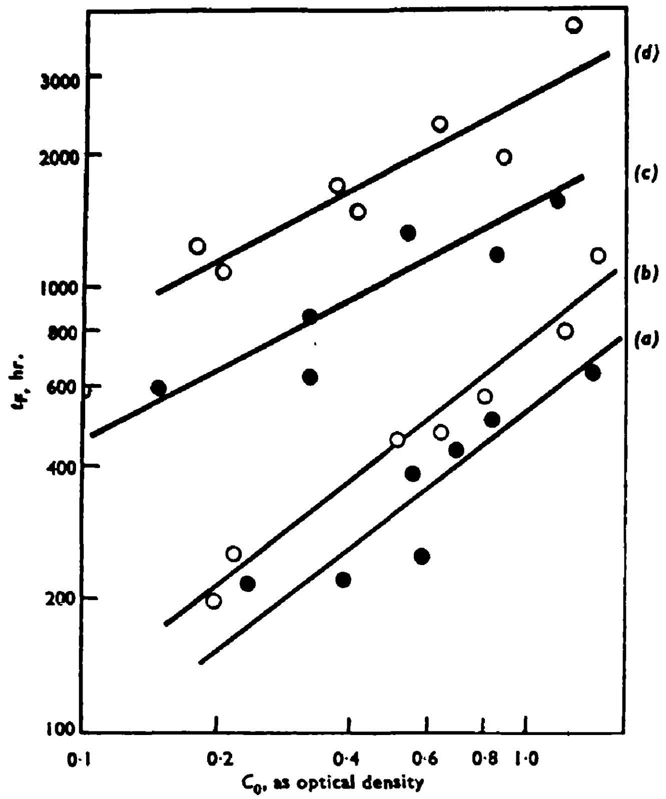
FIG. 15 – Ideal Systems of Growth of Dye Particles with Increase in Total Concentration, in Ratio 1 : 2 : 4



a b c = Theoretical curves for systems A, B, C respectively

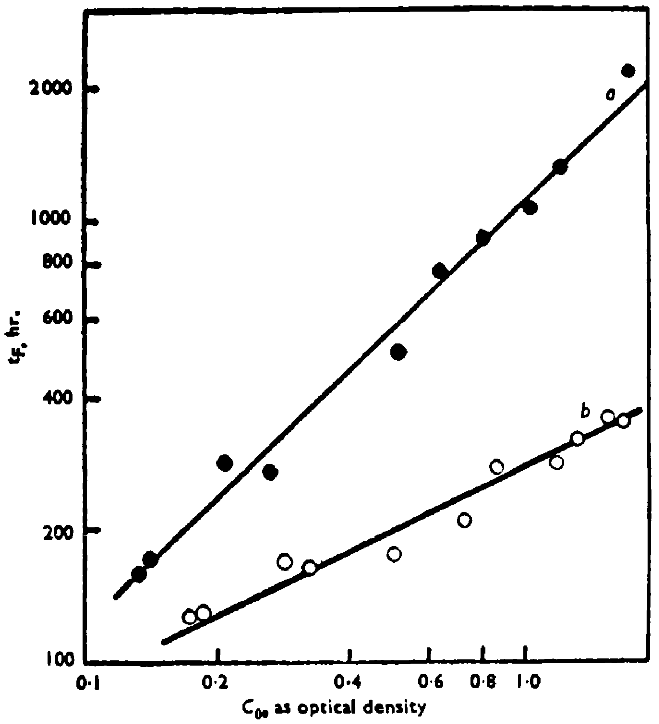
p_1q_1, p_2q_2, p_2q_3, p_2q_4 = Typical curves obtained in practice

FIG. 16 – Typical Characteristic Fading (CF) Curves



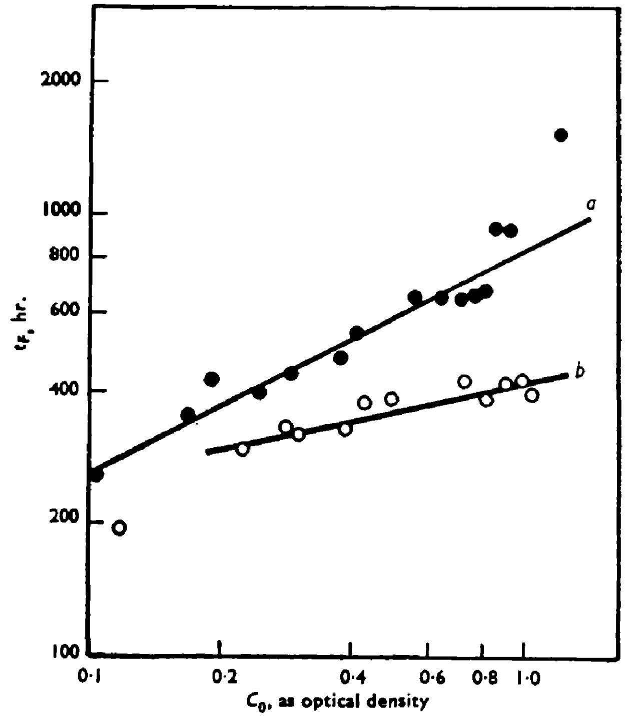
(a) Caledon Green 7G (ICI)— untreated
(b) Caledon Green 7G (ICI)— treated with cinnamic acid
(c) Caledon Yellow GN (ICI)—untreated
(d) Caledon Yellow GN (ICI)— treated with cinnamic acid

FIG 17 – CF Curves for Vat Dyes on Nylon Film



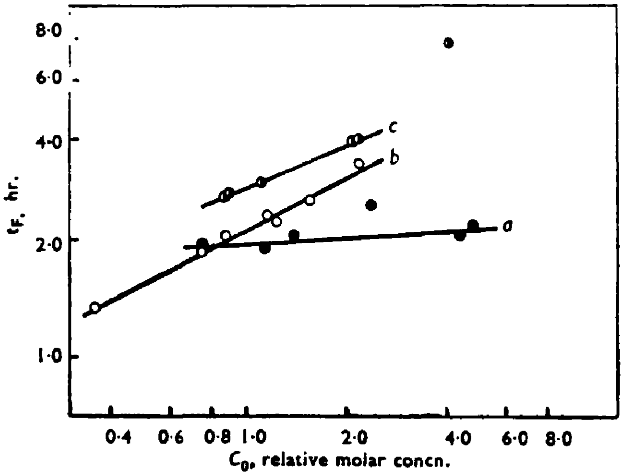
(a) Untreated (b) Soaped

FIG. 18 – CF Curves for Durindone Blue 4BC (ICI) on Cellophane Fibre



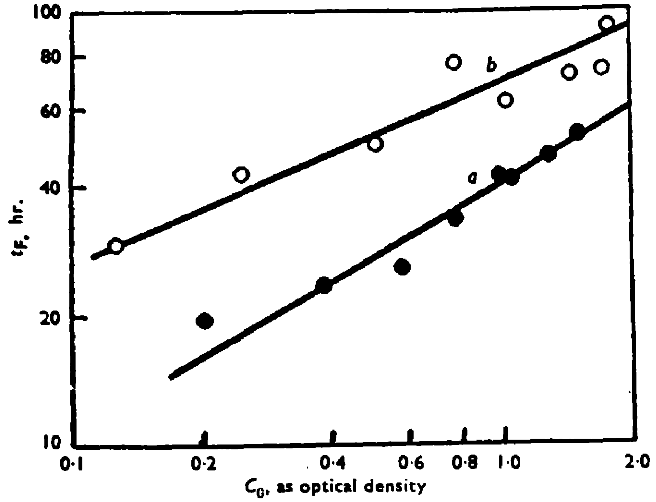
(a) Untreated (b) Soaped

FIG. 19 – CF Curves of Durindone Red 3B (ICI) on Cellophane Film



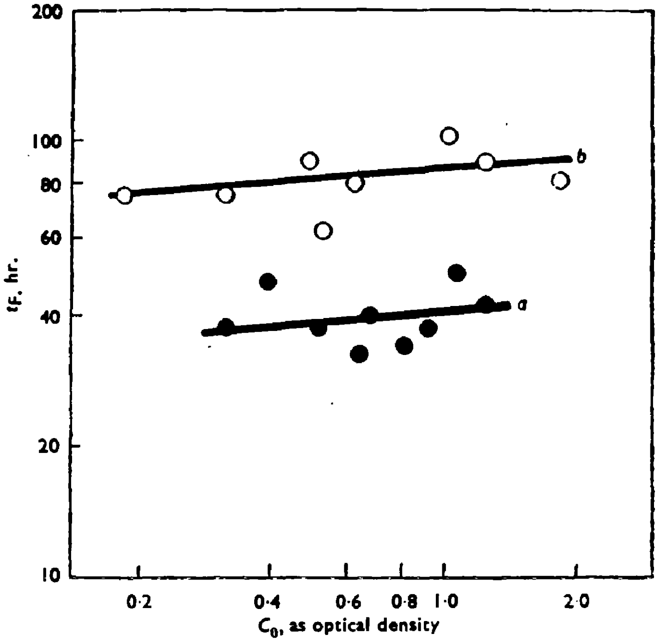
(a) Untreated dye
(b) Molybdophosphoric acid lake (equimolar)
(c) Molybdophosphoric acid lake (25% molar excess of acid)

FIG. 20 — CF Curves of Victoria Blue BO in Lithographic Varnish Film



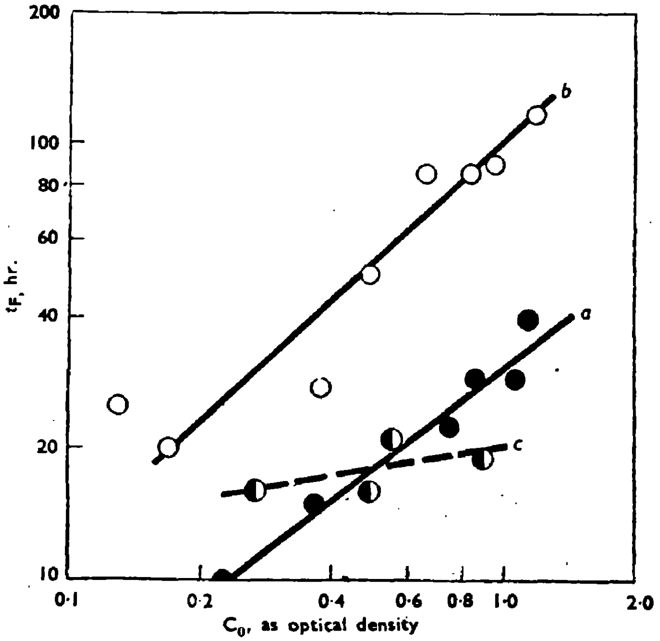
(*a*) Normal film (*b*) Gel film, fresh

FIG. 21 — C_F Curves for Chlorazol Sky Blue FF (ICI) on Cellophane Film of Different Porosities



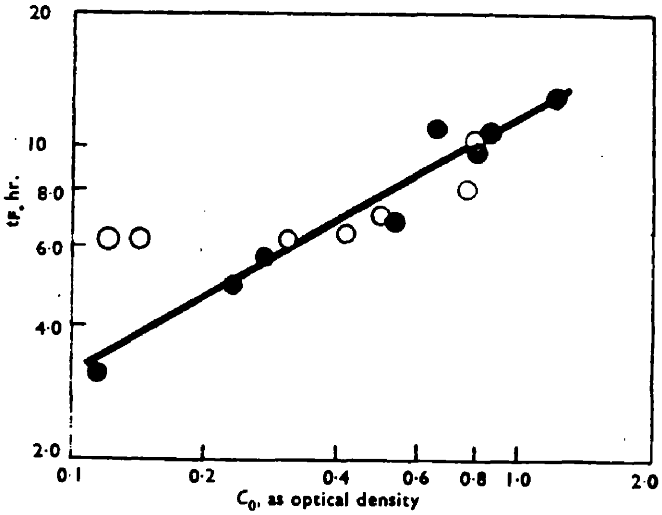
(*a*) Normal film (*b*) Gel film, fresh

FIG. 22 — C_F Curves for Chlorazol Rose B (ICI) on Cellophane Film of Different Porosities



(*a*) Normal film
(*b*) Gel film, fresh
(*c*) Gel film, aged

FIG. 23 — C_F Curves for Chlorazol Sky Blue FF (ICI) on Cellophane Film of Different Porosities



● Normal film
○ Gel film, aged

FIG. 24 — C_F Curves for Chlorazol Orange PG (ICI) on Cellophane Film

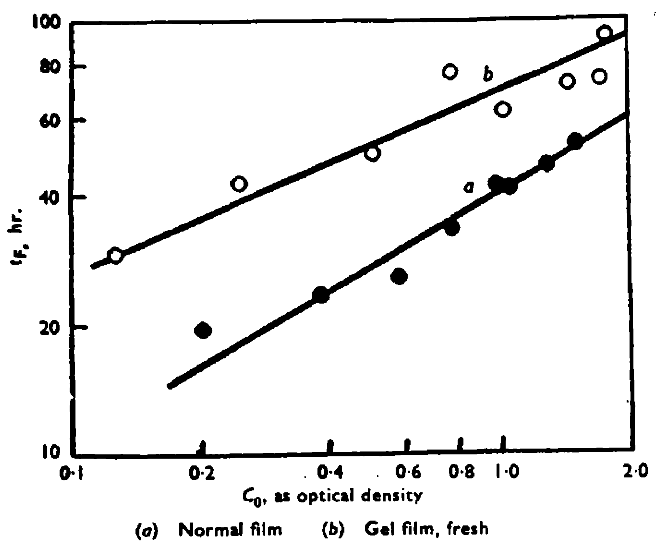


FIG. 21 — C_F Curves for Chlorazol Sky Blue FF (ICI) on Cellophane Film of Different Porosities

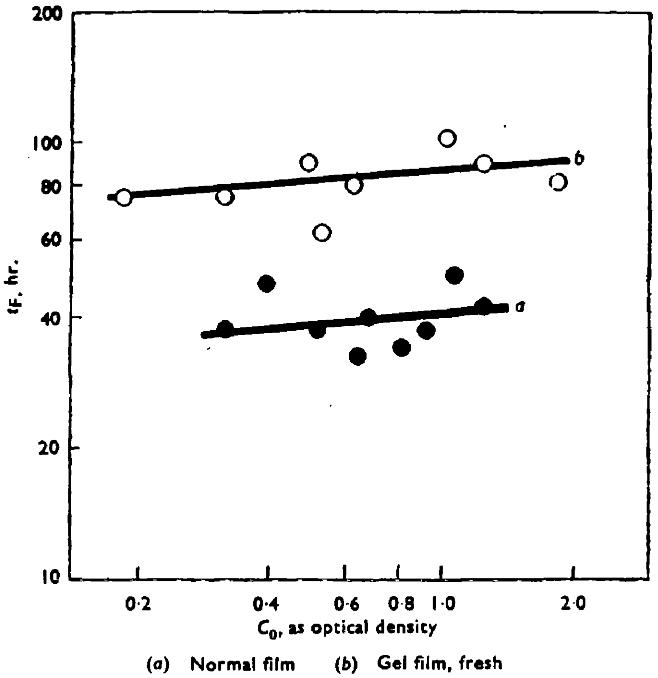


FIG. 22 — C_F Curves for Chlorazol Rose B (ICI) on Cellophane Film of Different Porosities

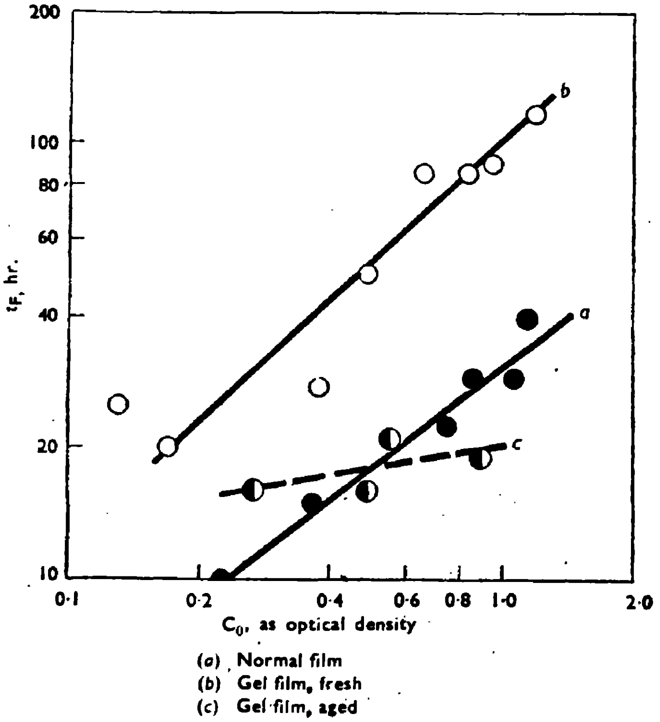


FIG. 23 — C_F Curves for Chlorazol Sky Blue FF (ICI) on Cellophane Film of Different Porosities

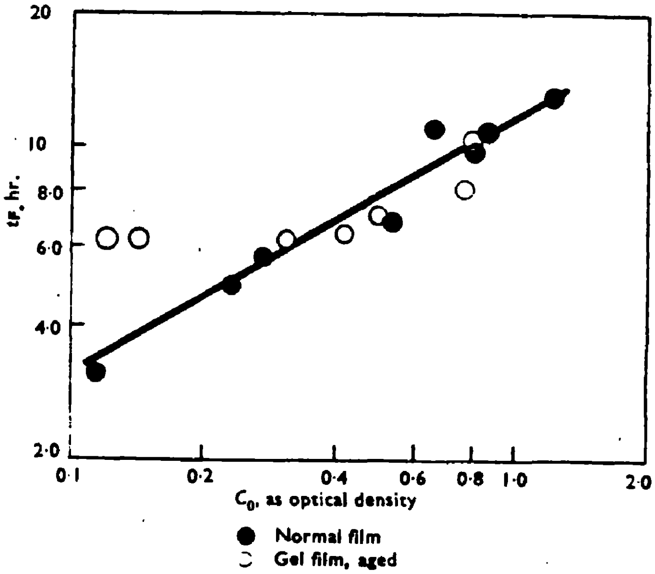


FIG. 24 — C_F Curves for Chlorazol Orange PG (ICI) on Cellophane Film

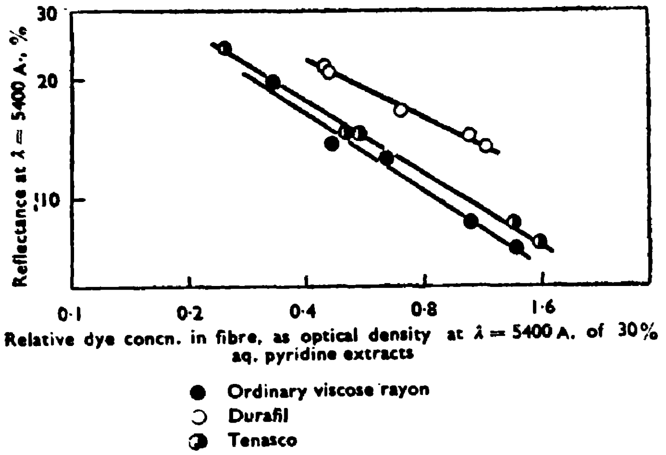


FIG. 25 — Relationship between Concentration of Chlorazol Rose B (ICI) and Reflectance of Viscose Rayon Fabrics

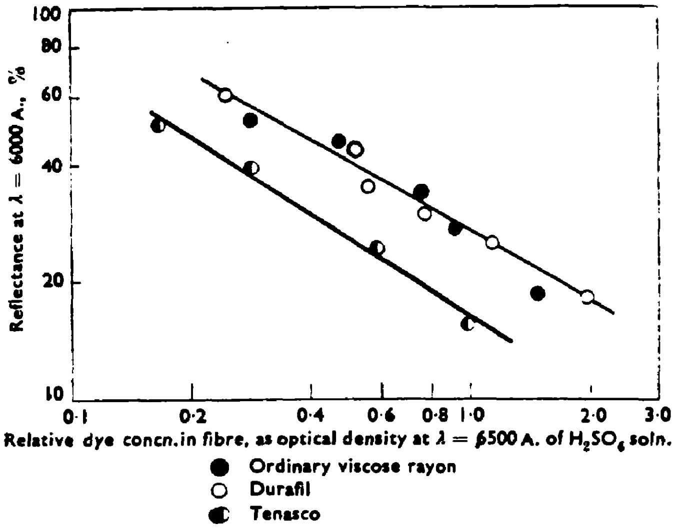


FIG. 26 — Relationship between Concentration of Chlorazol Sky Blue FF and Reflectance of Viscose Rayon Fabrics

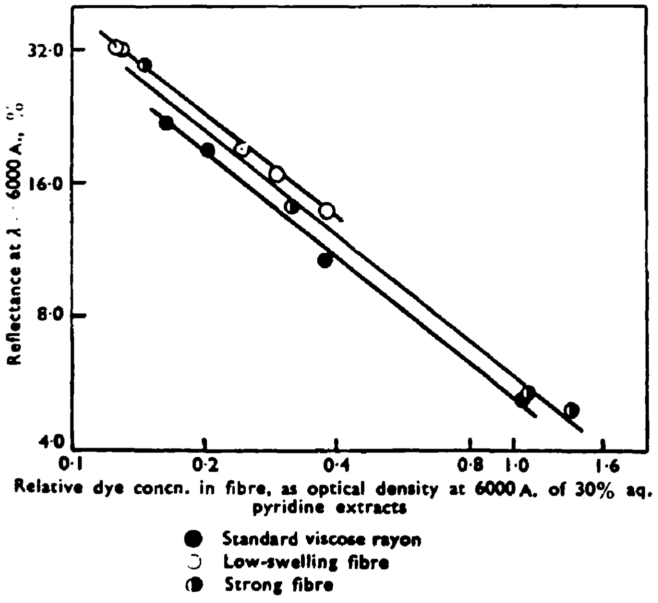


FIG. 27 — Relationship between Concentration of Chlorazol Sky Blue FF and Reflectance of Viscose Rayon Fabrics

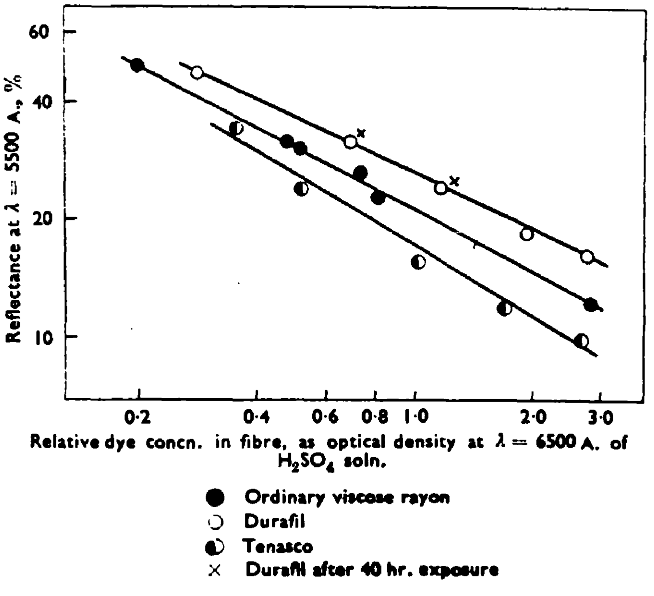


FIG. 28 — Relationship between Concentration of Chlorazol Fast Helio 2RK (ICI) and Reflectance of Viscose Rayon Fabrics

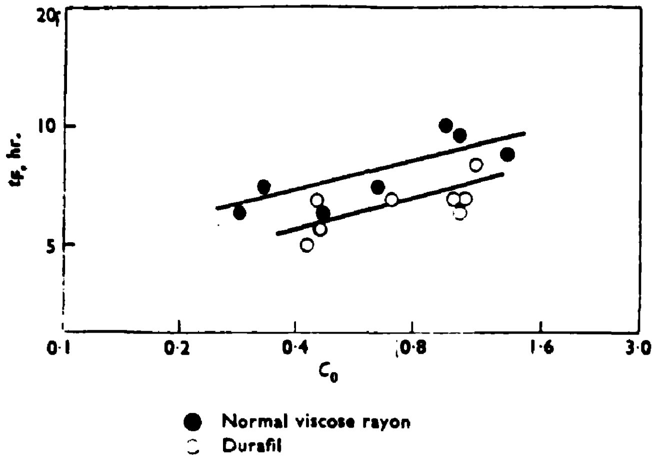


FIG. 29 — CF Curves for Chlorazol Rose B on Viscose Rayon Fabrics

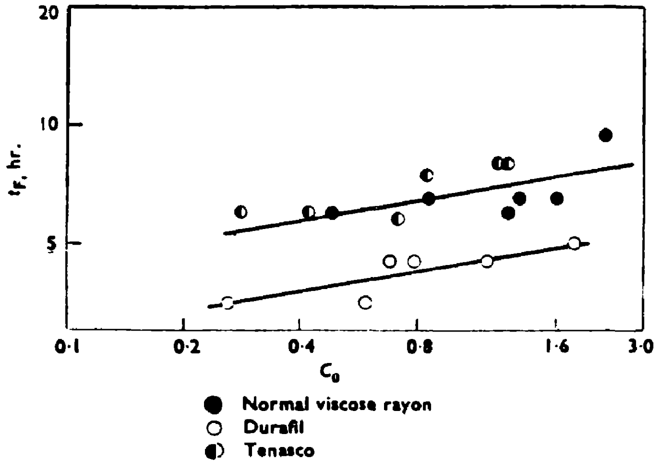


FIG. 30 — CF Curves for Chlorazol Sky Blue FF on Viscose Rayon Fabrics

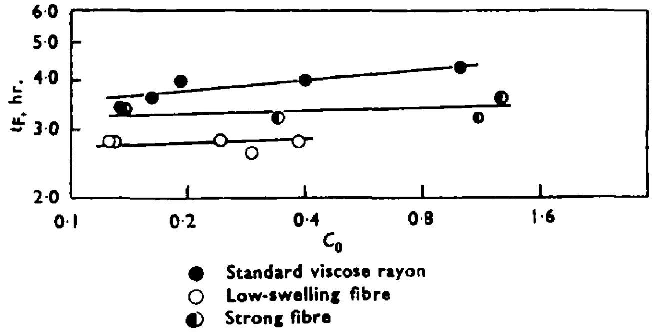


FIG. 31 — CF Curves for Chlorazol Sky Blue FF on Viscose Rayon Fabrics

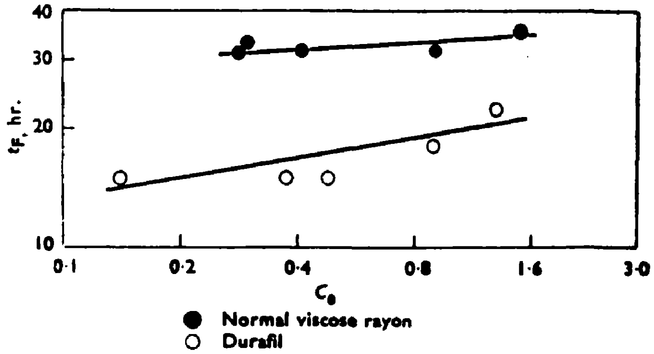


FIG. 32 — CF Curves for Chlorazol Fast Helio 2RK on Viscose Rayon Fabrics

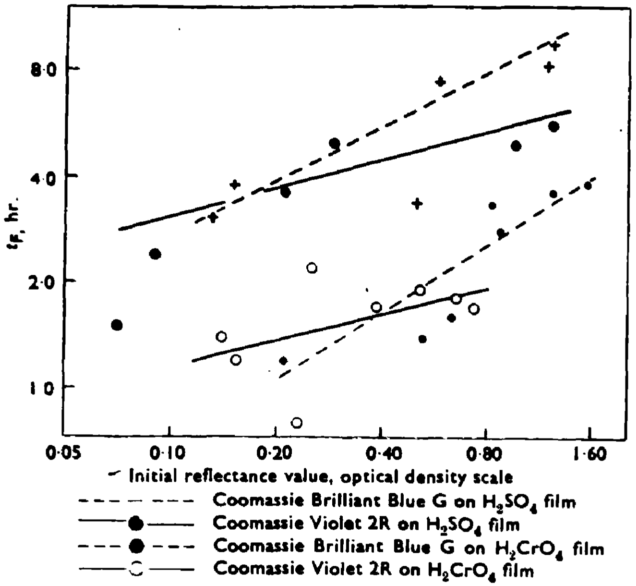


Fig. 33—CF Curves for Acid Wool Dyes on Anodised Aluminium Films

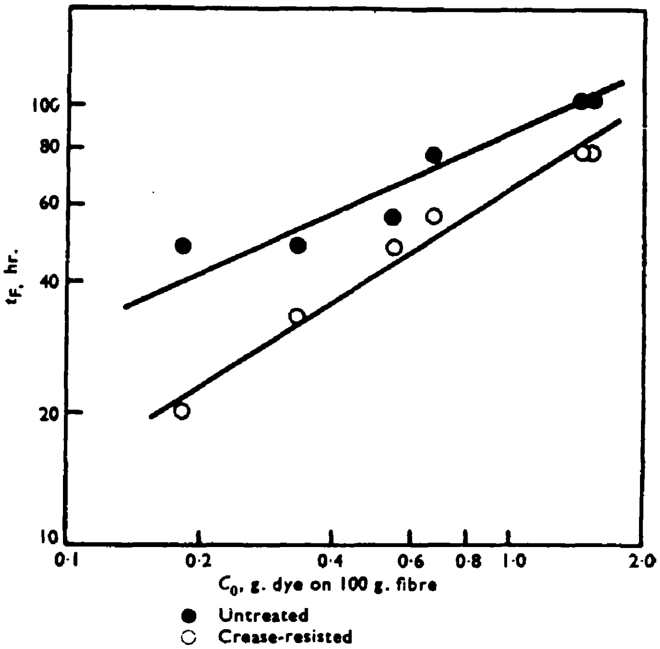


Fig. 34—CF Curves for Durazol Red 2B (ICI) on Viscose Rayon (Visual Estimation)

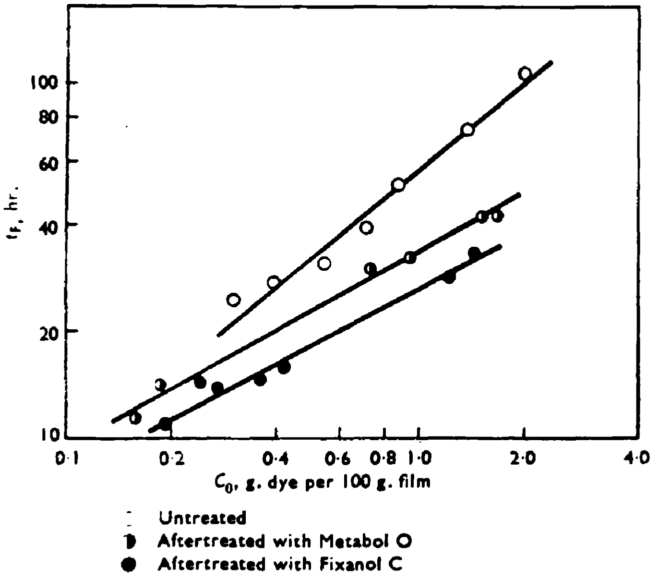


Fig. 35—CF Curves for Chlorazol Sky Blue FF on Cellophane Film

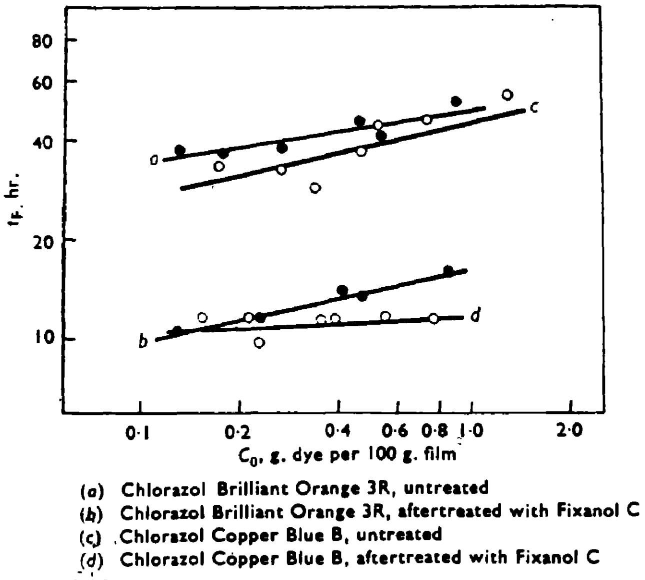


Fig. 36—CF Curves for Direct Cotton Dyes on Cellophane Film

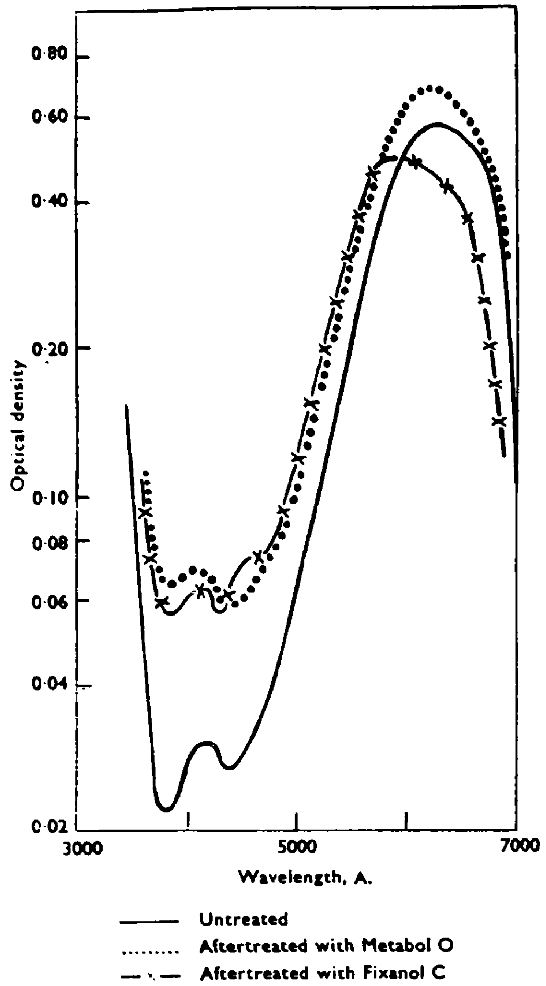


Fig. 37 — Light Absorption Curves for Chlorazol Sky Blue FF on Cellophane Film (Arbitrary dye concentrations)

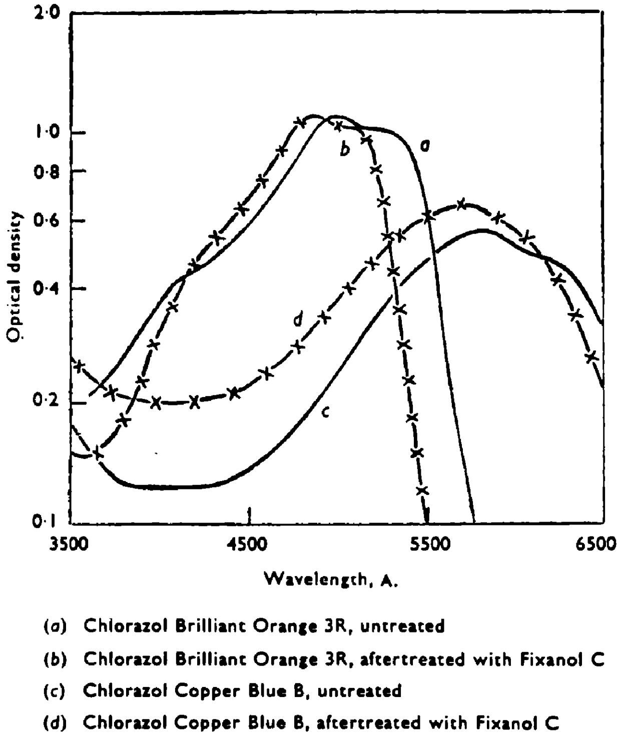


Fig. 38 — Light Absorption Curves for Direct Cotton Dyes on Cellophane Film

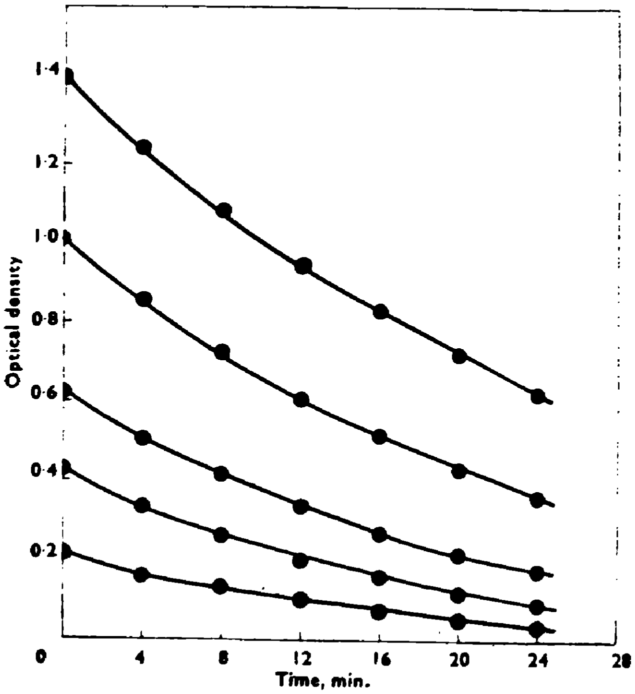


Fig. 39 — Typical Fading-rate Curves for Transparent Films (*mero*Cyanine Dye in Collodion Film)

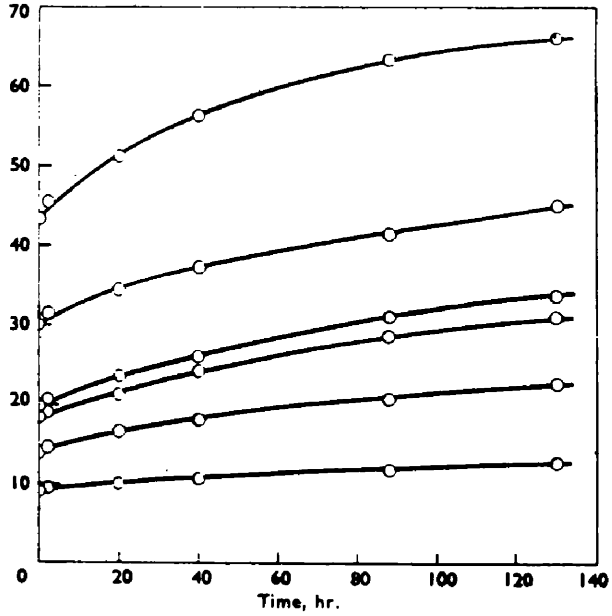
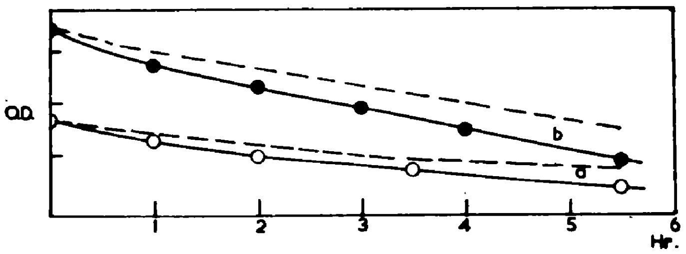
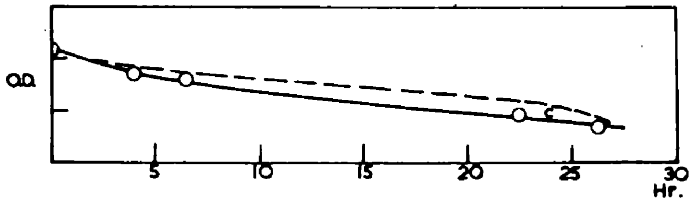


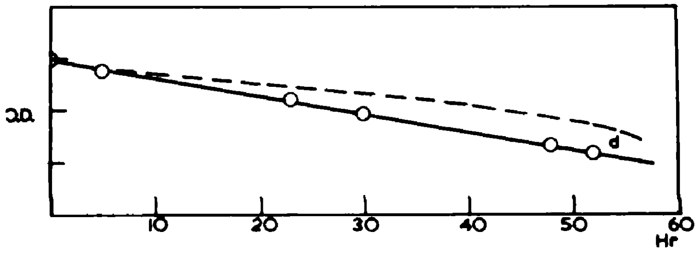
Fig. 40 — Typical Fading-rate Curves for Fabrics (Chlorazol Sky Blue FF on Normal Viscose Rayon Fabric)



a Dye IIId on Collodion.
b Dye II on Collodion.



c Dye IIIc on Collodion.



d Dye II on Methyl Ethyl Cellulose.

The broken lines are plotted with log. opt. density as ordinates.

Fig.41. Fading-rate Curves for Azo Dyes on Various Substrates.

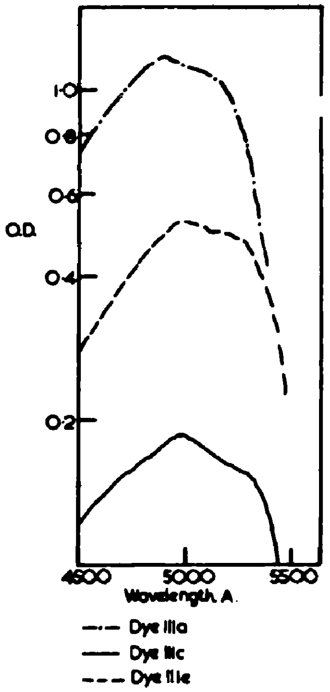
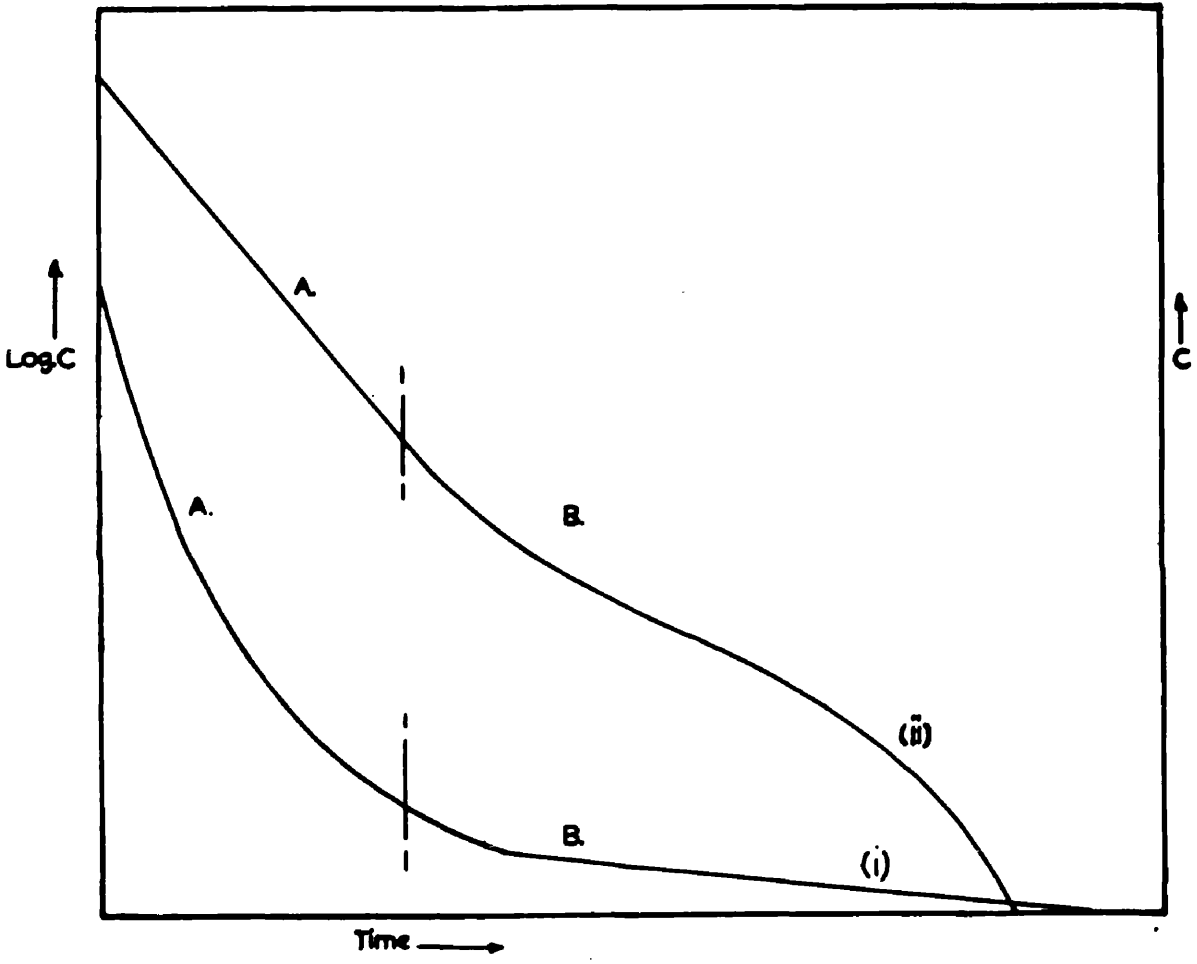


Fig.42. Light Absorption Curves for Dyes in Pyridine.



A. Monolayer and smallest aggregates fading — first order.
B. Largest aggregates fading — approaching zero order.

(i) Plotted with concn. ordinate.
(ii) " " log. concn. ordinate.

Fig.43. Theoretical Fading-rate Curve for Dye Present in the Substrate as a Heterogeneous System.

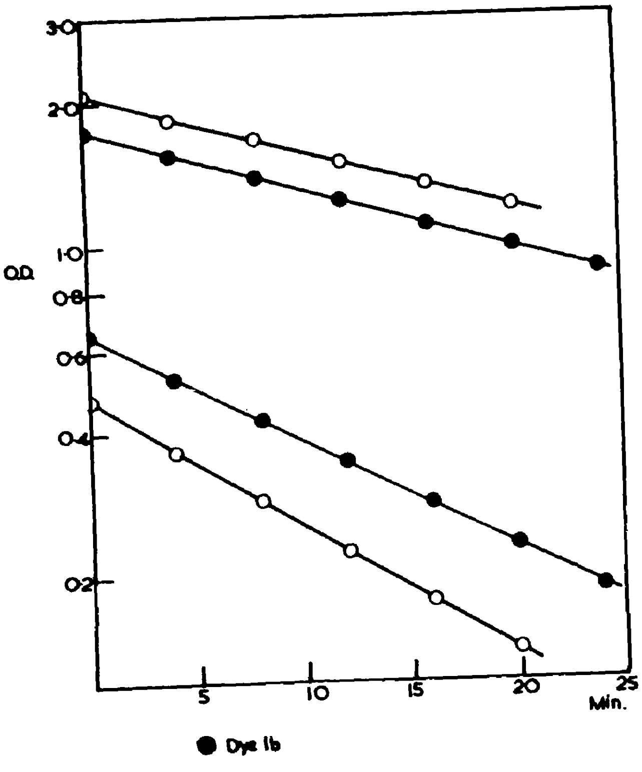


Fig.44. Log. Rate Curves for Fading of Merocyanine Dyes in Collodion.

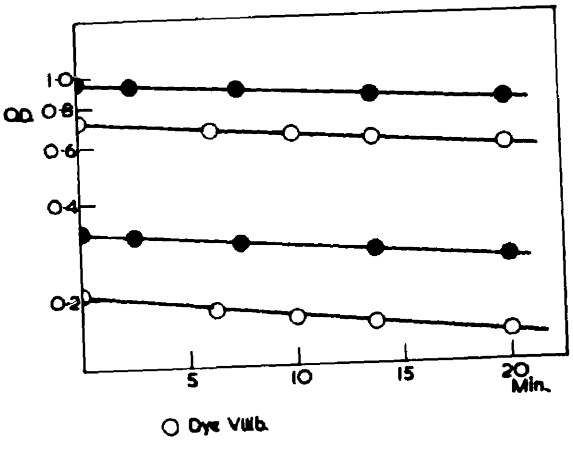


Fig.45. Log. Rate Curves for Azo Dyes Fading in Methyl Ethyl Cellulose.

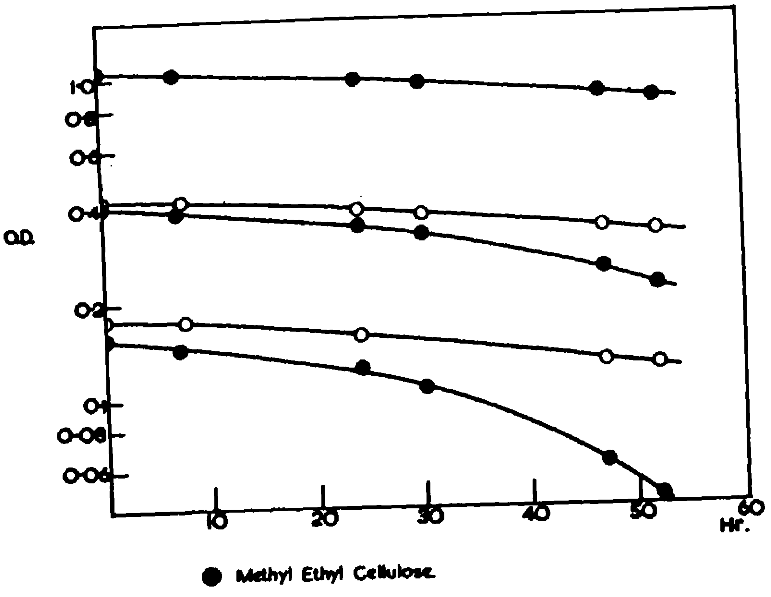


Fig.46. Log. Rate Curves for Fading of Brentamine Fast Red B→Brenthol AT Dispersions.

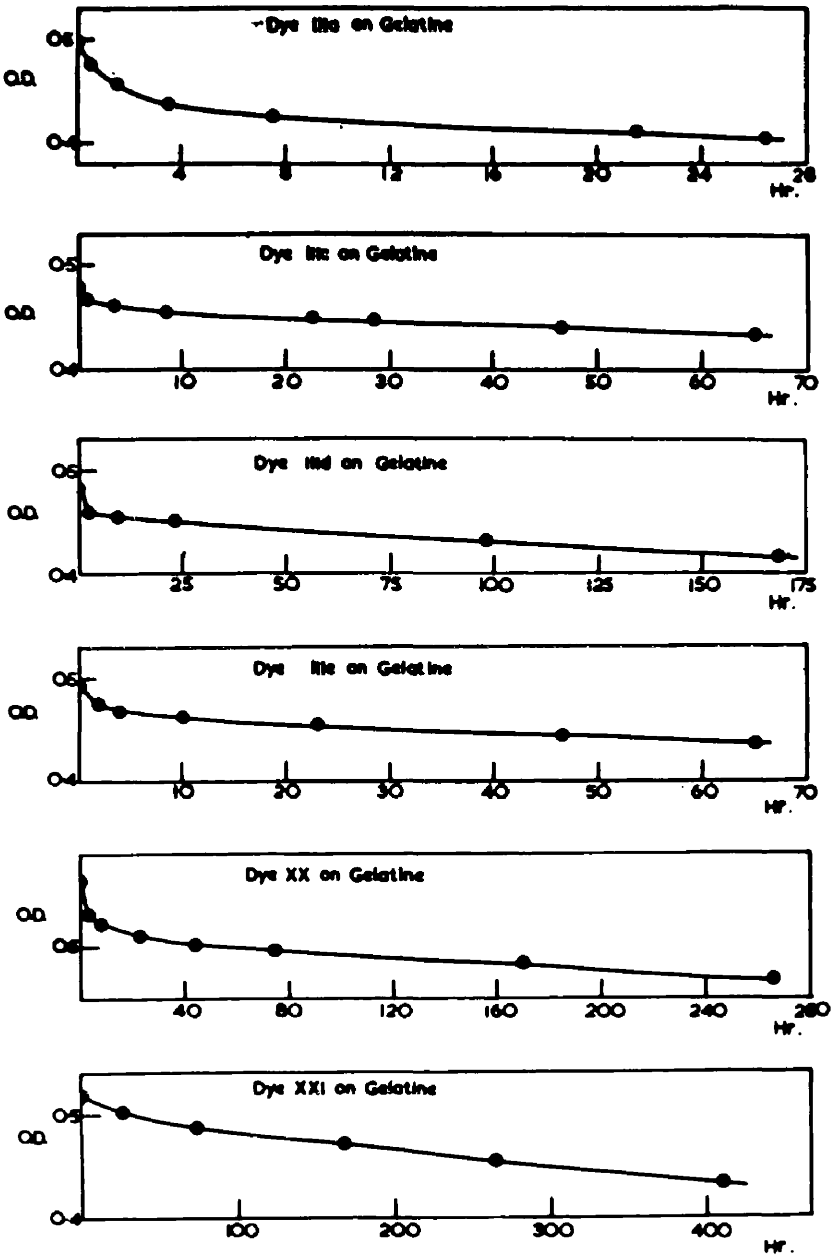


Fig. 47. Typical Fading-rate Curves.

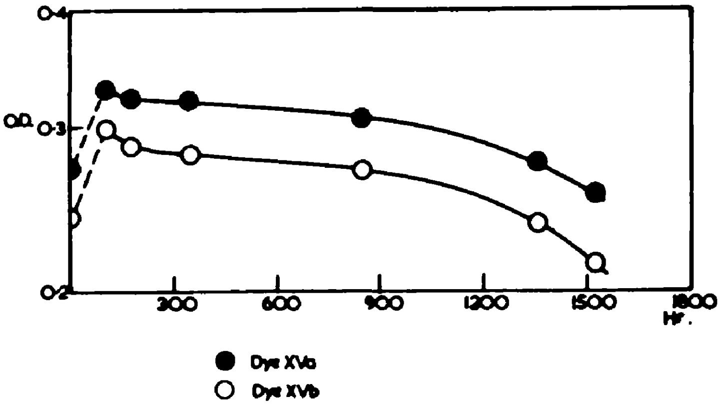


Fig. 48. Log. Rate Curves for Anthraquinone Dyes on Gelatine.

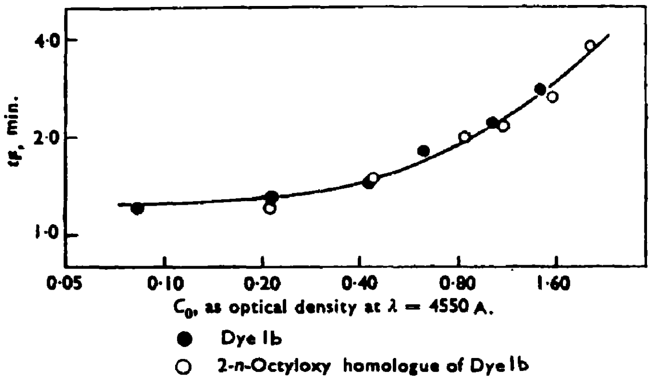


FIG.49— CF Curves for *mero*Cyanine Dyes in Collodion Film

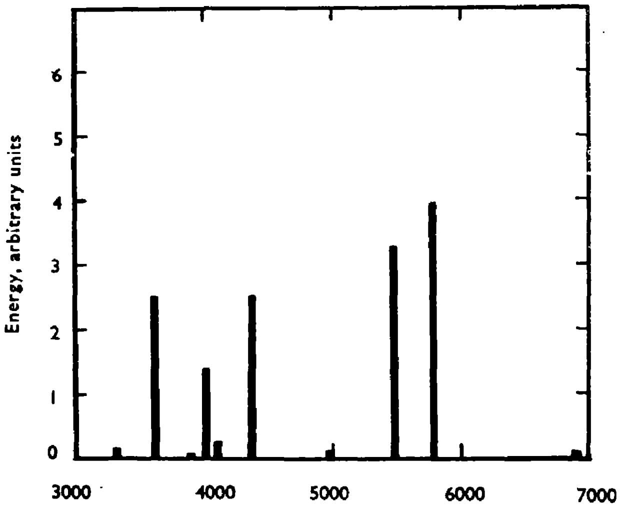
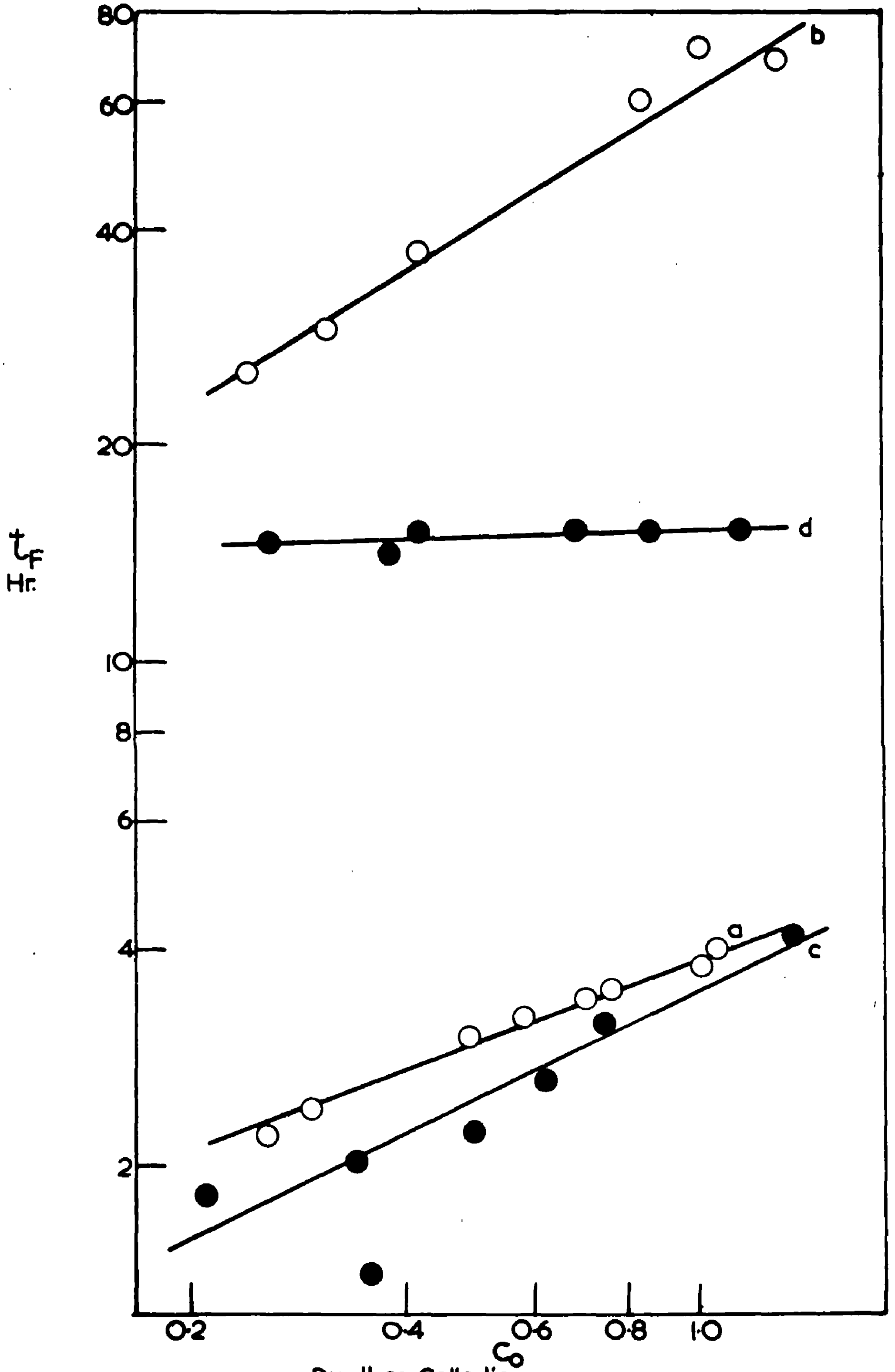


FIG. 50— Energy Distribution Curve of Osira (G.E.C.) 400-w. Lamp. A small amount of continuous radiation (too small to appear on this scale) occurs throughout the spectrum



a Dye II on Collodion.
b Dye II on Methyl Ethyl Cellulose.
c Dye IIId on Collodion.
d Dye IIIc on Collodion.

Fig.51. CF Curves for Azo Dyes on Various Substrates.

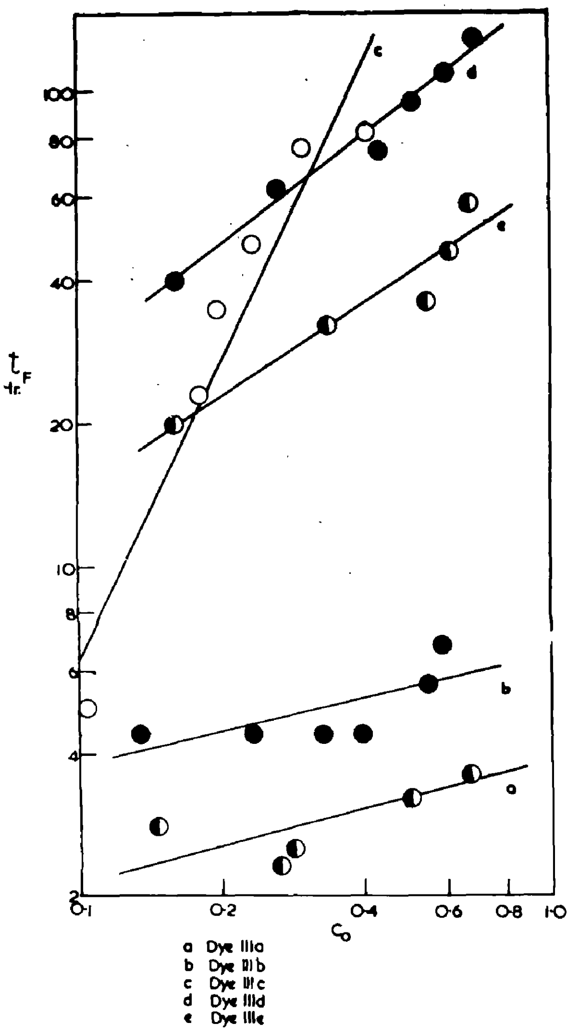


Fig.52. CF Curves for Azo Dyes on Gelatine–10% loss of dye

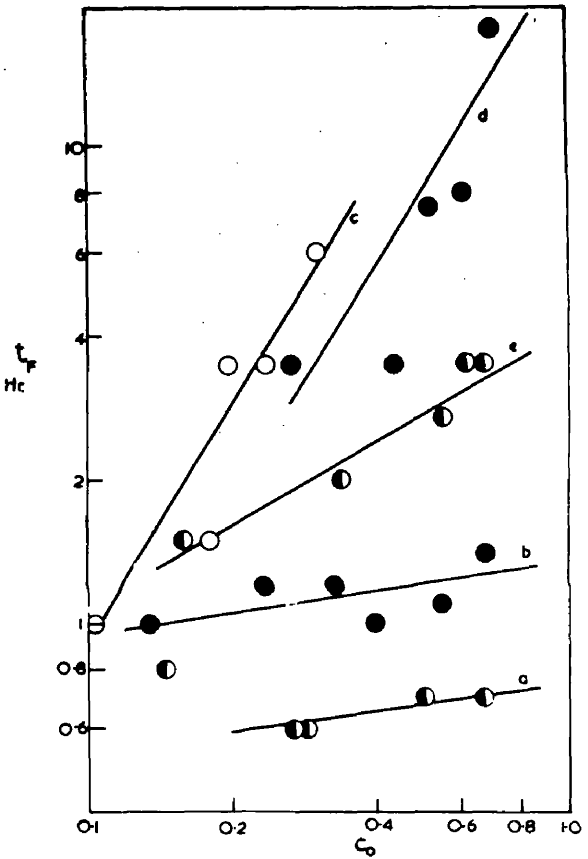


Fig.53. CF Curves for Azo Dyes on Gelatine–5% loss of dye.

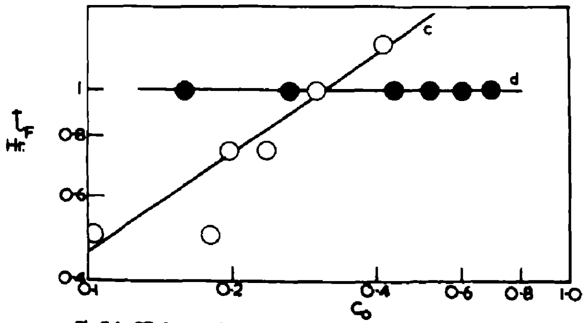


Fig.54. CF Curves for Azo Dyes on Gelatine–25% loss of dye.

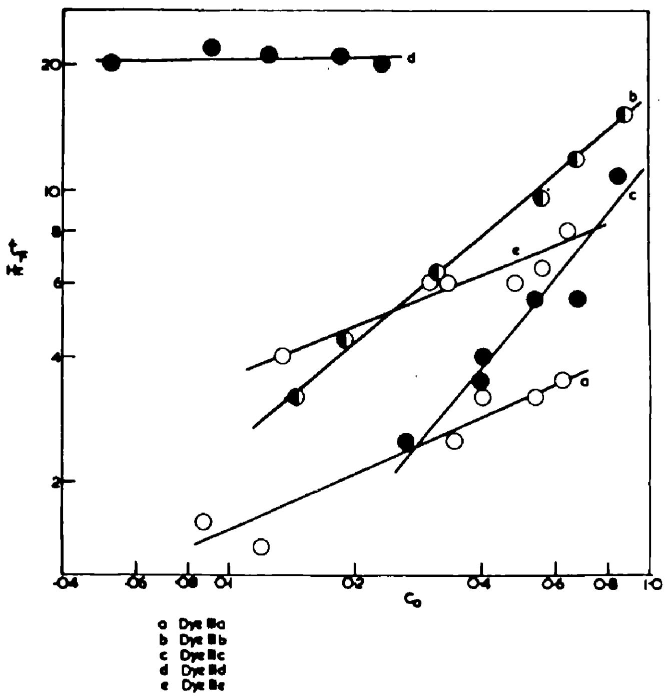


Fig.55. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

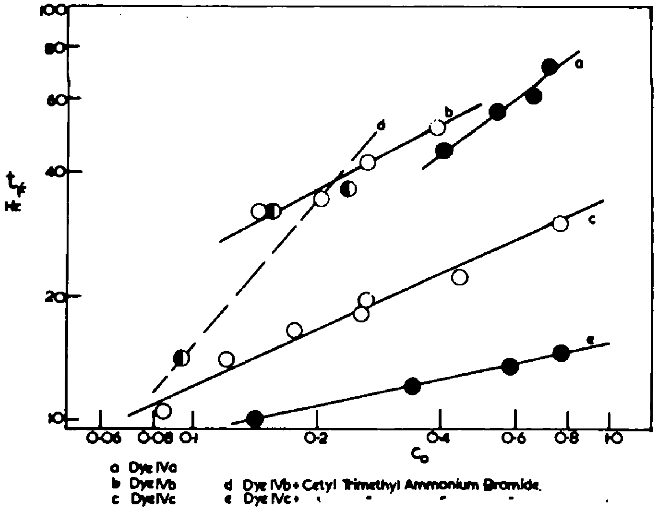


Fig.56. CF Curves for Azo Dyes on Gelatine.

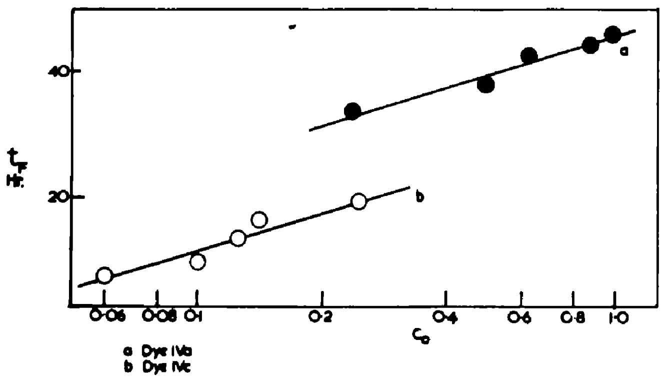


Fig.57. CF Curves for Azo Dyes on Methyl Ethyl Cellulose

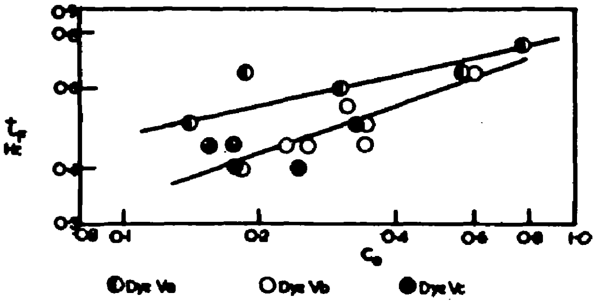


Fig.58. CF Curves for Azo Dyes on Gelatine.

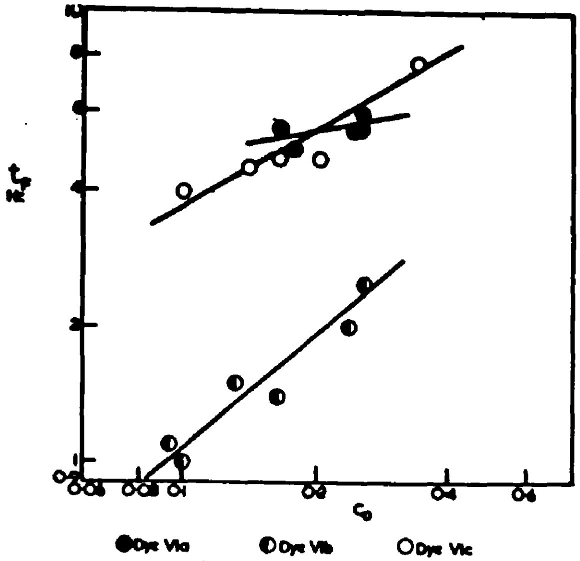


Fig.59. CF Curves for Azo Dyes on Gelatine.

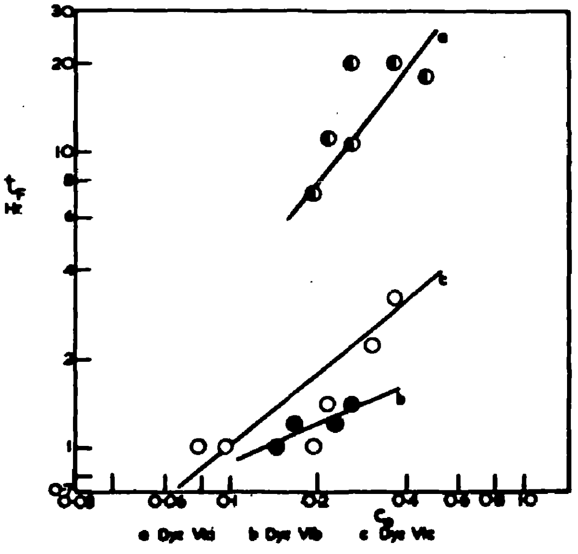


Fig.61. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

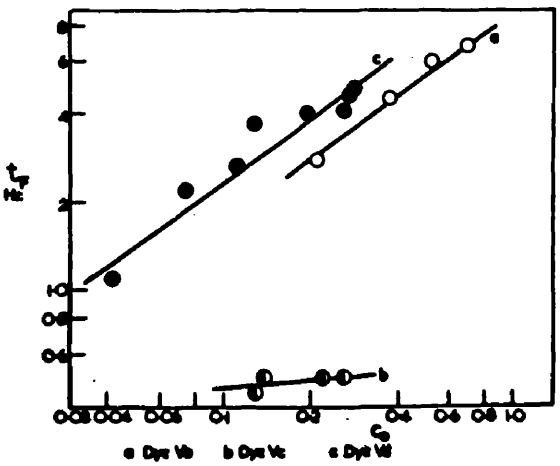


Fig.60. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

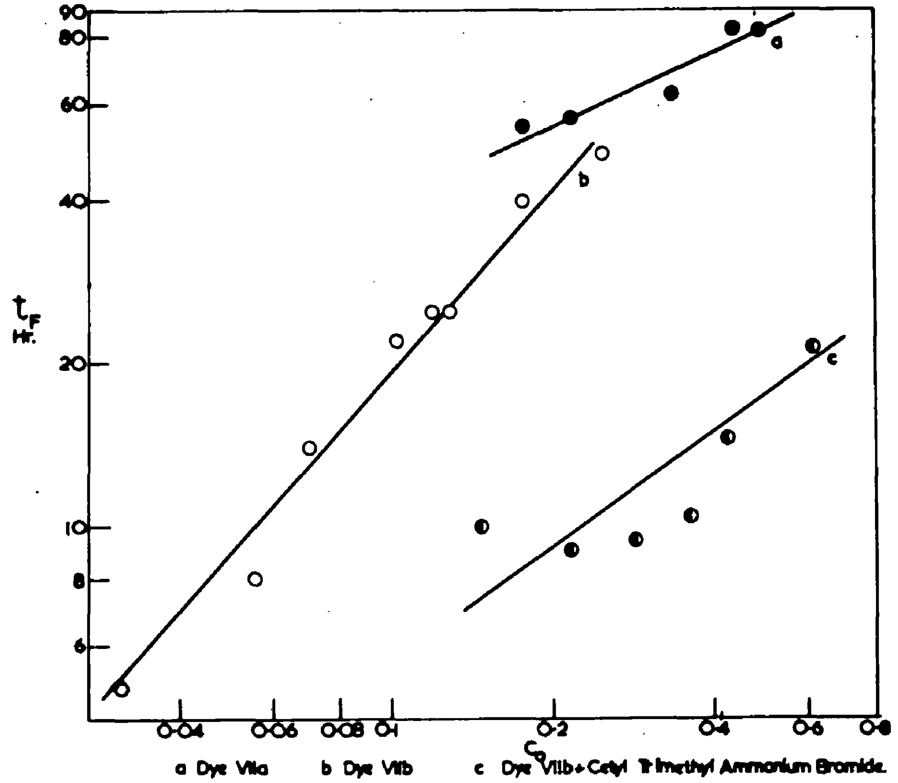


Fig.62. CF Curves for Azo Dyes on Gelatin.

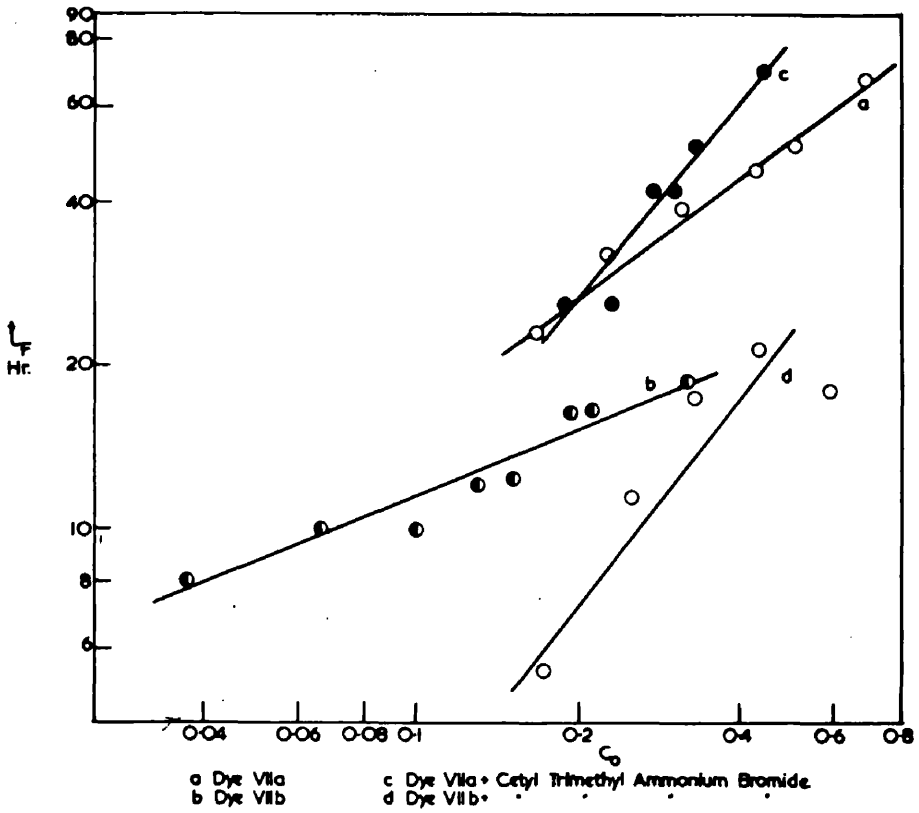


Fig.63. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

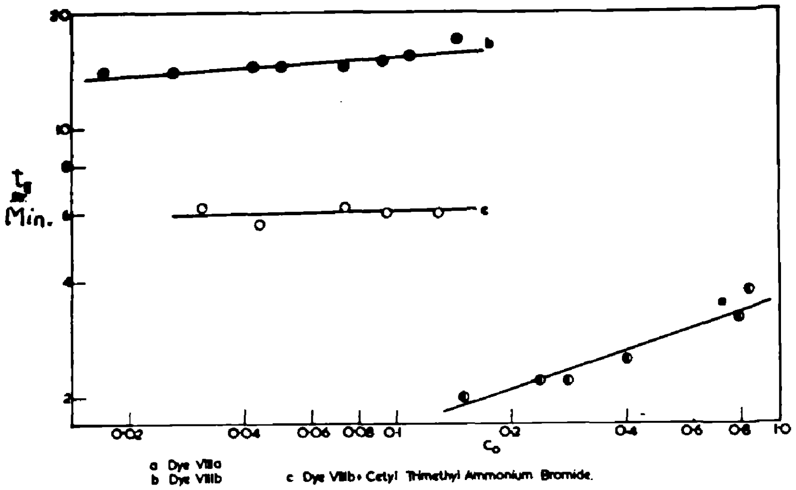


Fig 64. CF Curves for Azo Dyes on Gelatin.

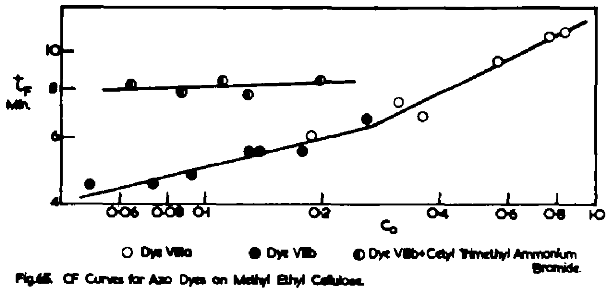


Fig.65. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

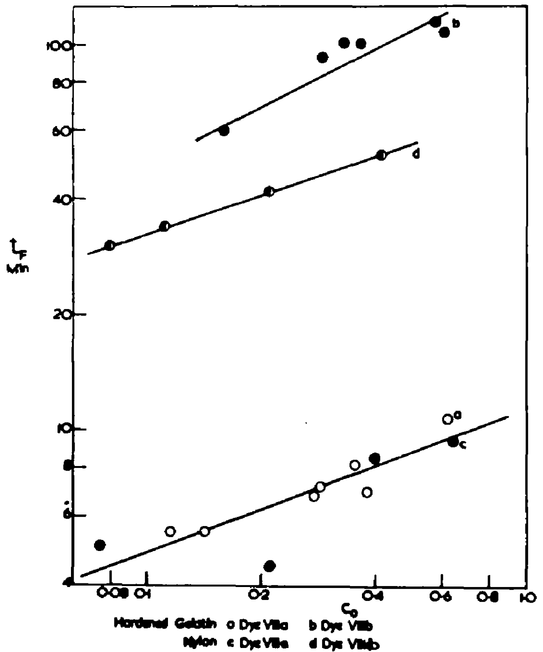


Fig.66. CF Curves for Azo Dyes on Hardened Gelatine and Nylon.

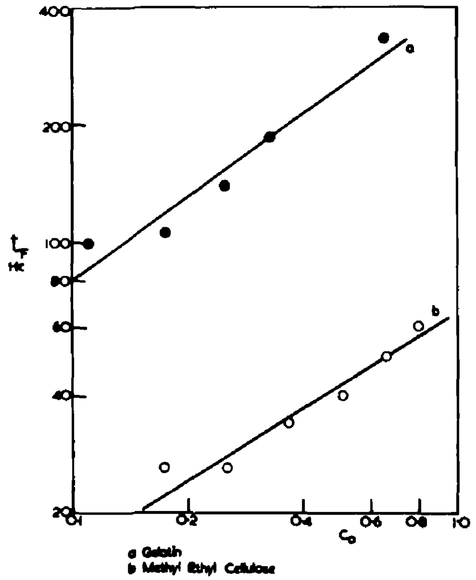


Fig.67. CF Curves for Dye IX on Various Substrates.

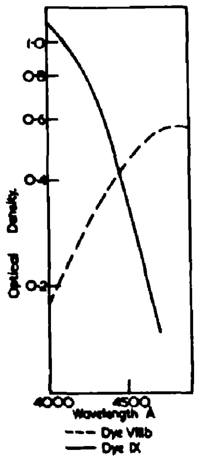


Fig.68. Light Absorption Curves for Azo Dyes on Gelatine.

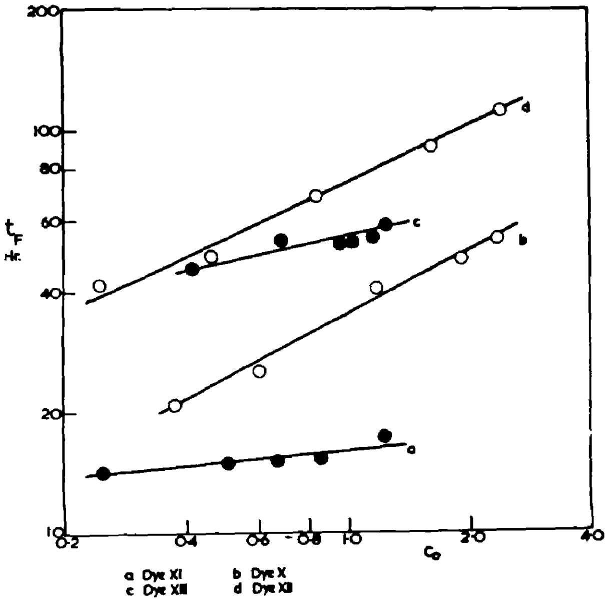


Fig.69. CF Curves for Colour-Coupled Azomethin Dyes on Gelatin.

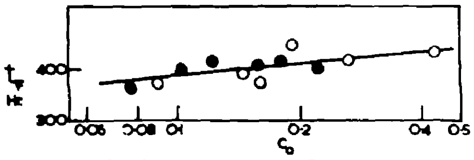


Fig.70. CF Curves for Anthraquinone Dyes on Methyl Ethyl Cellulose.

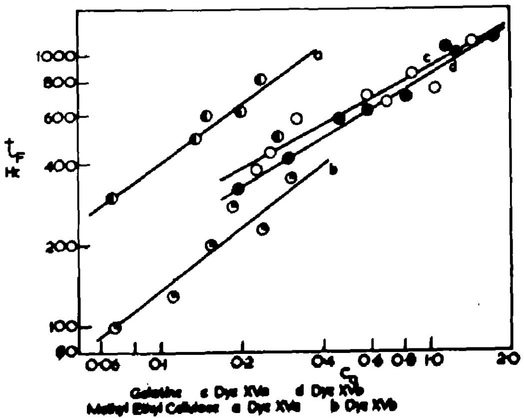


Fig.71. CF Curves for Anthraquinone Dyes on Various Substrates.

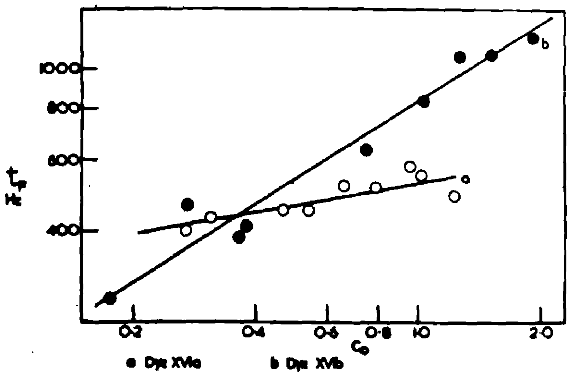


Fig.72. CF Curves for Anthraquinone Dyes on Gelatine.

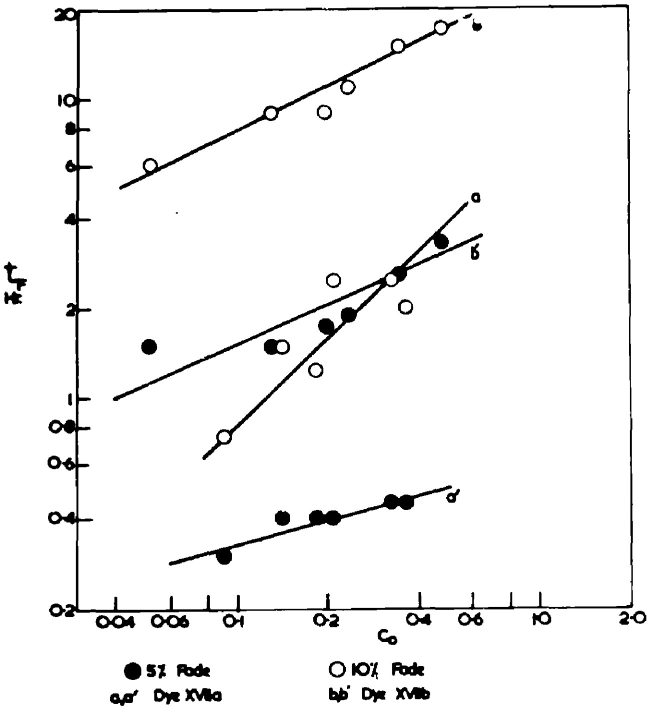


Fig.73. CF Curves for Azo Dyes on Gelatine.

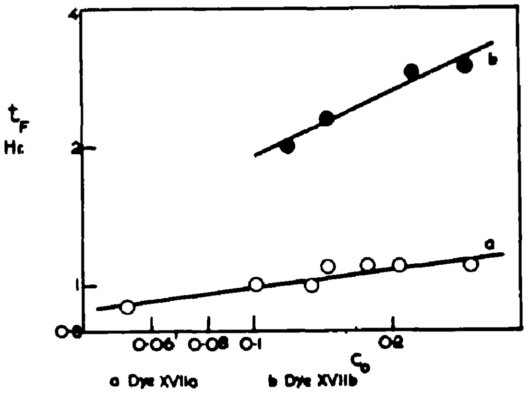


Fig.74. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

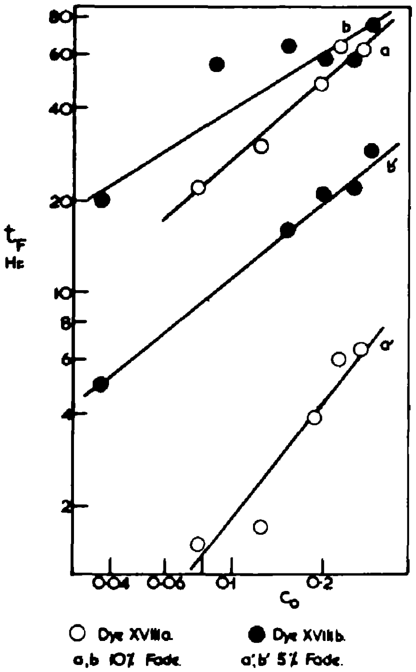


Fig.75. CF Curves for Azo Dyes on Gelatin

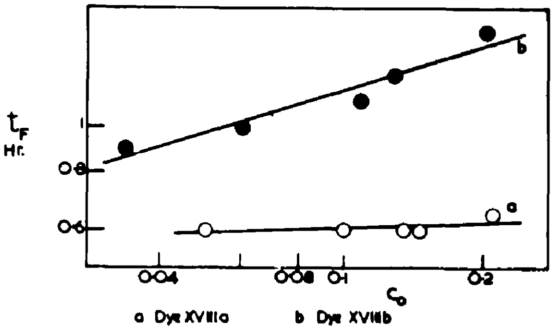


Fig.76. CF Curves for Azo Dyes on Methyl Ethyl Cellulose.

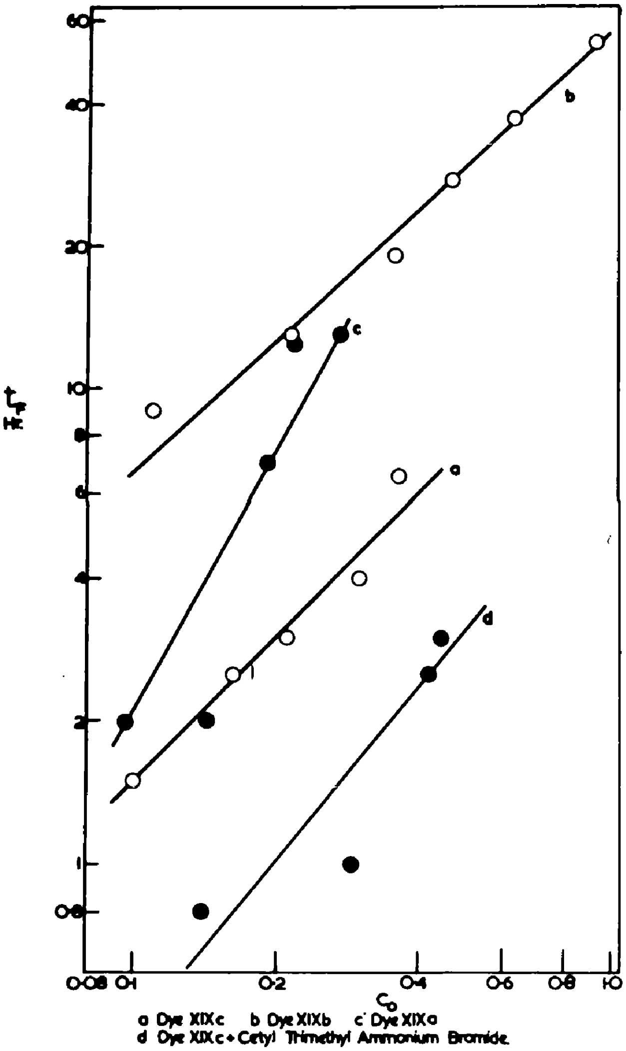


Fig.77. CF Curves for Disazo Dyes on Gelatine.

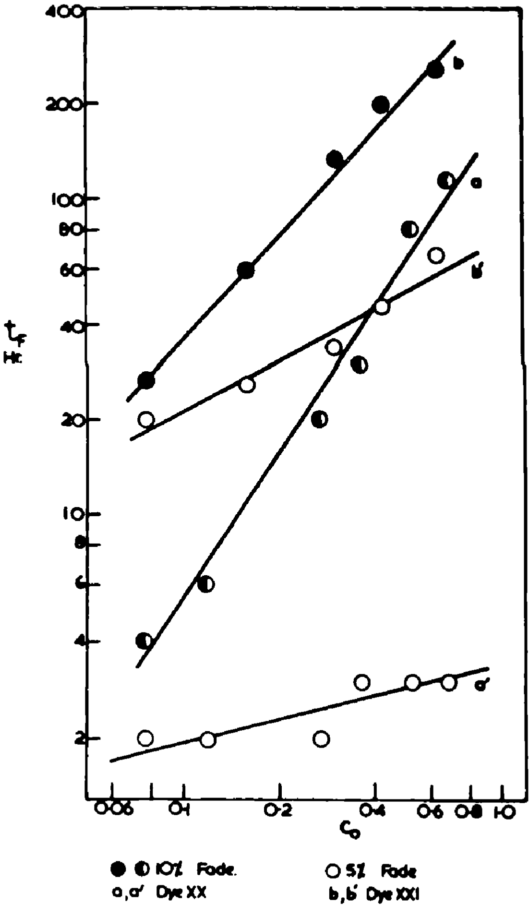


Fig.78. CF Curves for Disazo Dyes on Gelatine

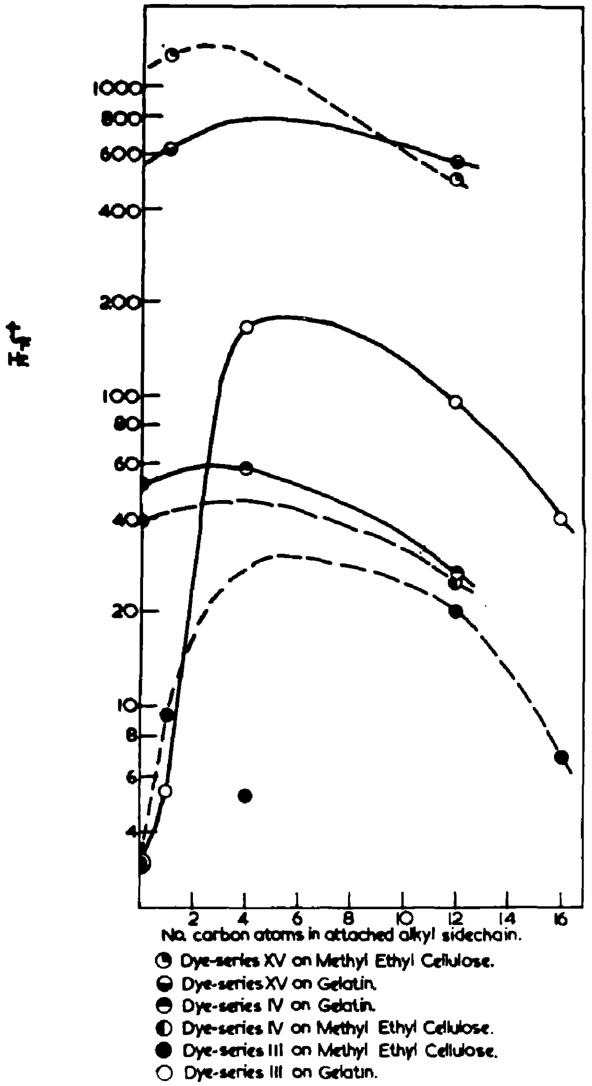


Fig.79 Relationship between Fading Time and Length of Attached Alkyl Chain, at Constant Initial Concentration.

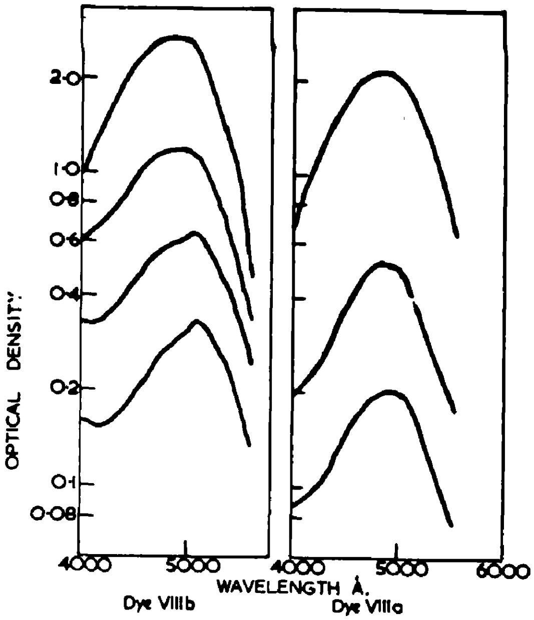


Fig.80. Light Absorption Curves for Azo Dyes on Transparent Nylon Film.

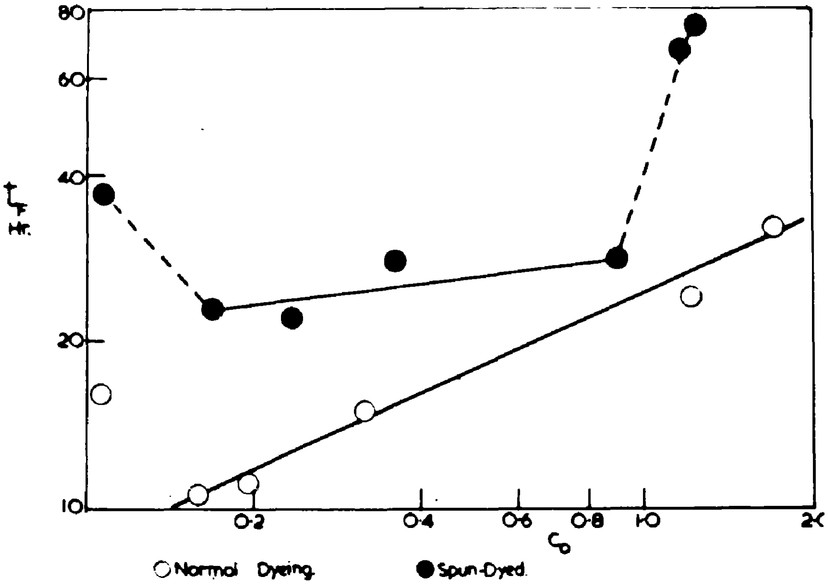


Fig. 81 CF Curves for Azoic-Dyed Viscose Fabrics.

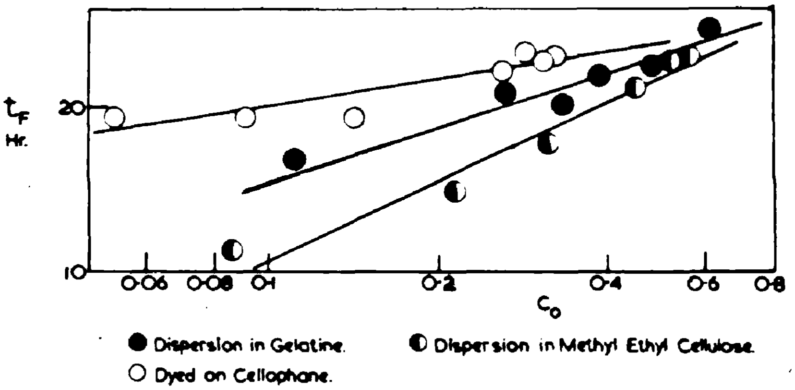
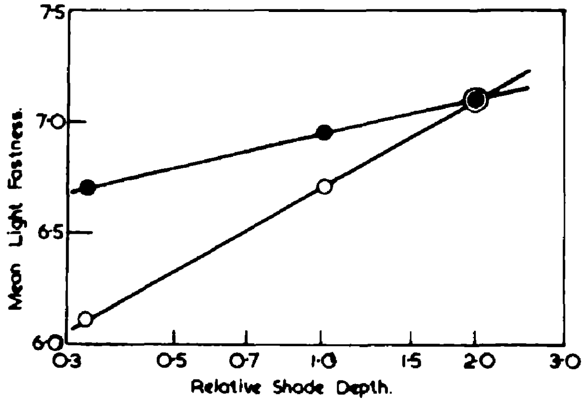


Fig. 82. CF Curves for Azoic-Dyed Transparent Substrates.



18 Helizarin dyes printed as pigments on spun viscose rayon.

18 Indanthren vat dyes applied to cotton from the vat. (A random selection of these dyes having identical fastness to the Helizarin dyes in heavy shades).

Fig. 83. Relationship between Shade Depth and Mean Light Fastness of Water-insoluble Dyes applied in Insoluble and in Temporarily Solubilised Forms.