STUDIES IN THE PHOTOCHEMISTRY OF DYESTUFFS.

by

N. Macaulay.

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Colour Chemistry Research Laboratory,
Technical Chemistry Department,
Royal Technical College,
Glasgow.

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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PUBLICATIONS.

The major part of the work contained in this thesis has been submitted for publication in the following papers entitled:

(a) Light Fading of Dyes in Gelatine, by C. H. Giles and N. Macaulay, Proceedings of the International Conference on the Science and Applications of Photography, Royal Photographic Society. To be published May, 1954.

(b) Researches Upon the Light Fading of Dyes, Part II. The Effects of Substitution in Azo Dyes and the Influence of the Substrate Upon Fading by H. R. Chipalkatti, N. P. Desai, C.H. Giles and N. Macaulay. J.S.D.C.

(c) Researches Upon the Light Fading of Dyes, Part III. The Influence of the Physical State of Dyes Upon Light Fastness, by C. H. Giles, (Miss) M. N. McKee and N. Macaulay. J.S.D.C.

CONTENTS.

INTRODUCTION.

The fading of coloured materials on exposure to normal atmospheric conditions is a problem of major concern to the dyeing, textile and photographic industries, in so far as the quality of many of the manufactured products depends to a definite degree on the light stability of the dyes and pigments used. It is not surprising, therefore, that an appreciable amount of research has been undertaken, over the years, in attempts both to elucidate the course of fading and to improve the light fastness of dyes already available. The former objective does not seem to have met with great success, partly because most investigations have been concerned with the fading of dyes in idealised, isolated systems rather than under the conditions likely to be met with in practice, where numerous other influences, e.g., the presence of moisture and atmospheric impurities, the nature of the substrate and the intensity of the illumination, serve to increase the complexity of the problem.

The following thesis describes investigations carried out in an effort to discover, firstly, the part played in the fading reaction by the substrate, and secondly, to what extent light fastness is influenced by the physical state of the dye in the dye-substrate system. It was also intended to attempt the identification of the products of fading of particular dyes following chromatographic separation, but unfortunately this part of the work had to be omitted,

and investigations confined to the measurements of fading rates.

As a guide to experimental work a comprehensive review of the available literature on the light fading of dyes was undertaken. This has been summarised in the subsequent pages.

THE MECHANISM OF FADING OF DYES.

Absorption and dissipation of light energy.

It is generally accepted that photochemical 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. The direct transition from singlet ground level to triplet level has also been considered by Lewis.

The electronic energy contained by the excited, let us say, dye molecule, after an interval of ca. 10^{-8} seconds, can

be degraded into heat energy by intermolecular collision, retransmitted as resonance or fluorescent radiation or may initiate chemical and dissociation processes. A number of formal schemes to explain these latter "electron transfer" reactions have been presented by Bowen, and are sufficiently important to merit inclusion here.

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

$$D^X + A \longrightarrow D^- + A^+$$

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

The existence of free radicals in the form of excited 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 dye.

A dismutation reaction may occur,

$$D^X + D \longrightarrow D^+ + D^-$$

and the ions so formed may react further to give a semi-quinone 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:-

$$\left.\begin{array}{ll} A^{+} + H_2O_2 & \searrow \\ A^{+} + O_2 & \longrightarrow \text{oxidation products.} \\ B^{-} + O_2 & \nearrow \end{array}\right.$$

Two or more of these reactions can take place simultaneously, depending on extraneous conditions such as in the substrate, leading, as in the case of the more complicated dyes, to a complexity of final fading products. Were these to be successfully separated and identified, the actual mechanism of fading would, in all probability still remain obscure, as any attempt to name the unstable intermediates could only be hypothetical.

Evidence of oxidation in fading.

The evidence available in the literature on the oxidative fading of dyes considerably outweighs instances wherein fading takes place by reduction. Thus Hibbert

obtained isatin from the fading products of indigo-dyed cotton; Haller and Ziersch obtained oxidation products from insoluble azo dyes dyed on cotton, while Harrison found that both in sunlight and in shortwave ultra-violet light, Methylene Blue dyed on cotton apparently faded by oxidation. A number of other dyes on cotton did not fade at all when exposed to sunlight in evacuated or nitrogen filled glass tubes. Many other investigators, e.g., Gebhard and Lazarev have shown that fading does not occur in the absence of oxygen, though this does not necessarily prove that fading is itself an oxidation process. Mounier, on the exposure to mercury vapour lamp of certain acid and basic azo dyes, in both oxidising and reducing atmospheres, found that only in the oxidising atmosphere was there any increase in fading rate. The same effect was obtained when oxidising agents were added to fibres dyed with the same dyes. Further, the colour reactions of the degraded products were the same as those obtained from the dyes faded in solution and by peroxide degradation. Couper, in a recent investigation into the fading of 1:4 bis(methylamino)anthraquinone on cellulose, succeeded in separating and identifying the majority of the products to be expected from oxidative fading.

Mudrovic reported that the polymethin dyes such as pinacyanol 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 pinacyanol 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.

According to Desai and Giles, substituent groups, e.g., nitro- and chloro- groups, which increase the resistance to oxidation of azo dyes, also appear to increase their light fastness on cellulose. Pinte and Millet at about the same time, and 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, e.g.,methoxy and methyl groups.

Evidence of reduction in fading processes.

Van Nostrand and Stillings showed that, on exposure to shortwave ultra-violet 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 CO and CO_2. Earlier Harrison had obtained the same result and found that 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 that 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. It appeared also, in other experiments, that nitro- groups in aromatic compounds suffered reduction in u.v. light in presence of cotton, but that amino- groups were oxidised.

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 ($< 2000A$) (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.

Neuweiler studied the photochemical bleaching of a large number of dyes in the presence of zinc oxide and Eosin. Both these substances 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 leuco form on exposure if either Eosin or zinc oxide is present, these last suffering no change. Azo dyes become irreversibly reduced to amines under analagous conditions. Thus photochemical reduction rather than oxidation takes place. Gelatine may take the place of the anodic depolariser. Mounier, and Seyewitz and Mounier found that certain nitrohydrocarbons were decolourised when irradiated on cotton, silk or wool. The 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.

On irradiation of azobenzene in iso-octane, Blaisdell obtained as final fading products, aniline and hydrazobenzene, the latter 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 aniline.

Atherton and Seltzer, in their work on the fading of aminoazo dyes on cellulose acetate, 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.

In light of wavelength $>$ 3400A. (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). This explanation is supported by the observation by Egerton that the extent of degradation of cotton behind glass is negligible in absence of oxygen.

It would appear that, in normal sunlight, even if the dye itself is not a photolytic sensitiser, some photolytic degradation of dyed cellulose fibres may occur with subsequent formation of reducing substances, as found by Harrison (1912), thus accounting for the reduction of nitro groups in aromatic compounds when faded on such substrates.

The available evidence on the fading of dyes by reduction on substrates other than cellulosic e.g., protein, is meagre. Potassium dichromate, however, is reduced to chromic salts when irradiated in gelatine, which is therefore insolubilised. Biltz and Eggert found that the quantum yield of ammonium chromate converted to an insoluble form by radiation of 4360A. is 0.5 and that for the amount of gelatine rendered non-swelling is 0.3. This means that two molecules of gelatine 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 gelatine. These high values, compared with those normally obtained in dye fading, may mean that the mechanism of energy dissipation by the excited molecule of chromate is

much less efficient than that of a dye molecule.

The oxidising action of H_2O_2 and activated oxygen.

Since, in certain circumstances, the formation of hydrogen peroxide and/or activated oxygen has been observed to accompany the fading of dyes, it has been suggested that these agents are a primary cause of fading by oxidation. Thus on irradiation of Acriflavine, dispersed on dry silica dust in dry oxygen at low pressure, a volatile oxidising agent was formed capable of oxidising leuco 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 H_2O_2 on irradiation(Kautsky et al.). Hydrogen peroxide is formed on irradiation of aqueous solutions of Eosin and Fluorescein (C.I. No. 766) in air (Blum and Spealman), and by irradiation of aqueous serum albumin solution at 2536A. H_2O_2 has only been indentified as a fading agent in the special case of photolytic sensitisation of cellulose.

The tendering action of certain vat dyes on cellulose and their catalytic fading effects on other, contained dyes on irradiation in air, has been the subject of considerable investigation (Egerton, Scholefield and Patel, Lanigan). The same effect is obtained in the presence of zinc oxide and titanium dioxide which absorb in the near u.v. All these

substances, whether dyes or white pigments form H_2O_2 when irradiated in aqueous suspension. Cellulose itself showing little absorption of visible or near u.v. cannot seriously be tendered thereby. It has been shown that the tendering action is due to H_2O_2 and/or activated oxygen, probably formed in the presence of the above sensitisers. The attack can extend to undyed fibre very close to, but not in contact with the irradiated material.

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.

The mechanism of photolytic tendering of cellulose by vat dyes has been studied by Bamford and Dewar, who have compared the tendering activity of many such compounds 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 :-

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

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

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 would 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 (usually oxidative) by which dyes break down under irradiation, but much of it is speculative and inconclusive, though the general opinion seems to be that some form of activated oxygen or a free radical derived from water or hydrogen peroxide is involved. Recently, Hillson and Rideal measured the photocurrent produced when each of a number of dyes of the triphenylmethane and azo series, absorbed on an electrode, was illuminated. The direction of the photocurrent so produced showed that the dye can be either oxidised or reduced depending on the conditions. Of the dyes investigated the triphenylmethane were generally the more reactive. Immersed in alkaline solution all were oxidised and all except two were reduced in acid solution. The two exceptions were oxidised. Reduction was found to occur only when the dye was in immediate contact with the platinum electrode, but oxidation could occur when the dye was at a distance from the electrode

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 :-

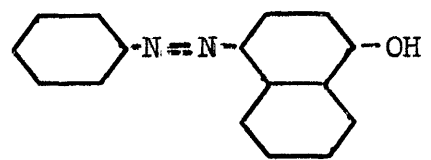
$$D^X + H^+ + e \longrightarrow DH^-$$

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

$$D + hv \longrightarrow D^X$$

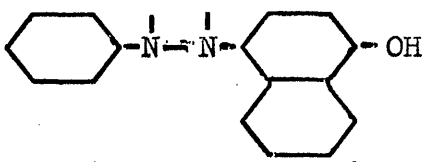
$$D^X + HOH \longrightarrow DOH^- + H^-$$

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



dye molecule.
Waxoline Red BN.

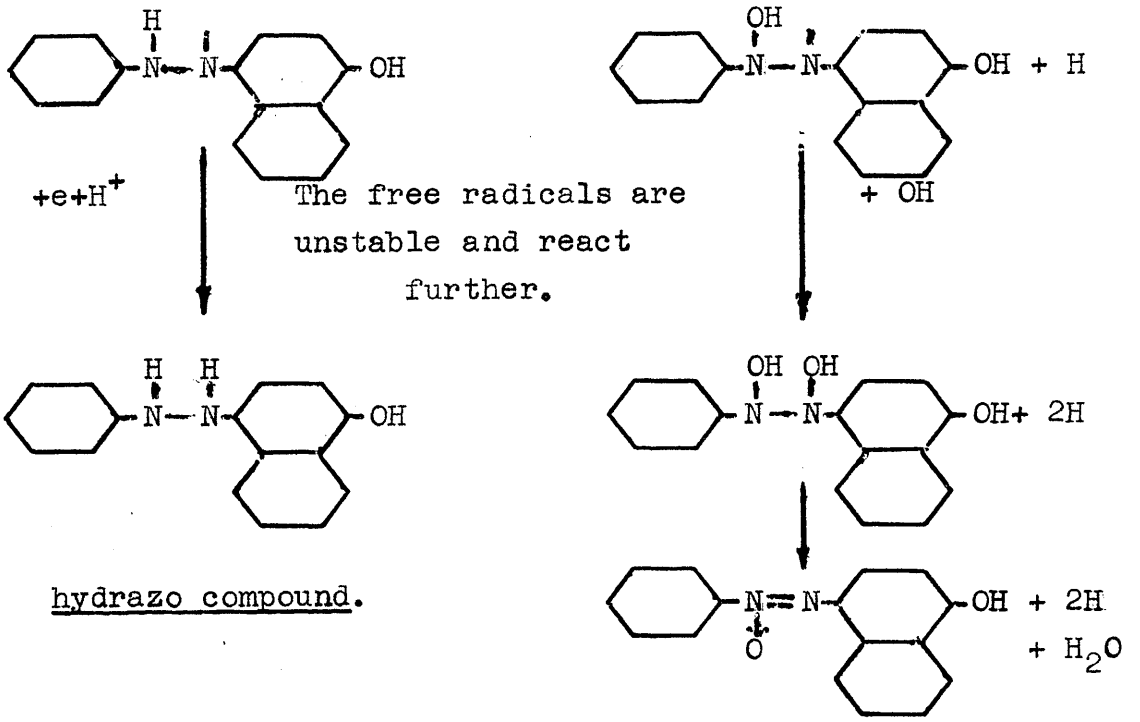
hv chemical collisions



excited radical

primary reduction step
$+e+H^+$ at electrode only

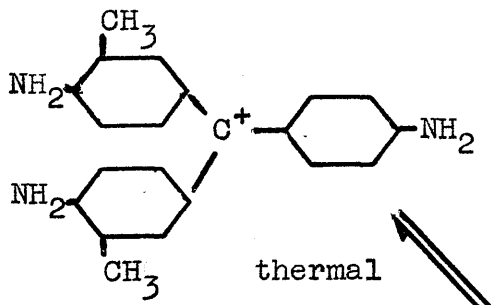
primary oxidation step $+H_2O$ at electrode and in solution.



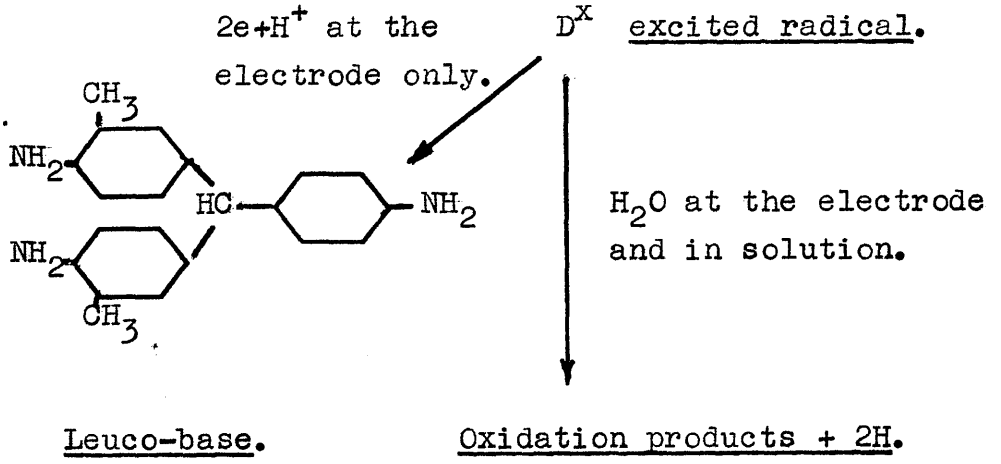
hydrazo compound.

azoxy compound.

Triphenylmethane dyes follow a similar scheme except that the oxidation leads to the complete disruption of the molecule.



Fuchsin. D^x excited radical.



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, 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. A net fading would then result if some of the hydrogen atoms are removed by side reactions and some of the excess dye-hydroxyl radicals are completely and irreversibly oxidised. The most likely mechanism for hydrogen atom removal is held to be reaction with oxygen to give HO_2 radicals which may react further to give H_2O_2.

The authors suggest that conditions on a textile fibre

are very similar to those in aqueous solution and that 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, fading would occur by a reductive mechanism, c.f. Blaisdell.

These suggestions are in fair agreement with the facts summarised above, which indicate 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. (Brownlie showed that moisture is essential to the fading of direct dyes on cotton). Yet they do not account for the fact that the presence of oxygen has several times been shown to be necessary before fading on fibres can occur, unless this promotes a different type of fading when no water except that which is very firmly bound is present in the fibre.

Atherton and Seltzer, purely speculatively, suggested the initial formation of an azoxy compound. Desai and Giles suggested a hydrolytic attack on the hydrazone form of the dye to give a quinone, and, first, a phenylhydrazine derivative which oxidises 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 sulphanilic 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 fading.

From the Stark-Einstein law of photochemical equivalence each molecule taking part in a photochemical reaction absorbs one quantum of the radiation causing the reaction i.e.

$$E = Nhv = Nhc/\lambda = 2.847/\lambda \times 10^5 \text{ Kcal./mol.}$$

where, E = energy absorbed by each molecule.

N = Avogadro's number.

c = velocity of light.

λ = wavelength of light.

h = Planck's constant.

The quantum efficiency (γ) of a photochemical reaction is defined as the ratio of the number of molecules of the absorbing material reacting to the number of quanta of energy absorbed, i.e.,

$$\gamma = \frac{\text{number moles. reacting.}}{\text{number quanta absorbed.}}$$

Measuring absorbed energy in kilocalories and chemical change in g-molecules destroyed,

$$\gamma = 2.847 \times 10^{5}/\lambda \times \text{g-mols. reacting/Kcals. absorbed.}$$

The quantum efficiency of normal dye fading is held to be very low, 10^{-5} to 10^{-7} (Morton) although no accurate determinations have been published. Yet, a number of observers have reported a surprising variation in efficiency depending on the wavelength of light used in the fading. Morton, for example, has reported that many dyes fade by the action of a comparatively narrow band of wavelengths near the absorption maximum of the dye, visible rather than u.v. light being the more efficient, though the light in question did not extend beyond 3650A. An exception was noted with direct dyes on cotton, aftertreated with " Fibrofix ", where the fading depends primarily on the radiation (3400A- 3900A), absorbed by the fixing agent itself. Taylor and Pracejus (1950) state that fading of dyed textiles is principally due to radiant energy of the visible spectrum. Appel and

Smith (1928), however, found that no fading occurred to certain blue dyes using light of the same wavelength as the absorption maxima of the dyes. Further evidence has been contributed by Blaisdell who reports 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 3030A and 3130A lines and inappreciable fading at 4050A and 4350A. For the yellow and orange dyes the most active wavelengths actually corresponded to a minimum of absorption of the dye-film system. Morton has ascribed the high rate of fading at 3030A to possible photolysis of the organic molecule since the absorbed photon is much larger than the bond energy. He further suggests that the fading mechanism in the u.v. might be different from that in the visible corresponding to different absorption mechanisms in these regions.

Atherton (given in the discussion of 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 which they used in their main investigation, and their initial destruction rates. These data are not very conclusive, but the author says they may perhaps show that the photoreaction is most rapid in the region 4400A - 4450A.

For the fading of certain colour-coupled dyes in gelatine, Collins found that the quantum efficiency was at a maximum in the near u.v. and fell almost to zero in the centre of the visible region. At this point the energy is ca. 50 Kcal./quantum which is sufficient to break a bond such as O-O (Burgess), and might therefore, be expected to affect the dye to some extent. Bamford and Dewar measured the quantum yield of a photosynthesised process of auto-oxidation of tetralin in the presence of Cibanone Yellow R at 4500A and 4000A and found it to be 0.007 and 0.03 respectively. The quantum yields for tendering, using a series of vat dyes, was of the order of 10^{-5}.

The concentrated sunlight instrument (Heliotest) was used by Luszcak and Zugriegel to determine the relative fading rates of some of the blue dyes of the German light fastness standards. They observed that each dye faded mainly in a particular waveband appreciably greater than that of the ultra-violet absorption maximum (λ). This band has a fairly definite boundary at 2λ, separating it from longer wavelengths that are almost devoid of fading action. An explanation of this phenomenon is given 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 ultra-violet luminescence. These quanta then correspond to wavelengths within the ultra-violet 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.

Experiments by Hill (1927) with a number of dyed woollen patterns exposed to mercury vapour light under several varieties of glass, demonstrated that fading increased both with intensity of u.v. radiation and with decrease in its wavelength.

Influence of the surrounding atmosphere on fading.

"Gas fume fading" on acetate rayon dyed with certain blue and violet anthraquinone dyes has been shown by Rowe and Chamberlain to be due to the combined effects of SO_2 and nitrous fumes produced by a combination of nitrogen and oxygen in the neighbourhood of burning gas flames. This type of fading appears to be confined mainly to the type of fibre and dyes mentioned. Couper has shown that the products of gas fume fading of one anthraquinone dye resembles those of light fading of the same dye.

The influence of temperature and humidity on fading.

The effects of temperature and humidity on the fading rate of dyes are substantially interdependent since an

increase in temperature proportionately decreases the atmospheric humidity. Furthermore, the moisture content (regain) of the dyed fibre is correspondingly reduced with a subsequent decrease in fading rate.

Hedges was able to control humidity values by placing aqueous solutions of glycerol or certain salts in small boxes containing dyed patterns fixed behind a " Vita " glass window for exposure to a " Hanovia " quartz mercury vapour lamp. The degrees of fading after a given period of time of a series of patterns exposed under various conditions were determined using the " Lovibond " colorimeter. The moisture content and the effect of temperature change at various humidities were observed and the temperature coefficient calculated at temperatures ranging from 10 to 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 Schwerzaw are in agreement with these values.

Fading was found to accelerate with each rise in humidity establishing a linear relation between percentage loss of dye and the moisture content of the sample, down to 5% moisture content for certain dyes on cotton and wool. A sharp change in this relationship was noted for dyes on silk, which showed a much steeper colour loss - moisture content

curve, (below 10% moisture content).

As a means of predicting fading under varying conditions, Hedges proposed the formula, $F = K/T(R + C)$, where K and C are constants; F, percentage loss of dye; T, the temperature; and R, the regain of the fabric. Lead, however, pointed out that the moisture content of exposed fabrics cannot ~~be~~ 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 at 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.

Influence of dye concentration.

In examining the fading of wool cloth dyed to different percentage depths of shade with a number of dyes, Barker, Hirst and Lambert measured 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 approx. 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 be originally present. This, of course, is the condition normally obtaining in photochemical reactions when the whole of the active radiation is absorbed, the number of molecules decomposed then becoming proportional to the time of exposure. This is known as a reaction mechanism of zero order (c.f. Bowen), so that, if the dyed fabrics do absorb the whole of the active radiation, the relationship established by Barker, Hirst and Lambert is normal.

These workers also observed an empirical relationship between fading and the square root of the time of exposure. Cunliffe and Lambert (1932) 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 pattern. They discovered that this point, in most cases, moved steadily towards " white " with the progress of fading. They obtained the relation :-

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

where F = the amount of dye faded and a and 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 c and 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 F and 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 (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 :-

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

where f and g are constants, the slope 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 :-

$$F_t = 100\left[1 - e^{-t(a \log C_o + b)}\right] \qquad \text{(vi)}$$

Sommer studied the same subject and noticed (1931) 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_o), i.e.,

$$\log t_F = a' \log C_o + b' \qquad \text{(vii)}$$

where a' and b' are constants. 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.

Several thousand individual light fastness gradings published in the trade literature of various manufacturers have been examined by Eaton, Giles and Gordon. Three grading figures for each dye are published, representing fastness in pale, medium and heavy shade depths, of given values. It was found that when the data for each dye/fibre system are averaged, a linear relation appears between (mean) log C_o (initial concentration on the fibre) and (mean)n, the light fastness grade. Furthermore, the curves for each dye/fibre system differ in slope and the slope differences are statistically significant (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 basis of the derivation is the assumption that the dye disappears in the fading reaction according to the mass law equation:

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

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, and A is the (total) dye concentration present at time t . By integration from t = 0, A = A_o, to a time t_F when a fraction α of the dye has disappeared, we obtain:

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

By taking logarithms, we obtain:-

$$\log t_F = (1-r) \log A_o + (r-1) \log (1-\alpha) - \log(1-r) - \log k$$

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

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

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

The influence of structural effects on the fastness of azo dyes.

Azo dyes form the largest class of dyes used commercially. They have been used experimentally in the major part of this thesis, hence it is advantageous to summarise some

of the more general effects of structural change on these dyes.

Azobenzene, the basic unit of azo dyes, 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, possible 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. Kiprianov and Ushenko, however, consider that the lowering of the light fastness of certain dyes of the azo, polymethin and triphenylmethane classes is due to the distortion of the planar molecule by substituent groups.

Influence of a second benzeneazo nucleus in the diazo-component.

Only one item of quantitative evidence is available regarding the effect of a second benzeneazo nucleus in the diazo component of simple azo dyes. Certain manufacturers' data show that o-amino azotoluene as a diazo base enhances the fastness a little, to about the same extent, in fact, as a m-chloro group.

The influence of meta and para substituents.

The quantitative methods employed by Kienle et al. and Pinte and Millet, have established the influence upon fading of substituents m- and p- to the azo group in benzeneazonaphthalene dyes. Since the azo group must be the point of attack in fading, the effect of m- and p- substituents will depend on whether or not they exert a protective effect on the azo group. 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.

In general it has been found that the logarithm 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.

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 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 β-naphthol, respectively, on wool (Boguslovsky and Sadov), and it extends to unsulphonated o- and p-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 o-OCH_3, noticed by Atherton and Peters might be due to chelation involving a CH...N bond.

Table I.

Fading rate data on sulphonated benzeneazo-naphthalene dyes(from Kienle et al.).

Group	Position	Reaction Rate / 10^{-6} (Reciprocal Seconds) on wool	on gelatin
OH	ortho	2.78	3.45
	meta	3.02	2.94
	para	2.63	2.54
OCH_3	ortho	2.41	2.85
	meta	2.08	3.25
	para	2.78	3.45
C_6H_5	ortho	2.71	3.35
	meta	2.94	3.35
	para	2.28	4.05
CH_3	ortho	2.35	3.35
	meta	2.09	3.35
	para	2.15	3.35
Cl	ortho	7.10	9.50
	meta	2.70	4.42
	para	2.55	4.19
COOH	ortho	1.00	1.92
	meta	2.21	3.36
	para	2.41	4.25
SO_3H	ortho	1.56	3.36
	meta	2.09	3.75
	para	1.61	4.54
NO_2	ortho	4.70	8.00
	meta	(2.41)	5.25
	para	(3.02)	5.96
H		2.09	3.62

This is supported by the data of Kienle et al. which are quoted in Table I. The o-COOH group protects the azo group and the o-OCH_3 does so too, but not so effectively. Both these might be forming chelate rings. The groups, e.g., CH_3, C_6H_5, Cl, NO_2, which do not chelate with the azo group have no significant protective action when in the o-position, even though bulky, so that steric effects cannot be operative; It is difficult to account for the slight protective effect of the o-SO_3H group, but this might perhaps be due to the electrovalent bond it forms with amino-groups in the substrate. The o-OH group shows no protective action; this again is to be expected. The OH groups referred to here are in the benzene nucleus; the o-OH group in the naphthalene residue is already chelated with the azo group in these dyes and it is known (Schetty) that in o:o'-dihydroxyazo dyes only one OH group is chelated with the azo group.

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 σ-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, this 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 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 tentative hypothesis that a substituent ortho- to the azo group increases or reduces 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.

Influence of the position of sulphonic acid groups.

A relationship between light fastness on wool and the position of sulphonic acid groups in the naphthalene nucleus of benzeneazonaphthalene dyes has been reported by Boguslovsky and Sadov. α-Naphthol dyes have the highest light fastness when the sulphonic acid group is in either position 4, 5, or 6, and the lowest when it is in positions 2 or 8. β-Naphthol dyes have the lowest fastness when it is in positions 3, 7,

or 8. It is difficult to see any reason for these differences, and failing another explanation, we might suggest that the position of these groups influences fading by affecting the size and shape of the aggregated dye in the fibre.

EXPERIMENTAL.

The source of irradiation.

In the evaluation of light fastness of dyed fabrics for commercial purposes, sunlight is the obvious choice as the source of irradiation since the conditions of test should approximate closely to the actual conditions of practice. Indeed, a large number of industrial firms still prefer sunlight fastness evaluation to that of any other. Sunlight in itself, however, has several major faults, e.g., variations in intensity and spectral energy distribution with time of day and season of the year. Moreover, fading by sunlight is usually a slow process, and for this reason a number of artificial light sources have been developed, usually of the carbon arc type, though a recent innovation has been the " Heliotest " apparatus (Gasser and Zugriegel) devised to give a 25-fold increase in intensity of the sun's emission. Commercial fading lamps usually employ the enclosed flame arc or the high intensity arc as the light source, e.g., the " Fadeometer " and " Fugitometer ", but these generally require a fair amount of attention and are costly both in initial and running costs, especially for intermittent laboratory work. Samuels et al. have reported the use of batteries of tungsten filament lamps by the I.G. in Germany, but the faults mentioned apply here also.

The lamps used in the present work as sources of illumination were chosen for their relatively constant

emission over long periods, low running costs and the very minimum of attention. These consisted of two General Electric " Osira " high pressure mercury vapour lamps of power 250w. and 400w. respectively with appropriate chokes in series but without condensers. An attempt was made to eliminate the slight fluctuation in the electricity supply by the fitting of a 230 volt constant-voltage transformer to the mains voltage supply but this cut down the lamp emission to such an extent that it had to be abandoned. The lamps were held in porcelain lamp-holders screwed to a wooden baseboard and surrounded by a cylindrical sheet aluminium screen (17in. dia. x 15in. high) fitted at vapour-stream level with $\frac{3}{4}$in. wide aluminium shelves, 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 air temperature within the screen was found to be constant for continuous running, being 41°C. and 56°C. for the 250w. and the 400w. lamps respectively. This was thought to be rather high and further investigation showed that the actual surface temperatures of the films ranged between 40 - 52°C. for the 250w. and 64 - 70°C. for the 400w. lamp for colourless and coloured films respectively.

The temperatures were measured by embedding thermocouples in the film on glass (Baxter). The temperatures obtained are much lower than Nordhammer found for the surface temperature of worsted fabric in the " Fadeometer ". Since, however, all 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 held to be adequate in so far as constancy in temperature was obtained. Uncontrolled lower temperatures, such as obtained by absorption of the infra-red emission by a water screen, would be more sensitive to variation in laboratory temperatures.

Nevertheless, an apparatus, embodying temperature and humidity controls was designed (Fig. 1) but unfortunately never reached a constructional stage due to the burden of commitments on the workshop staff. This apparatus would also have been of value in the investigation of fading under conditions of vacuum and in the presence of gases e.g., oxygen, nitrogen, and hydrogen.

The apparatus consists of a mercury vapour fading lamp, vacuum vessel, and light source for optical density measurements, as detailed below:

Fading lamp.

G.E.C. " Osira " high pressure mercury vapour lamp with choke and shutter, fitted to baseboard.

Vacuum vessel.

(a) As shown, fitted with quartz or "Vita" glass window with external filter holder attached (not shown).

(b) Pattern holder and rotating device with oil seal at wall of vessel.

(c) Heater (H) with thermostatic control (T). Gas and film surface temperature measured by low temperature thermo-couples. (No electrical connections shown).

(d) Cooling coils and motor (M) for fan. Heater, cooling coils and motor attached to back plate for convenient removal or alteration.

(e) Photocell box sealed into side of vessel containing filter. Iris diaphragm with operating mechanism, and photo-cell are fitted to removable slide.

The complete vacuum vessel is supported on metal rails to facilitate variation in illuminant intensity.

Light source for O.D. measurement.

" Spekker " lamp with shutter and lens for focussing filament on photocell; removable from rails.

The emission spectrum of the "Osira" mercury vapour lamp is reproduced in Fig.2 . In addition to the normal mercury lines a small amount of continuous radiation is emitted but this is too small to appear on the diagram. The inner envelope of the lamp is constructed of special refractory glass and absorbs all radiations below 3300A.

Hence 3650A in the ultra-violet is the lowest wavelength emitted. About 7.5% of the total energy is concentrated in the bands between 3500A - 4500A and 5500A - 6000A .

Measurement of fading.

Visual estimation;

In order to standardise the procedure of light fastness evaluation tests, the Society of Dyers and Colourists developed a series of blue standards which have been adopted by the British Standards Institution. The standards, increasing in fastness from no. 1 - 8 are spaced evenly on a geometric scale from standards no. 1 - 6, each fading at about half the rate of the one next below. Standards nos. 7 and 8 are more widely spaced.

It was intended to use these standards as a means of measuring the relative fading rates of a series of dyes on opaque substrates since the reflectance attachment for the Unicam S.P.500 spectrophotometer was not available. However, in a test exposure in the fading lamp, it was found that the standards did not fade in the order specified, nos. 1,2 and 3 having a preliminary hue change with a definite fade being observed first in the case of standard no. 3 rather than no.1 or even no.2 . This anomalous behaviour has been attributed to the differences in light absorption properties of the dyes used in preparation of the standards

coupled with the characteristic line-emission spectrum of the fading lamp. Because of this, fading on opaque substrates was measured merely as 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).

Spectrophotometric measurement.

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 absorption properties of the solute due to alteration in degree of association and aggregation (Vickerstaff). 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 ultra-violet.

The characteristic absorption curve for each dye in its substrate was determined from wavelengths of 3500A-7000A

at intervals of 100A except at maxima and minima, where the interval was decreased to 50A or 25A according to the sharpness of the curve. Such curves covering the total range of emission of the fading lamps were required for total absorption comparisons between the dyes.

Determination of dye concentration.

Opaque substrates:

In the cases where the dye has no direct affinity for the substrate it has been incorporated by purely mechanical means, and the concentration calculated directly from the quantities of dye and substrate employed. Where the dye has affinity for the substrate, the concentration has been taken as that added to the dyebath and calculated to give the required depth of shade. In such cases, exhaustion of the dyebath has been carried out as far as possible, but where necessary the concentration of dye remaining in the exhaust liquors has been determined by spectrophotometric means and subtracted from the original quantity present.

Transparent films:

Most of the experiments involving films required only relative concentration values for subsequent calculation and comparison, and where applicable optical density figures have sufficed, (see, however, p.72). In certain cases, e.g., where different sized particles have been incorporated into

films to give an optical density range within the Unicam scale, the exact concentration has had to be determined. This has been done by dissolution of a standard quantity of film in a suitable solvent followed by calibration and optical density measurement. Where evenly formed films were obtained, the concentration was calculated from the quantities of dye and film employed in the preparation.

Preparation and purification of dyes.

A series of meta- and para- substituted dyes of 1-benzeneazonaphthalene-2-hydroxy-3:6-disulphonic acid was prepared by diazotisation of the substituted aniline and coupling with naphthalene-2-hydroxy-3:6-disulphonic acid (R-acid), in the usual manner(Fierz-David and Blangey). Purification of the dyes so formed was attempted by recrystallisation from water as the only suitable solvent found, but this was rendered difficult by the gel-forming property of the dyes at higher concentrations. Precipitation of the dyes from solution by addition of ethanol also proved unsuccessful; the dyes were therefore used without further purification for part of the work, i.e., fading on opaque substrates. It was assumed that the impurities in the dye consisted mainly of salt. Estimation of the dye purity was carried out by the titanous chloride method.

Since the effect of impurities might have been more

critical in the case of fading on film substrates, further attempts were made to purify the dyes, until eventually a high degree of purity was obtained by making use of ion-exchange resins, thus: a 4ft. exchange column was set up of 1in. bore glass tubing, in two connecting halves, the upper containing a cationic resin "Dycatan", and the lower a laboratory prepared anionic resin. An approximately 2% aqueous dye solution was passed through the column at the rate of 200ml. per hour, the treated solution evaporated to dryness, the dye ground down, and the purity estimated as the free acid. Before use, the dyes were converted to the sodium salt by neutralisation with sodium carbonate. The cationic and anionic resins were regenerated for 12 hours after each run by soaking in 2N HCl and 5% Na_2CO_3 respectively. The dye purities were estimated (Table II), both by titanous chloride and by oxidation method of analysis (Arshid).

Preparation of alkyl ethers of sulphanilic acid → phenol.

Sulphanilic acid was diazotised and coupled with phenol (Fierz-David and Blangey). A mixture of 15g. (M/20) of the dye so formed, 8.25g. (M/20) n-hexyl bromide, 5ml. 10N sodium hydroxide solution and 50ml. ethanol was agitated under reflux overnight. The precipitate was filtered and recrystallised from boiling water. The preparation of the octyl ether was carried out similarly.

The solubility of these compounds in cold water was

found to be very low; consequently they were not used as originally intended in gelatine films.

Calculation of relative fading rate from fading curves.

For all opaque substrates used a just perceptible fade was assumed to represent an equivalent decrease in the surface dye concentration, and the time of exposure required to give a just perceptible fade taken as the time for an equivalent fade in each case. In dealing with films, however, it was found that initial fading in a large number of cases was rather irregular due, probably, to alteration in the physical state of the dye on exposure to the temperature in the fading lamp. Consequently the decrease in concentration ΔD, Fig. 3. 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 exterpolation 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.

Derivation and employment of Hammett sigma-values.

In chemical reaction where rate and equilibrium are determined by potential energies alone, e.g., side chain reactions of meta- and para- substituted benzene derivatives and in the reactions of substitution in the benzene ring, a simple and quantitative relation appears when two series of rate or equilibrium constants are compared, that differ with respect to the nature of the reacting group, the change which it undergoes during the reaction, or in the sense that the rate and equilibrium for a series of reactions are compared, e.g., ionisation constant of meta- and para-substituted benzoic acids against rate constant for the hydrolysis of similarly substituted benzoic esters; i.e., a straight line is obtained by plotting the logarithm of the ionisation constant of a benzoic acid against the logarithm Of the hydrolysis constant for the similarly substituted ethyl benzoate.

$$\log. k_h = \rho \log. K_i + A \qquad (i)$$

A similar relation holds for nearly all side-chain reactions of benzene derivatives.

Two series of constants thus linearly related to a third series are also related to one another, the slope of

the last relationship being the ratio of the slopes of the first two. Thus it is convenient to relate various constants to one standard of reference, in this case the ionisation constants of the substituted benzoic acids.

Equation (i) may be simplified,

$$\log.k_h = \rho(\log.K_i - \log.K_i^o) + (A + \rho\log.K_i^o)$$

and since, from equation (i),

$$A + \rho\log.K_i^o = \log.k^o$$

then, $$\log.k - \log.k^o = \rho(\log.K_i - \log.K_i^o)$$

therefore, $$\log.\frac{k}{k}o = \rho\sigma$$

where k, is any rate or equilibrium constant; k^o, the constant for the unsubstituted reactant; K_i, the ionisation constant of the substituted benzoic acid; K_i^o, the ionisation constant for the unsubstituted benzoic acid; σ, the substituent constant; ρ, the reaction constant for all substitutions, depending only on the reaction series.

The values of σ determined by Hammett and used in this thesis in conjunction with the fading rates of the corresponding benzeneazo→R-acid dyes are reproduced in Table II.

The influence of substrate in the fading of azo dyes.

Other than the published work of Kienle et al., Atherton and Seltzer, and Atherton and Peters, there is little precise knowledge on the effect of the substrate on the fading rates of azo dyes. One significant fact emerging from

a study of the above papers, however, is that on wool and gelatine as substrates Kienle et al. found that the slope of the curve of σ-value against the relative light fastness had a positive sign, i.e., the fastness decreased with increase in σ-value, while the other authors obtained the reverse effect on cellulose acetate. Desai and Giles detected the latter type of relationship in the fading of some insoluble azo dyes on cellulose and in oil media. The following experiments have therefore been carried out in order to ascertain whether the sign of the σ-value vs. light fastness curve is significant in so far as its variation may denote a different mechanism of fading on the substrates investigated.

The fading rates of R-acid dyes on inert substrates.

(a). Anodised aluminium:

Pure aluminium foil (0.002in.), rinsed in CCl_4 and cold water was anodised in 3% aqueous chromic anhydride "Analar" quality solution at 45°C. for 1 hour, using an e.m.f. of 40-45v. and a current density of 10 amp. per sq. ft. It was then thoroughly rinsed in water. The film is substantially pure alumina (Al_2O_3). Strips (5x5cm.) were cut and dyed in 50ml. of 0.02% dye solution at 60°C., then well rinsed and dried at 120°C. no sealing aftertreatment being given.

It was noted that the unsubstituted dye was not so firmly bound to the anodised surface as the other dyes of the series; it tended to strip off on vigorous rubbing. Notwith-

standing this, the strips were used as prepared.

(b). Asbestos:

Smooth white asbestos sheet (1.2g., ca. 1mm. guage), free of organic matter, was first rinsed in CCl_4, then in hot water, and impregnated with a 0.02M solution of dye, pressed between filter paper and dried thus between plate glass sheets at 100°C. This left approximately 0.3% by weight of dye in the sheet.

(c),(d),(e). Cellulose.

Three forms were used: (c), cellulose powder (for chromatography, Whatman); (d), bleached mercerised cotton sateen; (e), smooth chromatographic filter paper (Whatman). The last two mentioned were coloured by the method used for asbestos; the powder was simply impregnated with 0.01M dye solution, dried at 100°C., then ground to a uniform consistency.

Plaster of Paris.

An attempt was made to introduce the dye to this substrate, but was abandoned on discovering that most of the dye diffused out on slow drying to give an irregularly dyed surface.

Mounting and exposure of patterns.

All the dyed substrates with the exception of cellulose powder were mounted by stapling 5cm.x1cm. strips to a cardboard base, and a hinged flap attached in order to protect

one half of each strip from exposure, for comparison purposes. Cellulose powder was packed into 5cm.x1cm. rectangular apertures cut into thick card and sandwiched between glass plates which were then firmly bound with tape. One half of each pattern was protected by a hinged black card.

The samples were placed in the fading lamp and inspected at regular intervals for progress in fading by comparison of the exposed and unexposed portions. Altogether each experiment was carried out five times (Table III), and $\log. T_s/T_o$ plotted against the σ-value, Fig.4-8, where $\underline{T}_o$ is the time for a just perceptible fade for the unsubstituted dye, and $\underline{T}_s$ the corresponding time for the substituted dye. As was to be expected from a visual estimation of the fade the points obtained showed a wide scatter. The "least mean square line" was therefore, calculated using the equation,

$$b = \frac{\Sigma \underline{x}\underline{y} - \bar{y}\,\Sigma \underline{x}}{\Sigma x^2 - \bar{x}\,\Sigma x}$$

where $\underline{b}$, is the gradient of the line, and $\underline{x}$ and $\underline{y}$ represent σ-value and $\log. T_o/T_s$ respectively.

On examination of the curves, it will be seen that for each substrate, the gradient of the lines compare fairly well in slope, with the possible exception of that obtained for aluminium. In the latter case the difference may be due to chemical influences as it is the only case in which the dyes have an actual affinity for the substrate. The

mechanism of attachment of dye to Al_2O_3 on the surface of the metal is generally believed to be by hydrogen bonding, but how this should affect the fading rates is obscure.

In the case of certain substituents, e.g., p-NO_2, p-Cl, there appears to be a consistent deviation in the rate of fading i.e., the deviation of the value of log. T_o/T_s appears to be greater for these substituents. This could be due to inaccuracies in the values of "σ" used, in the first case, or to error in the visual observation of the first perceptible fade, as it is known that the sensitivity of the eye towards differences in depths of shade, varies to some extent over the visible region of the spectrum. Thus differences in depth changes are generally more difficult to distinguish in the yellow than in the red. Indeed it was noted during the experiments that the changes in shade depth of p-OCH_3, p-OC_2H_5, and p-CH_3 substituted dyes were much more easily detected with certainty, than those of -Cl and -NO_2 substituted dyes. Discrepancies in the values obtained for the nitro- substituents may be due to partial reduction of the nitro- group, to compounds more fugitive to light than the original. c.f., Seyewitz and Mounier.

One further suggestion is that fading is affected to some extent by the crystallisation properties of the dyes on the removal of the solvent, especially when the mode of preparation of the dyed substrate is taken into account, but

this aspect will be dealt with later in connection with aggregation of the dye in the substrate.

The most significant feature about the σ-value vs. light fastness curves is that without exception the gradients have a negative sign similar to that obtained by Atherton and Seltzer and in contrast to that obtained by Kienle et al.

Further experiments were carried out on nylon fabric dyed with the above dye series, and on wool dyed with the corresponding benzeneazo-β-naphthol series applied from glacial acetic acid, but estimations of the fade were generally extremely irregular and consistent results could not be obtained. It was decided therefore, in future work to make use of transparent substrates as far as possible, these having the advantage of exact spectrophotometric measurement of dye destruction. As examples of transparent substrates several materials were tried, "Cellofas A", "Cellofas B", polyvinylalcohol, polymethacrylate, but only the first was found to be suitable.

Preparation of "Cellofas A" films (methylethylcellulose).

A 4% aqueous solution of "Cellofas A" was prepared in the cold by stirring continuously for 24 hours, squeezed through nylon fabric, then centrifuged at 2500 r.p.m. for one hour in 4x250ml. containers to deposit fibrous material. The supernatant liquor was then used for film casting, 17ml. portions being mixed with 9ml. portions of 0.0005M dye solut-

ion and poured on "subbed" photographic glass plates. The sheets were levelled on a sheet of plate glass on a metal surface heated below by 4 x 100w. tungsten lamps. This procedure gave the most uniform films, but even so, inequalities in optical density due to drying irregularities were noted round the perimeter of the plates, and consequently only the central portions of the plates were used for subsequent fading.

A strip (50 x 11mm.) was cut from the centre portion of each plate and the film surface covered with a second equal-sized portion of similar glass, and the ends bound firmly together by tape to prevent movement in the event of the film peeling from the glass. This size of strip was suitable for direct insertion into the spectrophotometer cell-carrier. The strips were then exposed in the fading lamp and removed periodically for optical density measurements at the wavelength of maximum absorption as ascertained previously for each dye from their absorption curves. Three such experiments were carried out by exposure in the 400w. lamp and one in the 250w. lamp with the constant-voltage transformer in series (Table IV).

The fading rates obtained, show an almost linear relationship between decrease in optical density, i.e., concentration of dye, and time of exposure, rather surprisingly as it was expected that fading would follow approximately

the exponential law. c.f., equation (vi), p.28. It has since been found that a large number of the dyes later examined show the same linearity in fading rate, but as this question involves the study of all fading rate data subsequently obtained, it will accordingly be dealt with in the later discussion.

Values of the time required for an equivalent fade have been calculated over the period of fading from $D_1 = 4$, $D_2 = 10$ hours, for the 400w. lamp, and from $D_1 = 20$, $D_2 = 80$ hours for the 250w. lamp, since initial fading irregularities appear. The time of exposure required to give a 10% decrease in the value of D_1 was calculated from the mean fading rate between D_1 and D_2.

The least mean square line of relative fading rates vs. σ-value (Fig. 9) has the negative slope as for the foregoing inert substrates, the deviation of the points, however, has not decreased to the extent desired in spite of the use of the spectrophotometer, and the values of log. T_o/T_s for dyes with p-Cl and p-NO_2 substituents still appear to be too high, thus ruling out difference in spectral sensitivity of the eye as a major source of error in visual estimation.

The absorption spectra for these dyes in "Cellofas A" film (Fig. 11) show that only a slight increase takes place in the ratio of the shorter wavelength azo tautomer to the hydrazone tautomer as compared to absorption in solution,

Fig. 10, and it was thought hardly likely that the small differences in total absorption would affect the -value vs. fading curve to any degree, certainly not sufficiently to reverse the sign of the gradient. Nevertheless, "Cellofas A" films of these dyes were exposed to monochromatic light of wavelength 3650A by using a 2mm. Chance OX1 filter-glass in place of the normal coverglass, on exposure. The curve obtained, Fig. 9, shows no change in sign and only a small change in gradient, probably within the experimental error of the single test carried out. It would seem therefore, that for these particular dyes, small differences in total absorption have little effect on the nature of the σ-value vs. fading curve.

Fading on gelatine as substrate.

In order to substantiate the work of Kienle et al. and more recently, Chipalkatti, the fading rates of the dye series was investigated as follows:- 14ml. of a 6% aqueous solution of gelatine, of pure inert photographic quality, was mixed with 9ml. of 0.0005M dye solution and poured on a "subbed" photographic glass plate (4in. x 5in.) on a screw-levelled platform. On setting the film was placed in a steady stream of air from a fan until dry, this procedure ensuring the production of films having uniform optical density over their whole area. Strips were cut for exposure in the fading lamp as before.

The σ-value vs. fading curve (Fig. 12) shows the positive gradient also obtained by Chipalkatti on wool and silk (reproduced in Fig. 14, 15.) although the value of the gradient has decreased to a certain extent in the case of gelatine. It would appear therefore, that the class of substrate on which the dyes are faded is characterised by the sign of the σ-value vs. fading curve, positive for protein substrates, negative for inert substrates. It was thought feasible that this difference could be due to the effect on fading of the chemical bonding between the dye and the substrate in the former case, in contrast to the latter in which no actual chemical combination takes place between the dye and substrate, except in the case of anodised aluminium.

In protein substrates, dyes are generally believed to be attached at salt linkages between the polypeptide chains or by combination with free amino- or carboxylic acid end-groups or even the amido- groups in the protein molecule. By introduction of compounds containing these particular groups into a series of "Cellofas A" films it was hoped to reproduce the conditions of dye attachment prevailing in the protein substrate.

The effect of adjuvants on fading in "Cellofas A" film.

Films were prepared using 15ml. "Cellofas A" dope, 9ml. 0.0005M dye solution with further additions of, (a) 4ml. 0.2M aqueous n-butylpropionamide solution, (b) 2ml. aqueous

0.2M adipic acid solution, and (c) 2ml. 0.3% aqueous ethylenediamine solution respectively for each dye, and strips mounted for exposure in the normal manner.

From Tables VII. no departure from the normal order of relative fading associated with "Cellofas A" films can be detected; hence it may be concluded that none of these groups are instrumental in producing the negative gradient obtained on protein substrates. As a further check, however, varying concentrations of "Nylon 66" salt were added to similar films, thus: 15ml. "Cellofas A" dope and 9ml. 0.0005M dye solution was cast with addition of 2ml. of (a) 0.10%, (b) 0.25%, (c) 0.50%, (d) 0.75%, (e) 1.00%, (f) 2.50% aqueous "Nylon 66" salt solution respectively for each dye. At higher concentrations the salt crystallised in the film and results for the films containing 1.00% and 2.50% were rather irregular. In the remaining films, Table VIII. the addition of "Nylon 66" salt was found to have little, if any, effect on the light fastness.

Hillson and Rideal, c.f., p.14, have suggested that either oxidation or reduction mechanisms of dye fading, as they found in solution, may occur in the dye-substrate system depending on the conditions prevalent in the system. The reviewed evidence appears to favour an oxidative mechanism of fading on non-protein substrates, but as the foregoing experiments have shown that a contrasting difference exists

between the mechanism of fading on protein and non-protein, it is perhaps not unlikely that the reduction mechanism prevails in the latter case. It appears that this mechanism is independent of the mode of attachment of dye to substrate and that the effective reducing agent is confined to the substrate alone. Dyes with no affinity for protein substrates should therefore, still show the characteristic positive gradient of σ-value vs. fading curve when introduced to protein films. Consequently a series of benzeneazo-β-naphthol dyes were prepared for fading in gelatine.

To give satisfactory films of this type, Waters and I.C.I. here recommended the addition of diazo- and naphthol-components to separate volumes of gelatine with subsequent mixing of the two gelatine solutions. It was found, however, that on setting this method gave rise to film of rather poor transmission; consequently, the two components were first mixed and rapidly added to the gelatine. The diazo component was prepared at 0°C. by slowly adding 1.75ml. 10% $NaNO_2$ to the solution of M/400g. amine in 7.5ml. 10% HCl. The solution was made up to 250ml. The naphthol solution was prepared by dissolving 1.46g. (M/100) β-naphthol in 6.6ml. 10% NaOH and diluting to 1000ml. Separate films were prepared by thoroughly mixing, (a) 1ml., (b) 2ml., (c) 3ml. of each of these solutions, adding to 16ml. 8% gelatine solution and the whole poured on a glass plate, allowed to

set and dried. The films obtained had a certain amount of opacity, but were thought to have sufficient transmission for the purpose of the experiment. Those prepared from 1ml. of each component were found to give the most suitable optical density values.

The data obtained, Table IX., give little evidence of any regular order of fading. This has been attributed to inaccuracies incurred during preparation of the films, or to differences in crystalline form of the dyes. Further experiments were not attempted with insoluble dyes in gelatine.

Fading on nylon and polyglycine as substrates.

Bamford, Boulton, Hanby and Ward have shown that for anionic dyes, the equilibrium dye absorption is dependent on dyebath p_h, indicating that the free basic groups in the polymer contribute to absorption. Considerable reduction in uptake of Azogeranine 2G was observed on acetylation of the polymer, while the absorption of direct cotton dyes was little affected. Peters, and Munden and Palmer found that the saturation absorption of a levelling acid dye in the case of "Nylon 66" was closely related to amino end-group content. It appears, therefore, that acid dye absorption by these polymers is due to the amino end-groups, the interaction between dye and "backbone" being insufficiently strong to allow dyeing when the amino end-groups are blocked.

Further examination of fading on protein substrates

was carried out on "Nylon 66" and polyglycine. These represent the simplest type of protein substrate available, and differ essentially from the substrates of this class previously studied as they consist of polypeptide chains containing no side chains.

Nylon: Transparent 0.003 in. nylon film in 2.5 x 4 in. strips was dyed in 400ml. of 5 x 10^{-6}M dye solution at 95°C. for 90 minutes, a little dilute acetic acid being added after 45 minutes to effect complete exhaustion. The material was then well rinsed and dried at 100°C. and a strip cut and sandwiched between glass plates for exposure, one set in the 250w. lamp and three sets in the 400w. lamp.

Polyglycine: Unsuccessful attempts were made to prepare polyglycine films by casting from dichloracetic acid. Fading was therefore examined by visual estimation as for other opaque materials. 0.5g. of powdered polyglycine was dyed at a liquor ratio of 100:1 in a bath containing 20ml. 0.0005M aqueous dye solution, 10ml. 10% Na_2SO_4 solution and 1.5ml. 1% sulphuric acid. The bath was raised to boiling point in 30 minutes, and held there a further hour to give maximum dye exhaustion. The dyed powder was filtered, washed with cold water, dried and mounted for exposure as for cellulose powder. Complete exhaustion was not obtained.

Tables X,XI, show the same linearity in fading rates as obtained in other tests. σ-value vs. fading curves in

both cases, Fig. 16,18, show the negative slope associated with inert substrates. We have therefore confirmed that the characteristic fading on proteins cannot be ascribed to the fundamental groups present in these polymers and in proteins in general. Hence it can be concluded that the particular fading agent effective in natural proteins is not present in these synthetic substrates. The possible nature of the fading agent will be discussed later.

Oxidation and reduction of dyes in solution.

If the differences in fading, as previously discussed, are due to oxidation in the case of cellulosic substrates and reduction in that of protein, it would be expected that the same dyes would show corresponding differences when oxidised or reduced in solution. With this in mind the following experiments were carried out, more on a qualitative than a quantitative basis.

Oxidation by hypochlorite.

(a). In alkaline solution: 8ml. of 0·16% NaOCl solution and 2ml. 0.0005M dye solution were rapidly mixed and the oxidation rates at 18°C. measured on the E.E.L. colorimeter, using E.E.L. filter no. 624. The p_H of the solution while reacting was 9.6 - 9.4.

(b). In acid solution: the above experiment was repeated using NaOCl brought to p_H 4 by addition of acetic acid.

Reduction by titanous chloride.

Reduction rates were measured on adding 8ml. 0.00006N $TiCl_3$ solution to 1.5ml. of dye, at a p_H of 1-2, using the same filter as above. No suitable reagent was found for reduction in alkaline solution.

In both acid and alkaline conditions the order of the oxidation rate gives rise to a result consistent with that of fading on non-proteins, Fig. 19, 20, acid oxidation rates being relatively greater than alkaline, corresponding possibly to higher hydrogen ion concentration in solution at p_H 4 than at p_H 9. Reduction data, Table XII, are rather more inaccurate but show a definite reversal in order of dye destruction, corresponding to fading on protein substrates. This result has been confirmed by reduction in sodium sulphite-hydroquinone solution (Baxter), although results from reduction with stannous chloride were found to be inconclusive. In general the above results agree with the hypothesis of dye reduction on protein and dye oxidation on non-protein substrates.

Peroxide oxidation of R-acid dyes in gelatine.

Chipalkatti found that the light fading on wool or gelatine of the series of R-acid dyes in acid, neutral or alkaline conditions and the rate of oxidation in solution by hydrogen peroxide under acid conditions are influenced in the same sense (positively) by the nature of the substituent

group in the dye. In alkaline solution the relative peroxide oxidation rates are influenced in the negative sense by substituents Fig.21 . It has been suggested that if H_2O_2 was responsible for fading on proteins, the relative fading rates on these substrates under alkaline conditions would be influenced in the negative sense also, corresponding to the oxidation in solution. Objection has been raised at this hypothesis on the grounds that the comparison involves two entirely different dye-substrate systems viz., in protein and in solution. To overcome this objection it was attempted to study the peroxide oxidation rates of these dyes on gelatine film under acid and alkaline conditions.

Accordingly, portions of coloured gelatine films prepared as already described were placed in a " Perspex" cage and allowed to stand in a desiccator in the dark over mixtures of 5ml. of 98% hydrogen peroxide and 5ml. ammonia (0.880 S.G.) or glacial acetic acid respectively. (The films were exposed in this manner to the acid or alkali alone for two days before the peroxide was introduced). The films were removed at intervals for optical density measurements in the spectrophotometer and the vessel recharged with fresh reaction liquor each time. The results obtained, however, appear to be rather inconclusive in the case of oxidation under acid conditions Table XIII, although substituents tend to have a negative influence on fading rates under alkaline

oxidation conditions Fig. 22. This enhances the validity of the hypothesis criticised above.

The influence of aggregation on the fading of dyes.

Previous work on the study of the mechanism of dyeing has largely led to the view that dyes are attached to the fibre, molecule to molecule. Direct molecular attachment will probably take place between dye and substrate in systems involving solution, but in systems involving fabrics or solid films in which the solvent has been largely dried out, the substrate only contains the equilibrium amount of sorbed water. Only at very low concentrations will there be solvation of the dye and true molecular attachment of dye to fibre. At normal concentrations the dye must obviously be largely deposited from solution, and the form the dye assumes will clearly influence light fastness, and perhaps other properties also, but no precise knowledge has hitherto been available on this subject. Astbury and Dawson in the study of the setting properties of wool fibres, examined by X-rays samples of dry fibre dyed with a few acid dyes, and in some cases they did actually detect evidence of dye crystallites; in other cases no such evidence was obtained. Presumably this does not rule out the possibility of amorphous aggregates of dye being present in the latter case.

Recent studies in the mechanism of fading have mainly been carried out in solution (Blaisdell, Hillson and Rideal), in order to simplify identification of the products formed. These systems however, are held to be idealised in that they consist of liquids in relatively free kinetic motion and in which any absorbing molecule is equivalent to any other: they do not necessarily represent the true state of a dye on a fibre. In the dye-substrate system, owing to the fact that air and/or water are essential participants in the reaction, only those molecules in contact with the external atmosphere can take part in the fading reaction. If the dye is present as aggregates or crystals the remaining molecules in the interior are therefore prevented from active participation in the fading reaction until such time as the molecules become exposed to the external atmosphere by destruction of the outer molecules or breakdown of the crystal or aggregate. A decrease in active surface area will therefore tend to give an increase in the light fastness for equivalent concentrations of dye present in the fibre. The reaction order may also be entirely determined by the absorption of the active radiation by the dye present in the interface and may not necessarily decrease with increase in total dye destruction, as it would do in an ideal system. The system will then have a constant and characteristic reaction order which we may call its apparent reaction order, c.f., Eaton, Giles and Gordon p.29 .

This will only apply to the early stages of fading since at the final stages the surface area will obviously diminish and the reaction order approached that obtained, e.g., in solution.

The subsequent experimental work was carried out to ascertain in what manner the fading rates of particular dyes on exposure, were influenced by aggregational effects promoted by various reagents, and the extent to which the results obtained conformed to the above hypothesis.

The influence of particle size on fading.

Several attempts were made to investigate the influence of the size of the dye particles on light fading. Samples of Caledon Brilliant Orange 6R were obtained of varying average particle size, and these were incorporated into gelatine films. The fading rates, however, were so slow that the experiment had to be abandoned. Similar slow fading rates were obtained for a merocyanine dye (II) in gelatine, although in this case, the films containing the finest particles, prepared by addition of the dye dissolved in acetone to a gelatine solution, faded at a measureable rate, Table XXIV., Fig. 23. No regular fading was noted for the dye in larger particle sizes. This at least shows that the finer particles of dye fade the quicker.

The problem was overcome by making use of a very loose to light photographic merocyanine dye (I). A series of films

were prepared in "Necol" label varnish adhesive, wherein the dye was assumed to be in an approximately molecular dispersion, by adding 0.5-4.0ml. of 0.3g./litre acetone solution of the dye to 8ml. of 80% acetone solution of the varnish, spreading on 4in. x 2.5in. glass plates and drying in the dark. A further series was prepared by precipitation of the dye in gelatine by the addition of 0.5-4.0ml. of 0.3g./litre acetone solution of the dye to 8ml. of 6% aqueous gelatine solution. The particles obtained were barely perceptible on the microscope. A final series of gelatine films containing larger particles of the dye was prepared by simply grinding the dye and dispersing in water. 0.13-1.50ml. of this suspension was added to 8ml. 6% gelatine as before. The concentration of dye on the latter films was obtained by drying off 0.2ml. of the suspension, dissolving the residue in acetone and comparing the optical density of the solution with that of a solution of known strength, Table XXIV (ii).

Table XXIV (i), shows that the dye in gelatine faded in an approximately linear manner for a certain time until an abrupt change in fading rate took place. The dye was found to be completely insoluble in water, hence the initial fading cannot be due to the fading of any dye held in solution in the films. No satisfactory explanation has so far been offered for the sudden change in fading rate.

The influence of soaping on the light fastness of insoluble azo dyes.

In 1929 Bean and Rowe carried out a series of experiments involving the soaping of various insoluble azo dyes on cotton. They found that the fastness to light increased with increasing size of dye particle in the fibre and attributed this to a decrease in surface area of the dye. Fading was done in the "Fadeometer"and in sunlight.

As further confirmation of the effect of aggregation, several insoluble azo dyes have been investigated on "Cellophane" film, aggregated particles being large enough for observation under the microscope after soaping but not before.

A naphthol solution was prepared by heating 2g. Brenthol AN (α- naphthylamide of 2:3-hydroxynaphthoic acid) with a little Calsolene Oil HS (I.C.I.) and hot water, adding 10ml. 10% NaOH, followed by 10ml. hot water and heating until dissolved. 160ml. water and 20ml. 10% NaCl were then added and the solution diluted to 1000ml. A diazo solution was made up by pasting 0.25g. Brentamine Fast Orange GC base (o-chloroaniline) in 2ml. concentrated HCl, adding 3ml. 10% $NaNO_2$ and 50ml. water and ice. The solution after standing for some time, was neutralised with sodium acetate and diluted to 500ml.

"Cellophane" paper (6in. x 4in. x 0.001in.) was wetted

thoroughly in cold water containing a few drops of Calsolene Oil HS, and worked for periods of time ranging between 1 and 15 minutes , in the naphthol solution in a developing dish. After thoroughly rinsing in brine solution and cold water, the "Cellophane" strip was immersed for 10 minutes in 100ml. of the diazo solution until the dye was fully developed. One half of each strip was gently boiled for 1 hour in a solution containing 2.5g. soap flakes and 2.5g. sodium carbonate per litre. It was then rinsed, dried at a 100°C. and mounted between glass for exposure. The experiment was repeated as above, but in addition $\frac{1}{3}$ of each film was left soaking overnight in cold water, then dried. Brenthol AS coupled with Fast Orange GC base was used in a further confirmatory experiment.

From the fading rate data obtained, Table XIV, it will be seen that after an initial irregular fade the decrease in dye concentration is linear with time of exposure. Fig. 27, 28, show the plot of the logarithm of initial concentration against logarithm of time of exposure for an equivalent decrease in concentration in each case. Soaping of azoic dyes produced a definite increase in fastness in each case for each dye treated. Steeping in cold water overnight had little effect on light fastness, presumably due to the fact that little aggregation could have occurred. The curves show little significant change in slope, since the plot seems to

become more scattered on aftertreatment by soaping, and therefore, rather inconsistent.

It was realised that the relationship between optical density and concentration of dye in the film might significantly alter after soaping of the films due to aggregation of the dye. The true concentration of the dye in the film before and after soaping was therefore, determined by dissolving a standard amount (12 x 40mm.) of each film in 8ml. 80% H_2SO_4 and measuring the dye concentration spectrophotometrically. The optical density values for each film were plotted against the optical density of the film in solution, Fig. 29, showing that only a small variation occurs, with little effect on the final results Fig. 27, 28. This is regarded as an extreme case, aggregational effects being much less in other cases.

The influence of aggregation on the light fastness of vat dyes on nylon.

The light fastness of vat dyes on nylon is poorer than that on cellulose. Butterworth and Crossland have shown, that with a number of vat dyes, cellulose fibres exhibit negligible dichroism when the dye is in the oxidised state, but show pronounced positive dichroism in the reduced leuco state. Polyamide fibres, however, show positive dichroism in both the oxidised and reduced state; so it may be inferred that the dye molecules in the latter fibres remain in a

relatively unaggregated state, thus on the present hypothesis, accounting for their lower light fastness. It has been suggested that the swelling of the fibre in presence of aqueous solutions of swelling agents, e.g., salicylic acid, cinnamic acid, benzoic acid, would tend to increase the light fastness by allowing more space within the fibre for aggregation of the dye. With this purpose in mind the following fading tests were carried out on a pair of vat dyes on nylon, untreated and aftertreated with cinnamic acid as swelling agent.

Nylon film (0.003in.) in 4in. x 3in. strips was scoured at 40°C. for 15 minutes in 0.5% Lissapol N solution, rinsed in cold water and dyed in a bath prepared thus:- 0.1g. Caledon Yellow GN300, 14ml. 20% NaOH and 200ml. water were heated to 80°C., 2g. Formosul G and 20ml. 1% Dispersol VL added and the temperature raised to 90°C. and maintained there for 10 minutes for complete reduction of the vat. After cooling the bath to 60°C., the nylon strips were immersed for various periods of time as required, then washed, air-oxidised, and soaped at 60°C. for 15 minutes in a 1% soap solution.

One half of each dyed strip was treated for 5 minutes at 50°C. in 500ml. of 1.5% cinnamic acid in 25% aqueous acetone. It was then washed in hot water, soaped at 60°C. for 15 minutes in 1% soap solution containing 0.5% NaOH

and washed and dried. Samples of nylon were dyed and after-treated similarly using Caledon Green 7G300.

Results are tabulated in Table XV, and show the linear relationship between fading and time of exposure as before. Log.C_o- log.t_F curves (Fig. 30) are rather ill-defined, but a definite increase in fastness for the aftertreated samples is apparent from the stepwise rise in the curve.

The influence of aggregation on the light fastness of direct cotton dyes on "Cellophane".

"Cellophane" film was obtained in two forms, one in the usual dried state, and the other as extruded, without drying and contained in a sealed package. On dyeing these films it was expected, since the undried film contained larger pores, that the dye would assume a more aggregated form in this film than in the previously dried film.

Strips of each film, 10in. x 1.5in. were therefore dyed at 80-90°C. for periods of time ranging between 1 and 15 minutes in a bath containing 30ml. 1% Chlorazol Sky Blue FFS (pure) solution in 400ml. water to give dyed film of the required optical density range. The film was dried at 100°C. and mounted between glass for exposure.

The assumption that aggregation in the undried film should produce an increase in light fastness, was justified by the stepwise rise in the curves obtained, Fig. 31, Table XVI.

Fading of direct cotton dyes on viscose fabric.

As a further investigation of the effect of aggregation, fading experiments were carried out on samples of viscose of varying crystallinity. The catalytic effect on fading of the delustreing agent TiO_2 was also studied. Samples were obtained as (a) standard fibro, (b) reduced imbibition fibro, (c) strong fibro, (d) TiO_2 delustred fibro. 1.5g. samples were dyed at 85-90°C. in baths of 40:1 liquor ratio containing 45, 30, 15, 7.5, 3.75 and 1.5ml. respectively of 2g./litre solution of Chlorazol Fast Helio 2RKS, 2.5ml. 5% Dispersol VL, and 3ml. 10% Na_2SO_4 to effect exhaustion. After dyeing to maximum exhaustion the exhaust liquors were diluted to 400ml., and their dye content measured spectrophotometrically; hence the true percentage of dye on each sample was calculated, Table XXII. The samples were cut into $\frac{1}{2}$in. strips and mounted for exposure. Measurement of fading was done visually.

On exposure to the fading lamp, the dyed samples, (c) and (d) became bluer, in the case of (d) to such an extent that fading assessment was difficult. Consequently experiment (d) was abandoned. At the lower concentrations the dyeings (b) and (c) certainly faded more rapidly than (a), but at higher concentrations the results obtained are rather inconclusive due to the method of fastness evaluation.
Fig. 32.

The fastness to light of basic dyes precipitated with heteropoly acids.

The fastness to light of basic dyes precipitated with phosphometatungstic acid, its salts, or similar heteropoly acids is markedly superior to that of the untreated dye. Neergard found that up to a certain maximum, light fastness increased in proportion to the amount of heteropoly acid adsorbed by the complex, in excess of that calculated as being necessary for the salt formation suggested by Richards. The adsorbed acid is believed to be present on the surface of the colour complex and fastness to light therefore proportional to the surface concentration of the acid. The increase in fastness is assumed to be due to retardation of the fading mechanism by preferential absorption of light energy, normally causing fading, by the adsorbed complex. It is suggested that this may alternatively be due to a decrease in the effective surface area of the dye aggregate owing to the sealing effect of the adsorbed heteropoly acid.

Samples of Victoria Blue BO, untreated, precipitated exactly, and precipitated with 25% excess heteropoly acid were obtained. Gelatine films of these dyes were prepared by addition of their alcoholic solution to aqueous gelatine solution and drying. On fading, no significant difference in fastness was observed between the films, and it was assumed that some breakdown of the complex must have occurred

on solution. Similar results were obtained by addition of the dyes dissolved in 50:50 methanol-toluene solution to Bedafin 2001 (I.C.I.) and subsequent baking of the films at 100°C.

Further samples of the same dyes were obtained in the form of printing inks ground to the same particle size in lithographic varnish and all of equivalent strength. Successful films were prepared by thoroughly mixing small amounts of ink into lithographic varnish containing 15% w/w of a drying agent, and the resulting coloured mixture carefully painted on to glass plates. The relative concentrations for the films were calculated from the measured optical density of a mixture of 0.0001g. ink in 6g. lithographic varnish. In the 1cm. cell in the spectrophotometer, these quantities gave optical densities of,

0.145, for Victoria Blue BO, untreated,

0.311, for exact precipitation,

0.281, for 25% excess precipitation.

The optical density values of the films were adjusted accordingly, Table XVIII.

Table XVII, and Fig. 33, contain the data for fading in lithographic varnish. The fading rate curves depart from the usual linearity to give much more pronounced curves, and $\log.C_o$-$\log.t_F$ curves show an increase in fastness in the case of both dye complexes, the increase being greater in the case

of the complex prepared by excess precipitation, as expected. For both complexes, the order of reaction has considerably decreased. The significance of these results will be discussed later.

The effect of dye dispersion on light fastness.

"Cellophane" strips, 10in. x 1.5in., were dyed with direct cotton dyes as before, using (a) Chlorazol Copper Blue BS, (b) Chlorazol Brilliant Orange 3R. One half of each dyed strip was treated for 15 minutes at 40°C. in a 6% Fixanol C solution, as dispersing agent, rinsed out in cold water and dried at 100°C. On treatment the dyeings became yellower in the case of (b), and redder in that of (a), this colour change corresponding to a slight shortening of the wavelength of maximum absorption in each case, as shown by the absorption curves, Fig. 35. On exposure in each case, the fastness to light was reduced, though little change in reaction order, as indicated by the slope of the $\log.C_o$-$\log.t_F$ curve, occurred, Table XIX, Fig. 36.

The nature of the effect of the Fixanol C aftertreatment was assumed in the above experiment to be purely dispersive, but for confirmation, the experiment was repeated, after-treatment being carried out as before, and in addition with Metabol O, a quaternary ammonium compound chemically similar to Fixanol C, but devoid of dispersive action. In this case "Cellophane" was dyed using Chlorazol Sky Blue FFS (100%)

Treatment with Metabol O was carried out at 40°C. in a 6% solution for 15 minutes. On treatment the dyeings became much redder when wet, but reverted to their original blue colour on drying at 100°C. It would appear from these colour changes that the reagents exert some chemical as well as dispersive action on the dye, Fig. 37.

Fig. 38, shows that both treatments have much the same effect on light fastness. It may be assumed, therefore, that the decrease in light fastness in this case is not wholely, if at all, due to dispersion of the dye to smaller-sized aggregates within the films.

The effect on light fastness of the soaping of vat dyes on cellulose.

The soaping of dyed fibres in many cases results in formation of aggregated particles of dye within the fibre, c.f., Bean and Rowe. Sumner, Vickerstaff and Waters have shown that the soaping of vat dyes in cellulosic fibres causes colour changes which they have attributed to the effect of crystallisation of the dye within the fibre. The same changes occur in water alone, but the rate of crystallisation is improved by the addition of a detergent. They observed that soaping of vat-dyed cotton may increase or decrease the light fastness of the dyeings, but in general with the dyes studied soaping has little effect. Micrographs taken of the dye Caledon Pink RL at intervals during ageing in colloidal

solutions (conditions held by the authors to correspond to changes produced by soaping of the dye on viscose film), show the change from irregular particles of dye to long needle crystals. Aggregation of azoic dyes produces particles of larger size with a consequent reduction in surface area, but in the case of the above vat dye, the change to a crystalline form appears actually to increase the effective surface area of the dye. According to the hypothesis held, light fastness should be reduced on soap treatment of these dyes, assuming that this decrease in surface area takes place in the dyes examined. The change in the light fastness produced by soaping a pair of typical dyes of this class on "Cellophane" was therefore investigated.

20ml. of a 1% suspension of Durindone Blue 4BC250 was vatted at 60-70°C. for 10 minutes with 7ml. 10% NaOH and 0.3g. "hydros". When the reduction was complete, the solution was diluted to 200ml. with warm water containing 1ml. NaOH and 0.1g. "hydros" and the temperature maintained at 50-60°C. Strips of "Cellophane", 10in. x 1.5in. were then dipped in this solution for various periods of time to give the required optical density range on air-oxidation. One half of each strip was then soaped for 15 minutes in 1 litre of 4g./litre soap solution.

This procedure was repeated using Durindone Red 3B400. The results obtained, Table XXI, Fig. 39,40, confirm the

hypothesis outlined above.

The effect of crease-resist treatment on light fastness.

The change in light fastness produced on crease-resist treatment of viscose dyed with Duranol Red 2B was examined. Table XXIII, gives the concentration of the dye on the fibre with the corresponding time for a just perceptible fade in each case. At all concentrations the crease-resist samples are appreciably less fast to light, Fig. 41.

The dyeings and aftertreatment were carried out thus: 3g. samples of the standard viscose fabric were dyed at 85-90°C. in dyebaths containing 3.75, 7.5, 15, 22.5, 30 and 37.5ml. respectively of 2g./litre Duranol Red 2B solution at a liquor ratio of 40:1, each bath containing 2.5ml. 5% Dispersol VL and 6ml. 10% Na_2SO_4. After dyeing the concentration of dye on the fibre was determined by diluting the exhaust liquors to 500ml. and measuring the dye content spectrophotometrically.

For crease-resist treatment a solution was made up by neutralising 200ml. 40% formaldehyde with 1% NaOH, adding 100g. urea and when dissolved, 9ml.(0.880) ammonia. This solution was refluxed for 3 minutes and cooled rapidly until below 20°C. A second solution was prepared by dissolving 9g. ammonium dihydrogen phosphate in 50ml. water, neutralising to p_H 7 with 10% ammonia, the whole added to the previous solution, and the mixture diluted with 50ml. water. One half

of each dyed pattern was worked in the cold anti-crease dope, squeezed uniformly and dried at 60°C. The samples were then baked for 3 minutes at 130°C., soaped for 5 minutes at 50°C. in a solution containing 2.5g. soap flakes and 2.5g. Na_2CO_3 per litre, and finally rinsed and dried. Half inch strips were mounted for fading as for opaque substrates.

The influence of surface activity on the fading rate of dyes.

In addition to the formation of aggregates of dye in the fibre due to dye-dye attraction between polar groups in the molecule, it is suggested that dyes exhibiting surface-active properties may further be influenced in their light fastness by deposition as monolayers on the substrate. The physical state assumed by the dye will depend on the balance of dye-dye and dye-fibre intermolecular forces in absence of solvent, i.e., deposition as a monolayer will occur, if either the molecule is surface active or the dye-fibre molecular attraction is greater than the intermolecular dispersive forces between hydrocarbon residues of the dye, e.g., when the hydrocarbon residue is small. Normal aggregation will occur when the dye-dye attraction predominates, e.g., when the hydrocarbon residue is large but not conferring surface-active properties. Surface activity may be conferred by the introduction of long alkyl chains, ca. C_{16}, into the dye molecule.

In the present work the fading rates of a number of dyes containing long hydrocarbon chains have been studied in comparison with those for the same dyes but with no chains, or shorter chains. Two pairs of colour-coupled photographic dyes in gelatine film were obtained*, prepared by immersion in the developer for varying intervals of time to give the range of optical density suitable for fading rate measurements. One dye of each pair contained a C_{17} alkyl chain. The films were mounted and exposed in the usual manner. Curves of $\log.C_o$-$\log.t_F$, Fig. 42, show the order of reaction for the dye containing the long chain to be much greater than that for the dye with no chain attached, in the case of both the magenta and cyan coloured films. The relative rate of fading appears to be greater for the magenta rather than for the cyan film, Table XXVI, but the extent of the decrease in the $\log.C_o$-$\log.t_F$ gradient between the unalkylated and alkylated dyes appears to be the same. This has been attributed to the suitability of the C_{17} dyes for monolayer formation within the film.

Results obtained for the fading in gelatine of two pairs of acid dyes** with and without attached hydrocarbon chains are also consistent with the above hypothesis (Black). Further work on this class of dyes was carried out in order to substantiate the evidence already obtained.

Films were prepared by the addition to 16ml. of 6% aqueous gelatine solution of 0.5 - 9.0ml. of 0.2% solution of

* Supplied by Ilford Ltd
** " " ICI Ltd.

Solway Ultra Blue BS (Dye I), and the same dye with a C_4H_9 chain attached, and a similar blue dye (Dye II), unalkylated and with a $C_{12}H_{25}$ chain attached. After drying the films were prepared and exposed in the fading lamp. The results, Table XXVII, Fig.44, show that the slope of the curves for the unalkylated dyes are both lower than that for the C_4 and C_{12} dyes. Since the slope for the alkylated dyes has significantly increased, it must be assumed that neither the C_4 nor C_{12} chains confer surface-active properties, but do increase the tendency for aggregation to occur, presumably due to dye-dye attraction, since the hydrocarbon residue is large. There is a very slight decrease in the slope for the C_{12} dye as compared to the C_4 dye, but this is probably within the experimental error of the technique employed. It is possible however, that the C_{12} alkyl chain is insufficiently long for conferring surface-active properties. Further lengthening of the chain may produce better results.

In order to ascertain the length of chain required for the surface-active effect to predominate in fading, a series of yellow merocyanine dyes, alkylated from C_2-C_{16}, were obtained. Unfortunately these dyes were water insoluble and could only be incorporated into gelatine films as a dispersion, a procedure which would probably nullify any aggregational or surface-active effects. Dyed films were therefore prepared by addition of 0.5 - 4.0ml. of 0.3g. /litre acetone solution

of the dye to 8ml. dope prepared from 80ml. " Necol " varnish diluted with 20ml. acetone. The solution was spread on 4in. x 2.5in. levelled glass plates and allowed to dry in the dark. Fading rates are given in Table XXVIII. Log. C_o-log. t_F curves, Fig. 45,46,47, are identical for each dye, within the limits of experimental error, and it may be concluded that no surface-active effects take place with these dyes in the substrate used. This is probably due to the non-polarity of the solvent used on this occasion. No further investigations on this subject have been attempted.

The influence of the illuminant emission wavelength on fading.

As a certain amount of controversy exists over the particular wavelengths of light most efficient in the fading of dyes, c.f. p. 20, a series of experiments wefe carried out in order to investigate the relative fading efficiencies for the five major emission lines in the spectrum of the mercury vapour lamp used in the present work. A series of filters were therefore obtained which transmitted each of the lines separately, to the exclusion of the remaining four. These have been listed, together with their percentage transmission and the total energy incident on the exposed films at each wavelength, Table XXIX.

Yellow, magenta and cyan colour-coupled films were each faded at the monochromatic wavelength noted, by means of

these filters, and from the absorption curves for each dye, Fig. 43 and the fading rates, Table XXXI, the relative quantum efficiencies were calculated, Table XXX.

Of the wavelengths examined, it is clear that fading is confined to the 3650A, 4047A, and 4358A bands, with very little or no fading occurring at the 5461A and 5780A bands, although appreciable absorption takes place at these wavelengths. In view of the rather inconsistent values of relative quantum efficiences obtained for the former three wavebands, it would be necessary to carry out futher investigations on this subject, before any definite conclusions could be formed.

DISCUSSION

AND

CONCLUSIONS.

The influence of substrate on fading.

The detailed data for the fading of the 1-benzeneazo-2-naphthol-3:6-disulphonic acid dye series on the various substrates investigated are given in Tables III-X, from which the final curves of -value vs. log. relative time of exposure for an equivalent fade, are derived, Fig. 4-22. In order to complete the available information concerning this subject, Fig. 14, 15, 21, reproduced from the work of Chipalkatti, have been included.

From a study of these curves it is apparent that the influence upon fastness of substitutuents on the dye molecule depends on the nature of the substrate, whether protein or non-protein. It is suggested, therefore, that fading on proteins and non-proteins follows an essentially different mechanism. Various tentative hypothesis offered to explain this difference are discussed below.

Fading on 'inert' substrates.

On non-proteins, e.g., cellulose, asbestos, etc., in which the dyes have no direct affinity for the substrate, the influence of the substituent on the relative fading of the dye is very similar. The explanation of the similarity in behaviour of these materials which seems to accord best with all the facts, is that fading takes place by an oxidation process, and that it does not involve any chemical reaction

with the substrate itself. There are some grounds for believing that cellulose molecules in the regions accessible to dyes are surrounded by firmly bound water molecules, and do not come into direct contact with the actual molecules (Allingham, Giles, and Neustadter.). It would seem therefore, that the dye must either remain in solution within the fibre or crystallise into submicroscopic dye particles. In the above case, crystallisation is quite likely to take place, especially as the dye has no affinity for the cellulose. Differences in absolute fading rates for any particular dye between the substrates may therefore, be due to variation in the physical state which the dye assumes within the fibre, e.g., differences in surface porosity may limit the degree of crystallisation or aggregation of the dye, thus influencing the dye interface exposed to the air. Protein substrates, on the other hand, possessing affinity for the dye, are not so likely to be affected by aggregational influences, although the chemical bonding between the dye and substrate in the presence of solvent may, to some extent, be disturbed in favour of aggregation of the dye molecules when the solvent evaporates.

Fading on protein substrates.

The change in sign of slope of the curve of σ value-fastness in the case of protein substrates must mean that a different mechanism of fading takes place. By analogy with the results obtained from oxidation and reduction of the dyes

in solution, it seems not unlikely that a reduction mechanism could also apply to fading on protein substrates. Several alternative hypothesis have been suggested, however, and these have been examined below.

Hydrogen peroxide as the fading agent on proteins.

The formation of hydrogen peroxide by irradiation at 2500A. of the protein, serum albumin, has been reported by Roberts. In the presence of an excited dye molecule, longer wavelength irradiation might be sufficient to produce the same effect in the case of protein fibres, the hydrogen peroxide so formed being responsible for the fading of the dye. It has been shown that oxidation by peroxide, of the R-acid dyes in acid solution is influenced in the same sense by the substituent group in the dye as in the light fading on wool or gelatine. In gelatine film under alkaline conditions, or in alkaline solution, the influence of the substituent is reversed on the peroxide oxidation of the dyes to give a negative slope. By analogy, if peroxide oxidation was resposible for fading, then in an alkaline medium, the relative fading rates should also be influenced in the negative sense. This, however, was found not to be so, Chipalkatti having shown that the influence of substituent on fading is the same when irradiation is carried out under acid, neutral, and alkaline conditions. In the presence of pyruvic acid no change in the relative order of fading takes place, Fig. 14. Pyruvic acid would have

destroyed any peroxide formed during irradiation, leaving the dye open to attack by the reagent responsible for fading on other substrates, possibly thus reversing the relative order of fading. It would appear therefore, that hydrogen peroxide plays little part in fading on proteins.

The influence of substrate constituents.

The nature of the chemical linkage between dye and substrate was next considered as a possible influence on the mechanism of fading on protein substrates. However, the results obtained for addition to "Cellofas A" films of the various adjuvants simulating the effective groups present in the protein molecule, showed that neither the amino, carboxyl, nor amido groups had any effect on the normal course of protein fading. The negative value of the slope obtained for fading on nylon and polyglycine further shows that the influence of the protein substrate on fading must arise from structural effects not present in these latter substances, but which occur in the natural protein fibres, wool, silk and gelatine.

The effect of variation in light absorption on the mechanism of fading.

Absorption curves for each member of the R-acid dye series are shown in Fig. 10, 11, 13, 17, in which optical densities are plotted on the logarithmic scale, in order to bring out any changes in absorption due to structural effects alone. Curves obtained for the members of the series, compared

in aqueous solution alone, and containing "Cellofas A", show no difference in ratio of azo to hydrazone tautomer, c.f., Burawoy, Salem, and Thomson, but in "Cellofas A" and especially in nylon films, an increase in azo tautomer relative to hydrazone tautomer is apparent. This effect is a general one for the series, and represents changes no more than consistent with those to be expected from aggregation of dye within the film on evaporation of the solvent. In gelatine the curves for the nitro- compounds undergo considerable alteration in their peak wavelengths, having a much higher absorption at lower wavelengths than formerly. This is probably due to the sensitivity of these compounds to p_H changes. The differences in total absorption, however, are not sufficient to account for the relatively larger change in fading properties.

Reduction hypothesis.

The hypothesis that reduction occurs in fading on protein substrates appears to be the most reasonable, at least for the series of azo dyes examined, although no really conclusive proof has been obtained. In the presence of pyruvic acid the relative order of fading remains unchanged, but a striking increase in fading rate occurs. This is the effect to be expected if the fading reaction is a reductive one. The experiments involving reduction in solution further bear out this hypothesis, but in this case the results may not be strictly comparable with those of fading on films, due to the

wide differences in dye-substrate systems.

The actual mechanism of fading is rather obscure, but it is unlikely that proteins behave as H-donors like hydrocarbon solvents have been suggested to do, as nylon and "Cellofas A" also contain high proportions of hydrocarbon groups. Blaisdell, however, has suggested that an excited dye molecule may react with NH- or CH- bonds in a fibre, rather than with the stronger OH bond in water. In proteins, the weak points are the C=O or NH bonds and these may thus react preferentially to water. Nylon and gelatine have relatively low absorption at and above 3650A., the lowest effective wavelength used throughout the present work, and it is not very probable that these substrates become photolytically excited, though wool undergoes decomposition on exposure to sunlight and air. The effect of photodecomposition of tyrosine molecules in wool and silk might have some effect on fading, but as gelatine contains no tyrosine, no general hypothesis on these grounds appears feasible.

The influence of aggregation on fading.

The general equation representing the photodecomposition of a substance in solution is of the form,

$$Kt = kx + \log_e \frac{1 - e^{-\alpha a}}{1 - e^{-\alpha(a-x)}}$$

where a, is the initial concentration, x, the concentration

change after a time t, and k and K are constants, and α the index of absorption, which is a constant for a given substance. With high absorption, the arithmetic term is very small, and may be neglected, so that the amount of decomposition is proportional to the time of exposure, and the reaction is thus regarded as zero order. With very weak absorption, such as obtained as the reaction proceeds, the first term is relatively small and the equation reduces to the usual logarithmic form for a monomolecular reaction,

$$kt = \log_e \frac{a}{a - x}$$

Photochemical reactions in general may therefore, be regarded as possessing an order anywhere between zero and unity. In the typical curve, decomposition will be linear with time for the initial period at high concentrations (high absorption), gradually changing to give the first order exponential curve as the reaction proceeds to low concentrations. Thus, in solution, the plot of log. concentration against log. t_f will result in a curve of zero gradient at very low concentrations, increasing as the concentration is increased to give a gradient which can be shown graphically to be 1.45 approx. at high concentrations.

This type of curve will theoretically apply to photo-decomposition when the substance is in solution or in approximate molecular dispersion, but not necessarily in the

case of a dye dispersed in a fibre substrate, where there is a tendency for the formation of dye aggregates, c.f., p.66. Here the rate of decomposition will depend to a large extent on the effective surface area of the dye particles, since the light fading of dye on fibres is believed to depend largely on the accessibility to the dye of atmospheric oxygen and water vapour. Azoic dyes and vat dyes by nature of their introduction into the fibre will be expected to exist as discrete particles or aggregates. It is quite probable that water soluble dyes may also exist as aggregates, depending on the solubility of the dyes and the amount of solvent available within the fibre in its air-dried state.

Thus, the fading of dyes in fibre substrates does not necessarily follow the same laws as substances molecularly dispersed in solution. In fact the characteristic fading order curves of $\log.t_F$ vs. $\log.C_o$ in the present work show, in contrast to the theoretical curve determined above, an approximate linear relationship holding within the limits of the concentrations used. The linearity of these curves confirms the validity of the results previously obtained by Eaton, Giles, and Gordon, c.f., p.28. The inapplicability of the normal laws of photochemical decomposition to dye-substrate systems is further emphasised by the fact that the majority of fading curves obtained experimentally, e.g., Fig. 3, show a definite linearity between decrease in dye concentration and

time of exposure, although the fading rates vary with the different initial dye concentrations. This must mean that physical differences exist between the state of the faded dye and that of the unfaded dye of unchanged dye content. The effect produced on the progress of fading, by fading products, is unknown, and might possibly constitute a further reason for the anomaly.

The characteristic fading order curves for the various experiments involving changes in the physical state of the dye in the substrate are given in Fig. 23-47. The significance of these curves will now be discussed.

Increase in light fastness with increase in aggregation.

The merocyanine dye I in collodion is assumed to be in molecular dispersion, this assumption being justified to some extent by the fact that the curve obtained, shows the characteristic increase in slope with increasing concentration, associated with the theoretical curve for photodecomposition in solution. The dye as dispersed in discrete particles, shows a much higher fastness to light, and this is held to be due to the marked decrease in effective surface area of these particles. The difference in substrates could be responsible for this increase to a certain extent, as it has already been shown, Tables IV, VI, that R-acid dyes are generally faster in gelatine than in "Cellofas A". In the present case it is doubtful if the substrate has much effect on the rate of

fading as it acts merely as a dispersion medium, with no affinity for the merocyanine dye. Differences in light absorption between the samples are marked, Fig. 25, but as the larger particles have the greater total absorption over the particular concentration range, this would tend to rather increase the value of the relative fastness for the latter samples, if variation in absorption properties is held to be responsible for the changes in fastness.

Direct evidence of an increase in light fastness of azoic dyes with increase in particle size is given in Fig. 27, 28. Soap boiling was sufficient to cause the growth of microscopically visible crystals from non-visible dye, Fig. 26. A similar increase in fastness, undoubtedly due to the aggregation of vat dyes on nylon is recorded in Fig. 30.

With the water soluble direct cotton dye on "Cellophane" film of different pore size, an increase in fastness was observed, Fig. 31, presumably due to the larger dye aggregates being formed in the "Cellophane" of larger pore size. It is interesting to note in this case that the increase in fastness is roughly of the same magnitude as the increase in particle size, assuming particles of the same dimensions as the pores, i.e., 1:2.5 (average pore size 20A:30A respectively).

Tests of the same nature on viscoses of different crystallinity give less accurate curves, Fig. 32, but do demonstrate some slight increase in fastness with decrease in

crystallinity, especially at lower concentrations of dye. An increase in fastness was also obtained on exposure of the phosphomolybdic acid precipitated lakes formed from Victoria Blue BO. It is not known however, whether the increase in fastness is due to purely chemical effects, i.e., if the lakes are intrinsically faster to light, irrespective of their physical form, or to aggregational effects. Excess precipitation further increases the fastness, supposedly by acting as a protective agent against light, but whether this is due to a reduction in effective surface area of the particles, caused by the screening effect of the heteropoly acid or merely to its preferential light absorption, remains doubtful.

Treatments involving reduction in light fastness.

As mentioned previously, the soaping of certain vat dyes on cellulose can conceivably produce an actual increase in the surface area of the dye within the fibre, by formation of long needle-like crystals in place of the original amorphous aggregates. Fig. 39, 40 show that this type of change may be taking place in the case of the two vat dyes concerned, with a resulting decrease in fastness, as indicated by the fall in position of the fading order curve. It might also be due, however, to the leuco-compound, which is still present, according to Sumner, Vickerstaff, and Waters, in the unsoaped film, being intrinsically faster to light than the oxidised dye, or to the oxidising process dispersing rather than aggregating

the dye.

Two further cases in which the light fastness is reduced on aftertreatment, are given in Fig. 36, 38, the surface-active cationic agent Fixanol C being assumed to assist the formation of a monolayer of dye in the fibre on dyeing, by acting as a spreading agent, while the urea-formaldehyde crease-resist process might restrict the size of the aggregates by blocking the pores of the fibre with resin. In both cases however, an alternative chemical reaction might occur, with the formation of more fugitive to light products, although absorption curves, Fig. 35, 37, show no evidence of chemical effects other than could be accounted for, by alterations in aggregation. The non surface-active cationic agent Metabol O, produced the same decrease in fastness as Fixanol C, and this would tend to support the view that chemical action predominates in this case, although the matter is far from conclusive. Crease-resist treatment reduces the light fastness on viscose, and it is reasonable to assume, in this case, that actual inhibition of aggregate growth takes place.

The significance of the characteristic fading order curve.

In the experimental work, fading order curves have been obtained which show quite a variety of change in slope and stepwise rise or fall The theoretical significance of

these curves depends, in the first instance, on the assumption that the fading reaction takes place in the surface layer of dye. The curves are related to the growth of this layer, in that either the number or the size of the individual dye particles in the system increases with rise in total concentration. In the first case, Fig. 49a., an increase in concentration results in a proportionate increase in the number of each particle present at the original concentration, to give the same distribution of particles whatever the concentration. Hence the surface area of the particles remains directly proportional to the total weight of dye, and the time required for a given percentage loss by fading is constant at all concentrations. This gives a reaction order of unity, represented by a horizontal fading order curve. This type of curve has been obtained with the water insoluble merocyanine dye I, Fig. 24(iii), in which the range of concentrations was obtained by mixing different amounts of the same dye dispersion into the films. Some of the water soluble dyes, Fig. 36, give curves of very low slope, a fact consistent with the retention of a large proportion of the dye as a monolayer in the substrate.

Most dye-substrate systems, however, give rise to curves of positive slope, thereby implying a non-uniform particle size distribution, Fig. 49b. In this case, the surface area increases as 2/3 power of the linear dimensions

to give a slope of 0.12, Fig. 50(i), provided that the illuminant is constant in direction and accessibility to each particle. An extreme case of the more likely unsymmetrical particle growth is shown, Fig. 49(c), in which the particle expands in one direction only, and the illuminated area remains constant. This represents an apparent zero order reaction with fading order slope of 1.45, Fig. 50(ii), wherein the total amount of dye faded is constant irrespective of concentration.

All the experimental curves obtained have slopes ranging between 0.01 and 0.8, thus satisfying the above theoretical requirements; the majority have a significant positive slope, indicating that the dye particles increase in size as the concentration increases. Except in the case of those systems producing very low slopes, this slope also indicates indirectly that the dyes examined, including those which are water soluble, exist in the form of discrete aggregates. The presence of water soluble dyes as true monolayers would give a curve of zero slope at low concentrations, rising as the formation of multilayers took place at higher concentrations, conforming with the condition of Fig. 49c. In a dye dispersion system, it may be considered that at higher concentrations, crowding would cut off irradiation from some of the particles, giving rise to an increase in slope. This type of curve would also become progressively steeper with

increase in concentration. With the exception of the insoluble merocyanine dyes in collodion, no such curves have been obtained, and the above conditions are held not to be valid for normal dye-substrate systems. Further, Fig. 24(iii), for the uniform dye dispersion system, has a zero slope even at high optical densities.

It may therefore, be concluded that a positive slope indicates some form of growth of discrete particles or aggregates in all cases. Fig. 50, illustrates the possible changes in slope on growth of the particles. These conditions have all been obtained in practice. cd represents the untreated dyed sample, the particles of which may grow, either to the same extent at all concentrations to give the same slope, c_1d_2, or to a greater extent at higher concentrations to give an increased slope c_1d_3, in addition to the overall increase in fastness. The latter would represent the more likely case in practice. If at higher concentrations (but not at lower) the growth of the particles is limited by the pore size of the substrate, a decrease in slope may occur, c_1d_1. Such would be the case in Fig. 32, where all the samples of viscose show approximately the same fastness at high concentrations, though there is a marked difference in fastness at low concentrations.

Conclusions.

From the foregoing discussion the following conclusions may be summarised.

Substrates may be divided into two distinct classes, (a) inert or non-protein substrates in which the substrate takes no part in fading other than that of a dispersion medium. (b) protein substrates in which the substrate appears to have a definite influence on fading.

In the former case fading is almost certainly an oxidative process involving the dye, water, and probably oxygen, though simultaneous partial reduction may occur. In the case of protein substrates the most probable fading mechanism appears to be that of reduction, but no confirmatory evidence is available.

Depending on the physical state of the dye within the substrate, absolute fading rates may differ from one substrate to another of the same class. In solid substrates an increase in the particle size of water insoluble dyes increases their fastness to light, by reduction in the effective surface area of the dye particles. The same effect seems to be operative in the case of water soluble dyes, indicating that these dyes are present in the substrate as discreet particles, the size of which depends on the physical nature of the dye-substrate system.

It is evident, then, that in addition to the intrinsic resistance of the dye molecule to photochemical degradation, fastness to light is determined by the physical form which the dye assumes after dyeing, or in the final drying process. This would indicate that a higher degree of light fastness might be achieved in practice by controlling drying or finishing processes to give maximum aggregation of dye in the fibre. Further, the low fastness of very weak shades might be markedly improved by the use of a pigment dispersion applied during spinning of the fibre.

Suggested further work.

(a) More tests of fading on " Cellophane " of various pore sizes, including small pore sizes.

(b) More tests of fading of powders introduced into films.

(c) Merocyanine I dye faded as a dispersion in " Cellofas ".

(d) A water-insoluble azo dye faded in "Necol" varnish.

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TABLES.

Table II.

Dye.	Substituent.	σ value.	Percentage Purity. (a)	(b)	(c)
(i)	p-OCH_3	-0.268	75.0	98.5	100.0
(ii)	p-CH_3	-0.170	86.0	100.0	99.0
(iii)	-H	0.000	100.0	99.0	98.7
(iv)	p-OC_2H_5	-0.250	72.4	94.0	99.0
(v)	m-NO_2	0.710	87.6	113.0	99.4
(vi)	p-NO_2	0.778	81.9	113.0	100.0
(vii)	m-Cl	0.373	85.4	100.5	100.0
(viii)	p-Cl	0.277	85.9	99.0	100.0
(ix)	m-CH_3	0.115	-	-	-

(a). Impure, $TiCl_3$ estimation.

(b). Purified, $TiCl_3$ estimation.

(c). Purified, N_2 estimation.

Table III. Fading rate data for R-acid dyes, on "inert" substrates.

Dye.	(a) t_{F_1} hrs. for expt. no. 1	2	3	4	5	(b) t_{F_1} hrs. for expt. no. 1	2	3	4	5	(c) t_{F_1} hrs. for expt. no. 1	2	3	4	5
(i)	137	60	128	69	181	60	60	60	69	60	181	137	69	79	69
(ii)	158	79	169	79	181	69	69	60	69	69	157	104	91	60	79
(iii)	194	208	194	240	276	104	137	69	128	104	240	104	91	60	79
(iv)	148	60	120	69	79	60	79	69	79	79	181	91	69	48	69
(v)	364	591	552	480	363	240	208	181	181	158	339	223	208	208	148
(vi)	295	128	480	418	363	224	169	208	120	137	363	-	128	120	158
(vii)	257	277	552	340	316	208	169	158	169	158	257	169	137	181	128
(viii)	169	148	208	208	257	91	91	79	120	91	208	137	91	158	91

Dye.	(d) t_{F_1} hrs. for expt. no. 1	2	3	4	5	(e) t_{F_1} hrs. for expt. no. 1	2	3	4	5
(i)	60	120	79	69	69	91	91	79	69	91
(ii)	79	-	104	104	79	104	91	91	79	91
(iii)	104	223	137	169	120	169	194	104	194	137
(iv)	60	91	69	60	48	91	104	79	69	69
(v)	240	364	591	633	836	240	277	418	364	390
(vi)	157	194	120	364	158	240	316	148	-	-
(vii)	257	316	390	418	780	181	223	277	277	148
(viii)	120	223	240	240	448	120	169	104	137	120

Table IV. Fading rate data for R-acid dyes, substrate: "Cellofas A".

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	47	163	257	327	401	518	565
(i)	5150	528	505	512	505	495	487	480	472
(ii)	5000	606	599	597	584	572	564	553	548
(iii)	4925	502	500	497	487	481	478	470	470
(iv)	5175	561	548	537	530	522	514	505	499
(v)	4850	582	580	580	575	572	572	570	568
(vi)	4950	761	760	754	751	749	750	740	740
(vii)	4900	558	554	548	546	543	541	537	536
(viii)	4950	518	515	508	503	500	496	490	488

D_1 at 200; D_2 at 600 hrs.

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3	5	6	7	9	11
(i)	5150	660	612	593	551	550	542	506	484
(ii)	5000	576	540	523	501	494	486	459	439
(iii)	4925	463	449	414	403	396	395	380	368
(iv)	5175	569	530	509	480	467	460	430	411
(v)	4850	566	557	552	544	545	543	532	517
(vi)	4950	652	648	640	632	627	626	615	600
(vii)	4900	555	547	541	532	526	526	513	507
(viii)	4950	534	520	510	497	487	487	470	451

D_1 at 4; D_2 at 10 hrs.

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3	5	6	7	9	11
(i)	5150	551	514	494	467	457	450	418	398
(ii)	5000	485	456	443	421	412	407	387	368
(iii)	4925	706	685	653	633	636	630	596	581
(iv)	5175	562	522	503	473	462	452	425	403
(v)	4850	572	562	560	555	550	550	539	532
(vi)	4950	660	664	648	640	640	633	628	620
(vii)	4900	615	604	600	586	580	581	567	564
(viii)	4950	512	497	487	474	466	464	449	436

D_1 at 4; D_2 at 10 hrs.

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3	5	6	7	9	11
(i)	5150	644	604	582	549	545	535	500	477
(ii)	5000	755	720	694	660	660	652	623	597
(iii)	4925	454	440	427	413	410	407	390	381
(iv)	5175	558	517	500	477	465	452	425	406
(v)	4850	580	571	563	558	557	556	546	540
(vi)	4950	660	660	654	640	641	638	631	620
(vii)	4900	580	570	565	555	549	549	535	521
(viii)	4950	612	593	585	569	564	562	521	532

D_1 at 4; D_2 at 10 hrs.

Table V. Fading rate data for R-acid dyes on exposure at 3650A., substrate: "Cellofas A".

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	23	29	47	70
(i)	5150	397	311	283	241	193
(ii)	5000	710	580	544	486	419
(iii)	4925	830	684	652	590	519
(iv)	5175	520	407	383	334	276
(v)	4850	473	420	395	371	358
(vi)	4950	454	392	349	318	290
(vii)	4900	700	624	574	540	513
(viii)	4950	549	470	407	364	316

D_1 at 30; D_2 at 80 hrs.

Table VI. Fading rate data for R-acid dyes, substrate: gelatine.

(a)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 29	48	71	95	117	139
(i)	5100	375	371	321	312	298	290
(ii)	5000	374	372	347	340	325	319
(iii)	4920	262	267	227	216	207	207
(iv)	5175	400	395	349	340	331	322
(v)	4250	381	372	336	321	312	298
(vi)	4500	915	875	803	752	715	686
(vii)	4750	289	285	250	241	230	221
(viii)	4900	360	346	306	292	274	262

(b)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 29	48	71	95	117	139
(i)	5100	354	342	299	290	279	268
(ii)	5000	380	370	324	311	297	290
(iii)	4920	269	263	228	222	210	208
(iv)	5175	380	363	321	310	295	287
(v)	4250	393	386	347	338	322	307
(vi)	4500	900	863	800	753	710	673
(vii)	4750	290	286	250	247	234	224
(viii)	4900	362	351	309	293	279	267

D_1 at 80; D_2 at 160 hrs.

Table VI. Fading rate data for R-acid dyes, substrate: gelatine.

(c) Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 29	48	71	95	117	139
(I)	5100	350	339	299	290	278	270
(ii)	5000	383	372	328	319	307	310
(iii)	4920	277	268	231	222	216	210
(iv)	5175	407	394	350	342	327	318
(v)	4250	382	375	337	323	309	301
(vi)	4500	925	881	818	768	730	685
(vii)	4750	282	273	253	244	233	224
(viii)	4900	390	385	-	-	-	-

(d) Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 29	48	71	95	117	139
(i)	5100	383	328	327	317	305	299
(ii)	5000	368	361	312	304	291	278
(iii)	4920	274	270	230	232	218	213
(iv)	5175	373	339	325	315	301	297
(v)	4250	392	386	344	332	320	307
(vi)	4500	900	862	791	756	715	683
(vii)	4750	287	283	257	248	238	229
(viii)	4900	352	344	301	288	271	258

D_1 at 80; D_2 at 160 hrs.

Table VII. Effect of adjuvants on fading rate data for R-acid dyes.

(a)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 3.5	6.0	8.5	12	15	20
(i)	5150	324	285	250	218	187	146
(ii)	5000	405	365	333	300	268	223
(iii)	4925	330	302	285	263	245	213
(iv)	5175	310	273	234	197	173	137
(v)	4850	380	363	357	350	340	318
(vi)	4950	685	662	654	633	618	574
(vii)	4900	414	396	378	368	352	327
(viii)	4950	492	477	440	421	396	360

(b)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 3.5	6.0	8.5	12	15	20
(i)	5150	392	374	346	326	306	272
(ii)	5000	452	450	425	411	388	357
(iii)	4925	436	423	402	396	382	357
(iv)	5175	440	415	384	362	334	295
(v)	4850	533	528	516	514	504	493
(vi)	4950	748	739	723	721	713	680
(vii)	4900	502	493	481	470	462	442
(viii)	4950	516	507	489	477	465	438

(c)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 23	27	40	110	184	230	
(i)	5150	390	362	343	284	185	110	63
(ii)	5000	607	565	532	450	317	183	135
(iii)	4925	368	345	337	296	206	134	97
(iv)	5175	316	289	280	230	148	75	46
(v)	4850	366	328	303	255	172	118	95
(vi)	4950	415	367	322	256	169	113	91
(vii)	4900	405	384	370	315	235	161	127
(viii)	4950	430	403	386	326	231	154	112

Table VIII. The effect of addition of "Nylon Salt" on fading rates of R-acid dyes, substrate: "Cellofas A".

(a) Optical density x10^3 at exposure (hrs).

Dye.	$\lambda_{max.}$ A.	0	3	5	7	8.5	11	12	16
(i)	5150	487	437	405	376	370	353	339	312
(ii)	5000	571	521	487	460	450	436	424	395
(iii)	4925	544	520	497	472	465	458	451	430
(iv)	5175	559	499	468	442	426	402	390	355
(v)	4850	616	610	600	583	586	580	571	563
(vi)	4950	736	720	708	691	692	682	675	667
(vii)	4900	550	532	522	508	506	498	491	477
(viii)	4950	531	503	485	470	465	451	444	424

(b) Optical density x10^3 at exposure (hrs).

0	3	5	7	8.5	11	12	16
450	410	379	352	346	335	319	297
526	482	447	413	413	400	387	367
454	427	406	380	380	373	363	349
460	415	388	363	355	338	327	300
466	461	450	432	437	430	429	421
620	654	646	620	628	617	602	593
497	478	465	448	441	434	427	413
612	580	554	534	525	512	510	490

(c) Optical density x10^3 at exposure (hrs).

Dye.	$\lambda_{max.}$ A.	0	3	5	7	8.5	11	12	16
(i)	5150	513	475	444	417	411	400	386	375
(ii)	5000	557	520	485	456	450	440	429	412
(iii)	4925	321	301	283	267	268	262	253	243
(iv)	5175	490	447	421	396	388	373	359	337
(v)	4850	503	503	493	470	473	468	458	448
(vi)	4950	676	711	695	662	660	648	629	606
(vii)	4900	-	-	-	-	-	-	-	-
(viii)	4950	578	554	538	522	515	507	497	479

(d) Optical density x10^3 at exposure (hrs).

0	3	5	7	8.5	11	12	16
450	420	391	361	353	340	334	330
512	492	459	432	424	417	404	393
443	415	392	373	365	358	344	337
436	396	378	358	347	332	320	310
540	488	455	432	408	395	376	360
700	655	612	577	550	519	495	463
-	-	-	-	-	-	-	-
530	495	473	454	436	432	416	401

Table VIII. The effect of addition of "Nylon Salt" on fading rates of R-acid dyes, substrate: "Cellofas A".

(e)		Optical density x10^3 at exposure (hrs).								(f) Optical density x10^3 at exposure (hrs).							
Dye.	$\lambda_{max.}$ A.	0	3	5	7	8.5	11	12	16	0	3	5	7	8.5	11	12	16
(i)	5150	426	394	365	337	330	320	310	304	433	405	380	355	347	339	325	327
(ii)	5000	525	488	458	427	418	409	393	387	458	434	410	380	370	362	341	337
(iii)	4925	497	464	440	418	410	408	391	388	383	338	317	296	281	273	254	245
(iv)	5175	454	418	390	370	353	341	329	316	442	424	404	390	379	378	364	360
(v)	4850	517	501	485	468	461	458	446	436	503	440	413	386	362	343	323	300
(vi)	4950	815	791	755	720	697	677	654	626	530	485	454	425	403	390	370	353
(vii)	4900	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
(viii)	4950	640	600	579	552	541	533	520	504	608	588	568	521	483	436	414	361

Table IX. Fading rate data for 1-benzeneazo--naphthol dyes, substrate: gelatine.

(a)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 4	8	11	14	19	25	41	65	86
(i)	5000	740	739	732	727	705	725	709	700	685
(ii)	4900	680	679	672	667	662	670	663	652	632
(iii)	5300	752	752	750	740	745	748	747	742	732
(iv)	4800	510	508	506	502	498	507	496	491	481
(v)	4900	760	748	744	739	725	730	700	655	614
(vi)	4700	374	358	345	342	331	317	297	277	264
(vii)	4900	673	664	656	652	643	651	632	626	612
(viii)	4600	530	530	523	538	-	-	-	-	-
(ix)	5000	643	640	617	622	620	626	608	598	580

(b)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 4	8	11	14	19	25	41	65	86
(i)	5000	693	721	727	721	720	740	720	708	691
(ii)	4900	700	700	695	690	686	693	680	666	640
(iii)	5300	750	746	746	743	743	748	748	747	740
(iv)	4800	512	511	512	503	503	513	508	496	481
(v)	4900	767	753	747	738	730	731	689	640	593
(vi)	4700	477	470	465	459	451	452	438	420	402
(vii)	4900	634	621	641	632	-	-	-	-	-
(viii)	4600	530	577	582	577	575	585	577	570	558
(ix)	5000	642	631	628	622	616	622	603	586	567

Dye number corresponds to substituent as for R-acid dyes.(Table II).

Table X. Fading rate data for R-acid dyes, substrate: nylon.

(b)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3.5	6	9.3	11.3	14.3
(i)	4750	547	522	514	494	437	438	437
(ii)	4950	544	517	508	490	480	470	453
(iii)	4900	510	485	471	463	450	441	425
(iv)	4725	510	501	493	480	461	450	428
(v)	4825	685	663	662	652	653	643	636
(vi)	4950	932	913	907	880	875	870	850
(vii)	4850	660	632	623	608	602	597	585
(viii)	4900	648	623	615	605	589	587	570

(c)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3.5	6	9.3	11.3	14.3
(i)	4750	539	528	518	497	436	438	430
(ii)	4950	528	528	492	476	460	445	422
(iii)	4900	644	624	609	591	580	568	547
(iv)	4725	492	478	469	451	432	417	393
(v)	4825	628	610	600	590	586	578	567
(vi)	4950	1048	1042	1017	1006	1000	980	966
(vii)	4850	656	640	634	616	608	606	591
(viii)	4900	655	633	626	608	596	591	578

(d)

Dye.	$\lambda_{max.}$ A.	Optical density x10^3 at exposure (hrs). 0	2	3.5	6	9.3	11.3	14.3
(i)	4750	548	541	527	509	461	472	448
(ii)	4950	546	520	513	495	482	470	444
(iii)	4900	604	582	572	554	543	533	511
(iv)	4725	494	482	474	458	442	426	400
(v)	4825	644	655	648	642	640	632	628
(vi)	4950	852	877	860	840	840	820	811
(vii)	4850	644	626	617	603	596	588	580
(viii)	4900	653	633	626	608	596	591	573

D_1 at 5; D_2 at 20 hrs.

Table X. Fading rate data for R-acid dyes,

substrate: nylon.

(a)		Optical density x10^3 at exposure (hrs).													
Dye.	$\lambda_{max.}$ A.	0	20	42	64	87	161	207	254	324	394	511	605	676	750
(i)	4750	548	554	548	522	525	512	510	498	481	468	448	440	433	417
(ii)	4950	546	544	532	528	516	516	504	500	489	478	461	450	446	430
(iii)	4900	618	620	603	594	594	586	579	578	560	550	528	520	517	505
(iv)	4725	516	532	518	508	508	496	490	487	473	462	444	433	430	417
(v)	4825	680	688	674	674	672	668	665	660	656	651	642	639	636	630
(vi)	4950	987	982	973	960	960	960	950	955	943	938	930	923	920	910
(vii)	4850	667	673	653	640	650	641	624	624	625	600	598	598	594	580
(viii)	4900	708	712	679	672	672	667	664	660	653	641	630	624	614	608

D_1 at 100; D_2 at 500 hrs.

Table XI. Fading rate data for R-acid dyes, substrate: polyglycine.

Dye.	t_F	$\frac{T_O}{T_S}$
(i)	45	2.67
(ii)	80	1.50
(iii)	120	1.00
(iv)	45	2.67
(v)	300	0.40
(vi)	135	0.89
(vii)	235	0.51
(viii)	100	1.20

Table XII. Reduction rates of R-acid dyes in solution.

	E.E.L. reading after time (secs).											
Dye.	10	15	20	25	30	35	40	45	50	55	60	65
(i)	-	-	36	29	22	17	14	11	9	8	7	5
(ii)	33	25	20	15	13	10	9	8	6	5	4	4
(iii)	18	15	12	8	7	6	6	4	3	3	2	2
(iv)	42	31	25	20	17	14	11	10	8	7	6	5
(v)	approx. 5 secs. to colourless.											
(vi)	approx. 3 secs. to colourless.											
(vii)	16	14	12	10	8	8	7	6	6	5	-	-
(viii)	approx. 30 secs. to colourless.											

Table XIII. Oxidation rates of R-acid dyes in gelatine.
(a). In alkaline atmosphere.
(b). In acid atmosphere.

(a)		Optical density x10^3 at exposure (hrs).					
Dye.	$\lambda_{max.}$ A.	2.5	4.0	25	45	68	91
(i)	5150	330	375	380	361	315	100
(ii)	5000	460	493	502	468	358	129
(iii)	4950	355	384	390	352	252	87
(iv)	5150	358	374	397	328	276	83
(v)	4700	342	362	367	312	300	218
(vi)	3900	428	468	471	469	429	348
(vii)	4900	337	322	330	274	232	142
(viii)	4950	466	440	450	378	336	143

(b)		Optical density x10^3 at exposure (hrs).						
Dye	$\lambda_{max.}$ A.	22	46	70	140	209	230	324
(i)	5100	542	551	548	500	420	400	337
(ii)	5000	500	508	510	487	448	440	375
(iii)	4920	408	419	402	392	373	359	311
(iv)	5175	425	422	419	377	312	245	206
(v)	4250	504	504	489	438	404	375	285
(vi)	4500	908	892	860	780	693	649	425
(vii)	4750	326	337	333	318	278	264	204
(viii)	4900	436	443	440	408	373	385	283

Table XIV.(i). Fading rate data for Brentamine Fast Orange GC Brenthol AN on "Cellophane". $\lambda_{max.}$ 5050 A.
(a). Untreated.
(b). Soaped.

(a)

Exposure. (hrs).	Optical density x10^3.									
0	347	430	556	595	806	830	920	1050	1810	2180
22	346	426	554	598	798	849	909	1064	1867	2220
46	340	420	548	581	782	838	900	1058	1866	2232
69	329	406	532	578	773	825	881	1045	1849	2240
92	319	398	526	567	761	820	875	1035	1828	2210
163	300	380	501	543	732	800	848	1003	1789	2190
212	282	367	484	525	714	780	825	977	1773	2123
259	267	354	469	512	694	759	810	970	1765	2117
331	249	334	442	487	673	733	776	937	1732	2100
403	227	314	420	461	640	704	741	910	1698	2050

(b)

Exposure. (hrs).	Optical density x10^3.							
0	294	400	458	618	729	748	910	1512
22	279	383	439	598	706	723	888	1491
46	272	373	431	589	700	720	876	1484
69	266	366	420	580	684	703	871	1468
92	261	361	417	572	681	700	869	1462
163	254	356	404	554	665	688	850	1453
212	250	350	399	552	659	683	841	1434
259	248	349	392	546	652	681	842	1437
331	240	340	385	542	640	670	827	1422
403	237	329	378	532	633	661	820	1408

D_1 at 100; D_2 at 400 hrs.

Table XIV (ii). Fading rate data for Brentamine Fast Orange GC Brenthol AS on "Cellophane". $\lambda_{max.}$ 4700 A.
(a). Untreated.
(b). Soaped.

(a)

Exposure. (hrs).	Optical density x10^3.								
0	360	608	700	743	854	960	1165	1639	1970
20	382	652	752	820	937	1037	1277	1820	2080
45	339	598	700	769	880	975	1263	1764	2009
68	318	573	683	748	850	950	1210	1737	1987
141	278	521	614	688	769	875	1132	1639	1870
189	270	508	594	652	733	846	1096	1588	1813
310	217	440	517	572	639	750	976	1459	1653
405	174	385	456	500	560	680	890	1360	1540
524	145	336	399	440	480	613	805	1264	1438

(b)

Exposure. (hrs).	Optical density x10^3.								
0	248	393	665	745	825	875	913	1123	1600
20	258	410	692	772	853	910	955	1163	1655
45	217	369	646	723	808	862	905	1140	1599
68	212	365	636	717	800	851	888	1120	1581
141	194	340	607	682	768	816	850	1055	1548
189	195	341	602	680	767	812	845	1047	1530
310	180	319	565	640	730	770	800	992	1480
405	155	294	528	608	684	732	759	940	1427
524	135	269	493	569	642	697	713	898	1369

D_1 at 140; D_2 at 400 hrs.

Table XIV(iii). Fading rate data for Brentamine Fast Orange GC Brenthol AN on "Cellophane". $\lambda_{max.}$ 5050 A.

(a). Untreated.
(b). Steeped.
(c). Soaped.

(a) Exposure. (hrs).	Optical density x10^3.							
0	124	231	457	582	758	1233	1683	1838
46	140	248	464	608	779	1296	1726	1884
166	101	201	382	507	658	1142	1573	1768
264	67	155	302	420	546	1007	1463	1630
384	50	122	237	330	437	861	1321	1480
504	35	95	187	262	353	740	1203	1358

(b) Exposure. (hrs).	Optical density x10^3.							
0	134	270	470	620	807	1299	1396	1884
46	148	284	479	643	822	1366	1437	1936
166	109	229	414	559	729	1259	1336	1828
264	68	181	341	481	623	1152	1203	1714
384	50	145	268	399	520	1036	1076	1609
504	35	118	214	330	424	910	938	1472

(c) Exposure. (hrs).	Optical density x10^3.									
0	108	234	316	379	495	880	975	1306	1334	1925
46	114	250	329	408	506	886	994	1332	1376	1930
166	94	226	300	381	453	848	950	1282	1337	1888
264	77	203	285	364	444	820	920	1245	1291	1849
384	72	195	272	350	422	793	890	1220	1261	1820
504	68	188	263	342	407	776	870	1182	1240	1784

D_1 at 60; D_2 at 280 hrs.

Table XV (i). Vat dyes on nylon. Caledon Yellow GN $\lambda_{max.}$ 4200A.
(a). Untreated.
(b). Treated with cinnamic acid.

(a)

Exposure. (hrs).	Optical density x10^3.						
0	179	225	419	450	606	1024	1309
7	176	227	425	460	620	1026	1315
23	142	195	389	423	591	975	1276
47	126	179	372	399	581	947	1257
119	100	147	325	327	540	875	1190
167	98	140	314	307	533	841	1162
287	67	110	268	241	478	756	1078
383	44	80	228	190	440	680	980
501	32	60	185	141	389	600	912

(b)

Exposure. (hrs).	Optical density x10^3.						
0	255	266	431	507	680	1051	1342
7	251	269	438	510	684	1053	1343
23	216	248	405	468	654	989	1310
47	204	229	397	446	641	958	1295
119	178	201	370	412	623	896	1276
167	175	203	370	405	620	875	1274
287	160	178	342	370	595	820	1235
383	134	154	312	339	569	765	1193
501	121	135	289	305	515	714	1165

D_1 at 140; D_2 at 400 hrs.

Table XV (ii). Vat dyes on nylon. Caledon Green 7G, $\lambda_{max.}$ 4200A.
(a). Untreated.
(b). Treated with cinnamic acid.

(a)

Exposure. (hrs).	Optical density x10^3.							
0	185	319	568	662	762	798	911	1557
7	171	317	540	648	742	783	911	1532
23	152	291	511	617	706	753	879	1481
47	132	272	481	604	673	740	868	1463
119	95	241	419	565	600	708	838	1438
167	97	242	407	566	588	710	840	1424
287	83	230	373	540	550	682	820	1384
383	62	219	344	523	524	656	797	1352
501	55	201	329	510	508	640	780	1338
622	48	195	316	501	490	630	768	1302
720	35	190	299	485	475	610	742	1297
839	25	175	278	468	453	590	722	1270

(b)

Exposure. (hrs).	Optical density x10^3.						
0	314	312	625	725	881	1345	1590
7	305	316	622	712	875	1328	1560
23	269	283	589	686	852	1304	1539
47	243	265	571	673	835	1288	1525
119	203	232	533	645	810	1248	1475
167	202	333	534	648	812	1247	1477
287	186	220	521	634	792	1212	1430
383	165	198	500	614	772	1183	1418
501	159	192	495	603	760	1163	1405
622	154	186	486	596	734	1145	1382
720	143	175	473	580	729	1140	1382
839	127	160	459	560	708	1115	1358

D_1 at 200; D_2 at 800 hrs.

Table XVI. Chlorazol Sky Blue FFS on "Cellophane".
(a). Normal pore size.
(b). Large pore size.

(a)

Exposure. (hrs).	Optical density $x10^3$.								
0	314	553	785	988	1206	1280	1484	1697	1875
1.5	256	470	684	877	1095	1159	1368	1578	1734
3.5	238	443	654	850	1074	1132	1347	1564	1730
7.0	224	422	630	821	1045	1105	1320	1533	1718
10.5	213	408	609	800	1021	1083	1302	1523	1718
34.5	180	357	547	728	948	1007	1222	1436	1650
58.0	162	318	497	674	892	960	1163	1380	1606
82.0	135	280	449	620	838	880	1105	1310	1547

(b)

Exposure. (hrs).	Optical density $x10^3$.						
0	176	325	648	920	1200	1640	1920
1.5	135	272	557	825	1092	1518	1804
3.5	129	266	544	815	1071	1486	1785
7.0	130	260	518	800	1060	1464	1760
10.5	124	254	519	789	1048	1455	1753
34.5	111	238	486	757	1000	1390	1727
58.0	108	228	468	732	970	1338	1687
82.0	95	211	440	710	930	1294	1637

D_1 at 20; D_2 at 80 hrs.

Table XVII. Fading data for Victoria Blue BO in lithographic varnish. (a). Untreated, (b). Precipitated exactly, and (c). precipitated with 25% excess phosphomolybdic acid.

(a)

Exposure. (hrs).	Optical density x10^3.				
0.00	145	269	291	535	1070
5.25	102	160	192	132	686
9.25	70	122	147	243	534
14.25	52	88	114	186	392
20.25	43	66	94	146	300

(b)

Optical density x10^3.						
168	329	371	481	528	654	925
96	220	253	340	365	470	672
54	157	187	264	279	378	560
24	105	135	201	209	309	482
0	74	102	155	161	240	407

(c)

Exposure. (hrs).	Optical density x10^3.					
0.00	314	322	390	720	740	1424
5.25	238	242	298	586	600	1120
9.25	188	192	248	508	520	1040
14.25	152	156	205	443	462	1056
20.25	117	125	167	400	418	984

D_1 at 5; D_2 at 15 hrs.

Table XVIII. Relative concentration of dye in lithographic varnish films.

(a)		(b)		(c)	
D_1	Rel. conc.	D_1	Rel. conc.	D_1	Rel. conc.
700	480	675	220	1135	408
640	440	478	158	608	220
350	240	370	124	590	211
200	140	347	117	303	111
170	115	260	88	246	90
105	75	225	75	240	88
		100	36		

Table XIX (i). Fading data for Chlorazol Copper Blue BS On "Cellophane".
(a). Untreated. $\lambda_{max.}$ 5800A.
(b). Aftertreated with Fixanol C. $\lambda_{max.}$ 5700A.

(a) Exposure. (hrs).	Optical density x10^3.							
0	218	328	443	563	638	715	890	1498
2	198	298	398	529	596	668	844	1458
4	197	289	387	522	582	658	824	1426
6	189	287	376	510	570	640	810	1403
8	194	294	374	508	567	636	808	1405
10	196	298	367	502	561	620	789	1386
25	172	262	331	460	520	570	744	1309
32	171	251	320	449	506	552	729	1285
43	162	240	304	431	490	530	708	1259
67	154	224	284	410	474	494	673	1205

(b) Exposure. (hrs).	Optical density x10^3.						
0	280	326	420	567	641	860	1222
2	248	304	373	514	587	782	1110
4	226	292	350	486	553	745	1055
6	207	270	325	460	513	709	1000
8	201	267	316	443	497	692	969
10	191	258	300	430	482	670	925
25	142	197	212	338	367	528	729
32	122	179	189	308	332	480	660
43	105	155	155	263	291	420	571
67	88	122	117	205	229	333	452

D_1 at 20; D_2 at 70 hrs.

Table XIX (ii). Fading data for Chlorazol Brilliant Orange 3R on "Cellophane".
(a). Untreated. $\lambda_{max.}$ 5000A.
(b). Aftertreated with Fixanol C. $\lambda_{max.}$ 4900A.

(a)

Exposure. (hrs).	Optical density x10^3.					
0	154	213	327	544	660	1080
2	146	220	307	522	610	1026
4	156	208	301	508	598	992
6	142	195	291	498	580	973
8	146	195	288	500	582	975
10	142	196	280	497	579	968
22	135	181	272	470	545	920
25	131	172	272	465	537	913
32	128	174	263	457	527	898
43	128	171	257	448	507	870
67	120	159	242	428	480	837

(b)

Exposure. (hrs).	Optical density x10^3.				
0	198	342	567	655	1078
2	193	333	555	626	1032
4	185	320	537	607	1001
6	173	307	515	581	983
8	173	300	503	570	975
10	167	288	491	554	963
22	124	221	411	463	853
25	120	214	399	449	830
32	108	197	373	421	784
43	91	172	334	374	717
67	72	135	277	304	606

D_1 at 20; D_2 at 70 hrs.

Table XX. Fading data for Chlorazol Sky Blue FFS on "Cellophane". (a). Untreated, $\lambda_{max.}$ 6250A.
(b). Aftertreated Fixanol C, $\lambda_{max.}$ 6000A.
(c). Aftertreated Metabol O, $\lambda_{max.}$ 6250A.

(a)

Exposure. (hrs).	Optical density x10^3.						
0	400	510	707	870	1046	1556	2190
20	299	392	545	720	880	1388	2028
24	296	384	539	712	875	1382	2022
30	283	372	522	700	860	1369	2015
56	261	345	485	662	824	1330	1980
81	228	304	434	615	775	1276	1912

(b)

Exposure. (hrs).	Optical density x10^3.					
0	397	522	975	1210	1700	1930
20	162	206	743	980	1567	1720
24	156	188	720	952	1532	1688
30	141	170	700	930	1503	1664
56	115	145	641	870	1430	1580
81	75	100	560	768	1308	1457

(c)

Exposure. (hrs).	Optical density x10^3.						
0	415	440	512	621	728	1560	1755
20	195	256	272	366	421	1251	1445
24	182	244	260	351	405	1222	1412
30	167	229	245	338	382	1190	1382
56	128	189	208	298	327	1107	1298
81	84	142	151	227	258	978	1163

D_1 at 20; D_2 at 70 hrs.

Table XXI (i). Fading data for Durindone Blue 4BC on "Cellophane".

(a). Untreated, $\lambda_{max.}$ 5900A.

(b). Soaped, $\lambda_{max.}$ 5900A.

(a) Exposure. (hrs).	Optical density x10^3.									
0	133	139	199	247	486	591	742	972	1113	1584
47	147	141	212	267	528	641	802	1049	1214	1709
167	138	130	207	262	518	635	797	1043	1212	1701
263	125	116	192	248	512	626	782	1030	1198	1694
383	117	110	187	243	495	613	778	1018	1193	1696
503	114	102	184	238	488	610	772	1015	1170	1680
671	94	84	166	217	461	586	740	975	1156	1645

(b) Exposure. (hrs).	Optical density x10^3.										
0	187	176	293	334	532	748	870	1193	1348	1585	1690
47	192	183	297	335	527	743	880	1208	1342	1611	1704
167	166	158	264	299	464	678	825	1126	1256	1490	1617
263	146	140	241	270	428	634	780	1065	1207	1439	1558
383	130	124	223	251	399	599	743	1021	1152	1400	1460
503	121	116	214	235	375	570	715	974	1116	1343	1409
671	100	94	188	205	332	518	672	920	1062	1290	1356

D_1 at 100; D_2 at 700 hrs.

Table XXI (ii). Fading data for Durindone Red 3B on "Cellophane.
(a). Untreated, $\lambda_{max.}$ 5300A.
(b). Soaped, $\lambda_{max.}$ 5300A.

(a)

Exposure. (hrs).	Optical density x10^3.													
0	114	172	195	245	290	409	372	555	666	728	780	693	837	902
5	130	193	219	271	321	444	410	605	677	788	832	740	890	970
22	105	170	193	249	295	417	383	576	654	755	810	718	870	938
45	102	168	191	250	295	415	382	576	650	753	809	714	863	945
117	96	162	189	240	285	405	372	560	639	767	799	708	849	925
166	108	170	194	247	291	410	377	563	638	760	798	701	849	925
286	108	164	188	241	284	401	372	553	632	750	785	698	850	913
382	95	154	177	228	270	386	352	535	608	728	760	677	823	890
502	90	147	165	220	263	379	348	528	600	717	755	666	814	880
622	90	147	166	215	260	374	342	521	594	710	753	666	810	880
790	67	133	160	201	247	358	328	506	577	688	728	643	792	863

D_1 at 100; D_2 at 700 hrs.

(b)

Exposure. (hrs).	Optical density x10^3.											
0	112	240	294	320	417	463	534	765	868	963	1043	1084
5	130	260	317	341	439	488	560	811	999	1000	1085	1125
22	108	234	289	311	406	451	527	761	860	959	1044	1072
45	105	227	282	307	395	440	507	741	837	935	1022	1050
117	99	214	272	293	380	424	490	717	808	900	976	1016
166	109	221	276	296	380	426	490	710	800	887	970	1008
286	106	213	265	285	369	410	473	690	776	861	938	962
382	93	200	250	269	347	392	452	664	742	828	908	930
502	91	194	246	262	338	382	440	650	728	812	888	918
622	90	189	238	254	328	375	432	640	713	792	870	890
790	75	174	221	234	307	355	409	610	680	766	838	863

Table XXII. Fading data for Chlorazol Fast Helio 2RKS on viscose.
(a). Standard fibro.
(b). Reduced imbibition fibro.
(c). Strong fibro.
(d). Delustred fibro.

Calibration.

	Wt. of dye g/400 ml. $\times 10^3$	2		10	20	50	
	Optical density of soln. $\times 10^3$.	79		398	774	1908	
(a)	O.D. of exhaust liquor $\times 10^3$.	36	90	224	251	1057	1708
	Wt. of dye in exhaust liq. g.$\times 10^3$.	0.95	2.30	6.00	6.80	27.80	44.80
	% dye on fibre.	0.14	0.35	0.55	1.60	2.14	3.00
	Time (hrs). for 10% fade.	30.00	33.00	48.00	56.00	78.00	78.00
(b)	O.D. exhaust liquor $\times 10^3$.	34	86	198	505	729	1201
	Wt. of dye in exhaust liq. g.$\times 10^3$.	0.90	2.20	5.20	13.20	19.30	31.40
	% dye on fibre.	0.14	0.35	0.65	1.12	2.70	3.90
	Time (hrs). for 10% fade.	8.00	30.00	33.00	48.00	56.00	103.00
(c)	O.D. of exhaust liquor $\times 10^3$.	38	72	188	372	720	1109
	Wt. of dye in exhaust liq. g.$\times 10^3$.	1.00	1.90	5.00	9.90	19.00	29.00
	% dye on fibre.	0.13	0.37	0.67	1.33	2.73	4.00
	Time (hrs). for 10% fade.	15.00	30.00	48.00	48.00	78.00	78.00
(d)	O.D. of exhaust liquor $\times 10^3$.	43	92	142	278	469	692
	Wt. of dye in exhaust liq. g.$\times 10^3$.	1.10	2.50	3.70	7.20	12.40	18.20
	% dye on fibre.	0.13	0.33	0.75	1.52	3.17	4.80
	Time (hrs). for 10% fade.	--	--	--	--	--	--

Table XXIII. Fading data for Duranol Red 2B on viscose.
(a). Untreated.
(b). Crease-resist treated.

Calibration.

	Wt. of dye g./500 ml. $x10^3$.	10		20			30
	Optical density of soln. $x10^3$.	471		975			2000
(a)	O.D. of exhaust liquor $x10^3$.	73	189	622	950	970	1085
	Wt. of dye in exhaust liq. g.$x10^3$.	2.00	5.00	16.60	25.00	25.50	28.60
	% dye on fibre.	0.18	0.33	0.55	0.67	1.48	1.55
	Time (hrs). for 10% fade.	48.00	48.00	56.00	78.00	103.00	103.00
(b)	Time (hrs). for 10% fade.	20.00	30.00	48.00	56.00	78.00	78.00

Table XXIV. Fading data for merocyanine dye II. precipitated in gelatine from acetone solution. $\lambda_{max.}$ 5050A.

Exposure. (hrs).	Optical density $x10^3$.						
0	375	426	607	850	1374	1488	1830
42	259	315	476	723	1192	1297	1587
115	256	311	460	699	1158	1259	1539
163	194	250	385	552	1035	1150	1420
331	164	239	380	524	1000	1122	1391
667	145	220	344	508	960	1078	1344
955	95	168	294	441	875	1005	1256
1291	85	147	282	439	850	975	1216

D_1 at 200; D_2 at 1200 hrs.

Table XXV (i). Fading data for merocyanine dye I.
(a). In collodion. $\lambda_{max.}$ 4550A.
(b). Ppte. in gelatine. $\lambda_{max.}$ 4980A.
(c). Dispersed in gelatine. $\lambda_{max.}$ 4980A.

(a)

Exposure. (min).	Optical density x10^3.					
0	83	213	428	625	1012	1426
4	58	159	336	506	855	1243
8	37	138	262	415	722	1086
12	25	101	199	335	609	945
16	17	73	155	270	515	830
20	10	52	118	217	431	720
24	8	36	92	175	365	622

(b)

Exposure. (hrs).	Optical density x10^3.					
0.0	210	452	699	905	1298	2010
3.5	182	378	560	730	1067	1760
7.5	150	280	400	520	800	1320
12.3	145	227	329	432	622	860
24.5	138	200	290	387	561	798

(c).

Exposure. (hrs).	Optical density x10^3.				
0.0	180	300	620	960	1431
3.5	175	290	590	910	1360
7.5	160	266	540	856	1280
12.3	151	241	496	812	1197
24.5	143	232	480	785	1167

t_f for a 50% fade calculated on initial optical density value.

Table XXV (ii). Relative dye concentrations and exposure required for a 50% fade, calculated on initial rate of fading.

(a).	Relative C_o.	0.15	0.30	0.45	0.60	0.90	1.20
	Relative t_F (hrs).	0.13	0.16	0.19	0.23	0.28	0.33
(b).	Relative C_o.	0.15	0.30	0.45	0.60	0.90	1.20
	Relative t_F (hrs).	10.60	9.80	8.70	9.00	10.00	13.00
(c)	Relative C_o.	0.23	0.45	0.90	1.80	2.70	
	Relative t_F (hrs).	34.70	35.00	30.00	31.50	36.00	

Table XXVI. Fading data for colour-coupled photographic dyes in gelatine.

(i). Magenta. a). unchained; b). with C_{17} chain. $\lambda_{max.}$ 5300A.

(ii). Cyan. a). unchained; b). with C_{17} chain. $\lambda_{max.}$ 6700A.

Exposure. (hrs).	(i)a. Optical density x10^3.					(i)b. Optical density x10^3.				
0	250	502	672	852	1205	376	614	1186	1920	2360
24	197	401	550	694	1025	341	554	1130	1867	2275
44	162	316	440	555	845	313	518	1071	1760	2170
70	124	232	335	436	700	272	456	1014	1652	1994
99	82	154	228	306	533	194	370	950	1610	2020
165	59	71	103	147	274	40	91	600	1175	1542

Exposure. (hrs).	(ii)a. Optical density x10^3.						(ii)b. Optical density x10^3.				
0	428	734	1042	1138	1343	1273	274	490	870	1668	2420
22	435	760	1070	1168	1363	1310	270	488	882	1700	2520
53	412	699	970	1031	1254	1170	249	453	833	1631	2400
70	402	652	920	980	1200	1109	240	447	821	1625	2349
94	374	612	830	880	1125	1033	219	414	780	1568	2300
166	310	556	760	800	1000	916	182	362	709	1480	2240
239	250	470	655	705	883	813	132	294	609	1308	2008

D_1 at 0; D_2 at 100 hrs.

Table XXVII (i). Fading data for acid dye I on gelatine.
(a). with no chain. $\lambda_{max.}$ 6000Å.
(b). with C_4 chain.

(a)

Exposure. (hrs).	Optical density x10^3.								
0	211	287	420	555	610	809	905	1032	1175
104	268	345	490	572	683	850	1000	1078	1295
176	260	312	470	549	668	820	970	1052	1240
344	259	306	460	533	650	800	945	1021	1242
512	260	298	450	515	630	768	925	987	1198
848	255	295	437	500	620	740	900	970	1156
1352	216	249	392	450	557	675	830	882	1094
1520	186	222	346	397	513	617	770	827	940

(b)

Exposure. (hrs).	Optical density x10^3.								
0	136	248	308	367	712	950	1219	1447	1840
104	171	262	382	390	792	1068	1352	1620	2050
176	156	266	354	382	780	1068	1328	1583	2020
344	160	254	350	363	760	1044	1300	1549	1965
512	164	258	344	359	742	1039	1278	1532	1975
848	151	252	328	342	717	990	1253	1500	1925
1352	125	220	289	302	661	930	1190	1435	1870
1520	100	196	258	269	620	890	1151	1386	1785

D_1 at 200; D_2 at 1200 hrs.

Table XXVII (ii). Fading data for acid dye II on gelatine.
(a). with no chain. $\lambda_{max.}$ 6000A.
(b). with C_{12} chain.

(a)

Exposure. (hrs).	Optical density x10^3.							
0	162	207	271	542	672	838	1101	1437
104	222	243	330	600	720	892	1102	1570
176	219	247	323	588	702	875	1082	1496
344	216	248	321	580	685	863	1058	1476
512	228	256	327	575	683	850	1040	1459
848	212	237	306	560	665	830	1000	1439
1352	186	207	274	520	620	780	940	1364
1520	156	186	253	490	571	749	899	1320

D_1 at 200; D_2 at 1200 hrs.

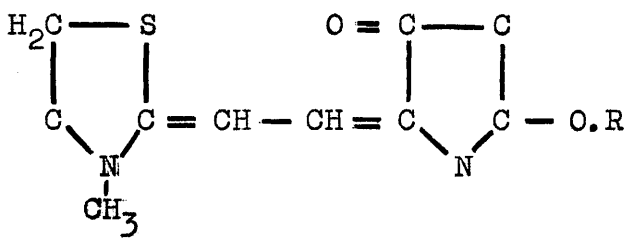
(b)

Exposure. (hrs).	Optical density x10^3.							
0	142	240	412	551	776	1041	1275	1748
104	161	299	474	598	825	1202	1334	1860
176	180	286	460	590	810	1186	1309	1803
344	181	280	458	582	799	1175	1298	1810
512	189	287	451	578	792	1165	1288	1761
848	174	270	434	558	772	1135	1255	1737
1352	143	236	397	515	720	1082	1190	1643
1520	130	213	370	480	677	1038	1158	1626

D_1 at 200; D_2 at 1200 hrs.

Table XXVIII. Fading data for merocyanine dyes of increasing alkyl chain length, in collodion film.

Dye general formula.



C atoms in chain.	Mol. Wt.	Concentration correction factor.
2	270	1.000
3	284	0.950
4	298	0.906
5	312	0.865
6	326	0.830
7	340	0.795
8	354	0.764
9	360	0.750
10	382	0.706
12	410	0.659
14	438	0.616
16	466	0.580

Table XXVIII (cont.).

R= C_2

Exposure. (min).	Optical density x10^3.					
0	172	457	912	1058	1345	2100
4	115	349	657	870	1133	1840
8	85	271	549	738	975	1644
12	62	226	460	630	840	1491
16	45	185	390	540	740	1306
20	32	148	329	464	644	1175
24	23	121	277	398	560	1077

R= i-C_3

Optical density x10^3.					
114	290	544	699	970	1682
75	212	410	548	792	1435
54	165	333	450	672	1277
42	132	272	372	573	1132
32	108	225	310	486	980
25	90	187	260	414	870
20	74	158	220	353	766

R= nC_4

0	85	285	527	700	900	1660
4	60	201	405	561	740	1453
8	46	154	328	460	630	1278
12	37	119	264	379	540	1138
16	33	92	217	312	440	1007
20	28	71	178	260	374	882
24	26	57	148	217	317	790

R= nC_5

143	332	568	820	940	1500	
94	244	437	657	765	1288	
70	192	352	550	641	1142	
50	152	288	460	552	1000	
35	120	235	388	470	870	
27	100	194	329	401	762	
18	82	162	279	348	682	

R= tert.C_5

0	116	289	477	658	875	1390
4	72	202	340	502	682	1153
8	50	152	258	396	554	980
12	37	116	202	314	452	840
16	26	92	158	253	374	720
20	19	74	127	204	306	614

R= nC_6

187	476	730	1082	1480	2070	
129	368	593	910	1292	1833	
91	289	487	760	1144	1680	
63	225	397	646	980	1490	
44	175	320	540	863	1333	
30	139	260	452	748	1204	

Table XXVIII (cont.).

R= nC_7

Exposure. (min).	Optical density x10^3.					
0	211	506	820	1122	1782	2500
4	143	390	660	913	1540	2160
8	100	308	546	780	1390	2020
12	70	241	446	650	1225	1840
16	47	198	377	558	1100	1680
20	34	152	301	465	960	1508

R= nC_8

Optical density x10^3.					
212	539	840	1090	1553	2025
144	415	683	910	1338	1825
103	327	568	768	1172	1648
74	260	470	648	1047	1513
50	198	377	553	890	1362
35	155	300	470	780	1195

R= nC_{10}

189	440	677	980	1500	1880
130	341	548	813	1304	1683
97	279	460	708	1158	1515
70	230	389	610	1037	1393
49	185	322	527	905	1248
34	151	269	453	810	1137
23	126	228	390	710	1028

R= nC_{12}

150	388	593	845	1284	1875
105	301	480	706	1136	1641
74	242	394	601	976	1463
51	191	329	514	875	1311
34	151	274	435	752	1180
22	122	232	372	672	1070
14	99	190	316	585	1024

R= nC_{14}

144	380	650	843	1337	1739
97	290	524	700	1165	1548
65	221	427	582	1010	1393
42	169	350	497	880	1246
25	131	285	418	770	1110
12	99	234	350	675	988
5	75	188	295	586	880

R= $-(CH_2)_3Ph$.

177	533	810	1075	1535	2040
122	429	660	900	1335	1775
85	348	560	774	1185	1672
60	286	472	668	1060	1484
39	232	396	580	940	1358
26	190	335	484	830	1250
14	155	280	420	723	1123

R= nC_{16} (see Table XXV ia.).

Table XXIX.

Wavelength. A.	Filter combination (Chance).	% Trans-miss-ion.	Relative incident energy.
3650	OX1	73	37.10
4047	OB10 OV1	18	5.05
4358	OY18 OB10	34	17.30
5461	OGr1 ON16	28	18.50
5780	OGr1 OY2	11	8.80

Table XXX. Relative quantum efficiency of fading at characteristic emission wavelengths of G.E.C. "Osira" H.P. mercury vapour lamp: colour-coupled dyes in gelatine. (a) Yellow. (b) Magenta. (c) Cyan.

Wavelength A.	3650	4047	4358	5461	5780	Blank
(a)						
$D_1 \times 10^3$.	682	710	721	721	758	758
$D_1 \times 10^3$.	370	579	591	664	711	711
$D^2 \times 10^3$.	265	184	183	10	0	0
Mean relative absorption, D_1-D_2.	233	424	636	164	130	-
Relative quanta absorbed.	86.1	21.2	110.0	30.4	11.4	-
Relative quantum efficiency.	391	1000	730	4	0	-
			D_1 at 10; D_2 at 50 hrs.			
(b)						
$D_1 \times 10^3$.	626	740	706	780	782	868
$D_1 \times 10^3$.	311	680	679	760	770	860
$D^2 \times 10^3$.	307	52	19	12	4	0
Mean relative absorption, D_1-D_2.	155	238	339	701	488	-
Relative quanta absorbed.	57.5	12.0	58.7	130.0	43.0	-
Relative quantum efficiency.	1230	1000	75	0	0	-
			D_1 at 150; D_2 at 350 hrs.			
(c)						
$D_1 \times 10^3$.	511	549	550	544	588	600
$D_1 \times 10^3$.	330	490	522	530	570	580
$D^2 \times 10^3$.	167	39	8	0	0	0
Mean relative absorption, D_1-D_2.	228	129	75	188	219	-
Relative quanta absorbed.	84.5	6.5	13.0	34.8	19.3	-
Relative quantum efficiency.	330	1000	103	0	0	-
			D_1 at 100; D_2 at 500 hrs.			

Table XXXI. Fading data for colour-coupled dyes in gelatine. (a) Yellow. (b) Magenta. (c) Cyan.

(a)

Exposure. (hrs).	Optical density $x10^3$.					
0.0	763	740	754	735	753	768
2.0	758	742	752	740	761	779
4.0	740	732	742	740	761	779
7.5	703	712	726	722	746	760
25.2	562	662	670	703	732	740
49.5	369	577	594	662	711	711
61.0	292	540	558	640	693	693
73.5	233	504	520	634	686	686

(b)

Exposure. (hrs).	Optical density $x10^3$.					
0.0	748	770	715	780	850	778
7.5	738	767	716	779	855	783
25.2	703	759	712	778	855	780
73.5	681	752	704	772	855	778
142.0	627	750	713	782	872	782
187.0	567	728	700	779	870	780
240.0	501	713	695	772	862	776
475.0	113	640	660	746	857	745

(c)

Exposure. (hrs).	Optical density $x10^3$.					
0.0	584	572	570	559	612	604
7.5	560	563	558	548	606	590
25.2	544	558	556	542	602	588
73.5	522	540	542	532	594	573
142.0	497	550	552	550	606	592
187.0	462	530	540	534	585	579
240.0	451	534	546	541	596	583
475.0	345	490	526	528	584	572

FIGURES.

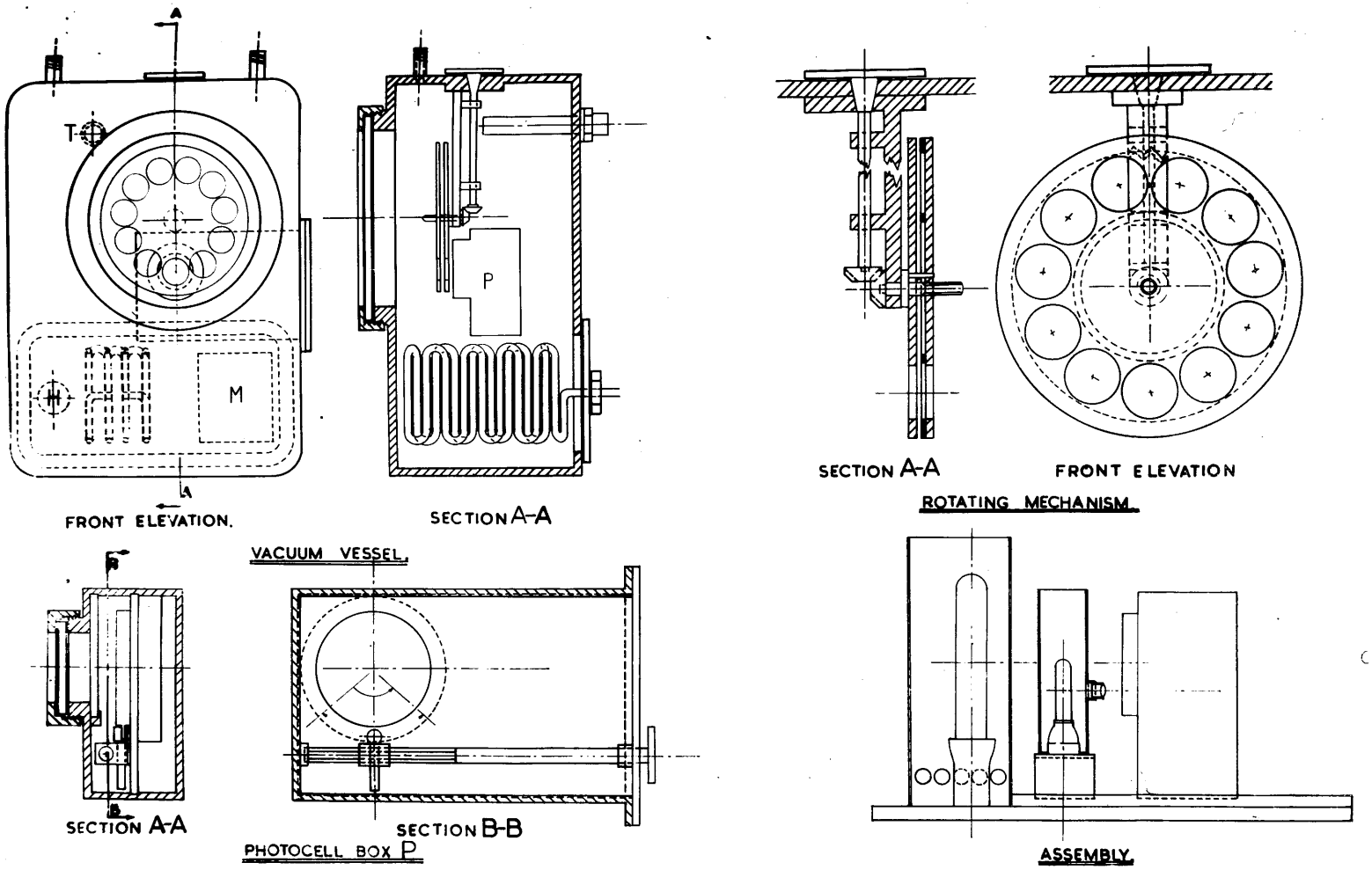

A
T
M
P
FRONT ELEVATION.
SECTION A-A
SECTION A-A
FRONT ELEVATION
ROTATING MECHANISM
VACUUM VESSEL.
SECTION A-A
SECTION B-B
PHOTOCELL BOX P
ASSEMBLY

FIG. 1.

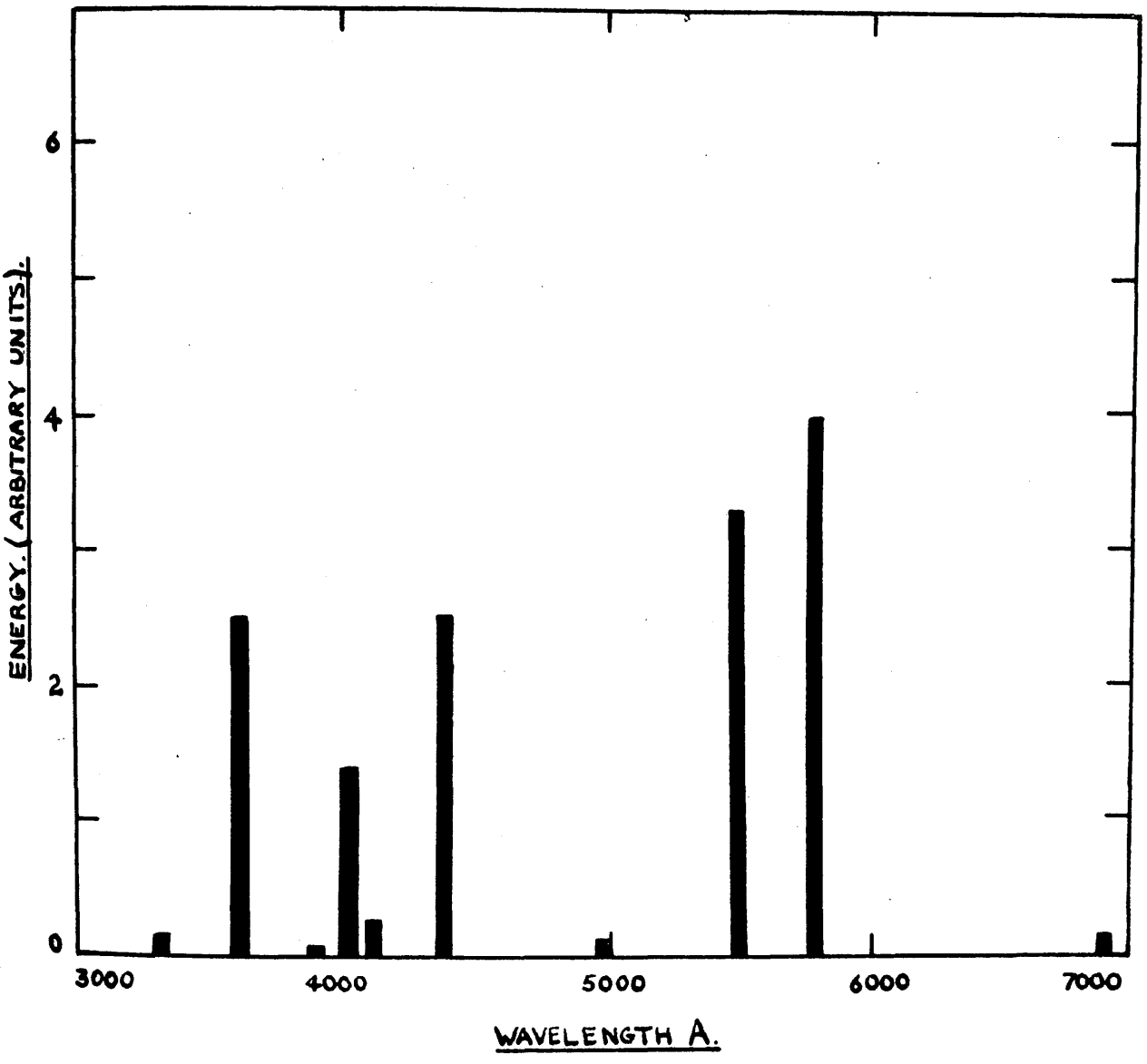


FIG. 2. ENERGY DISTRIBUTION OF "OSIRA" 400W. LAMP.

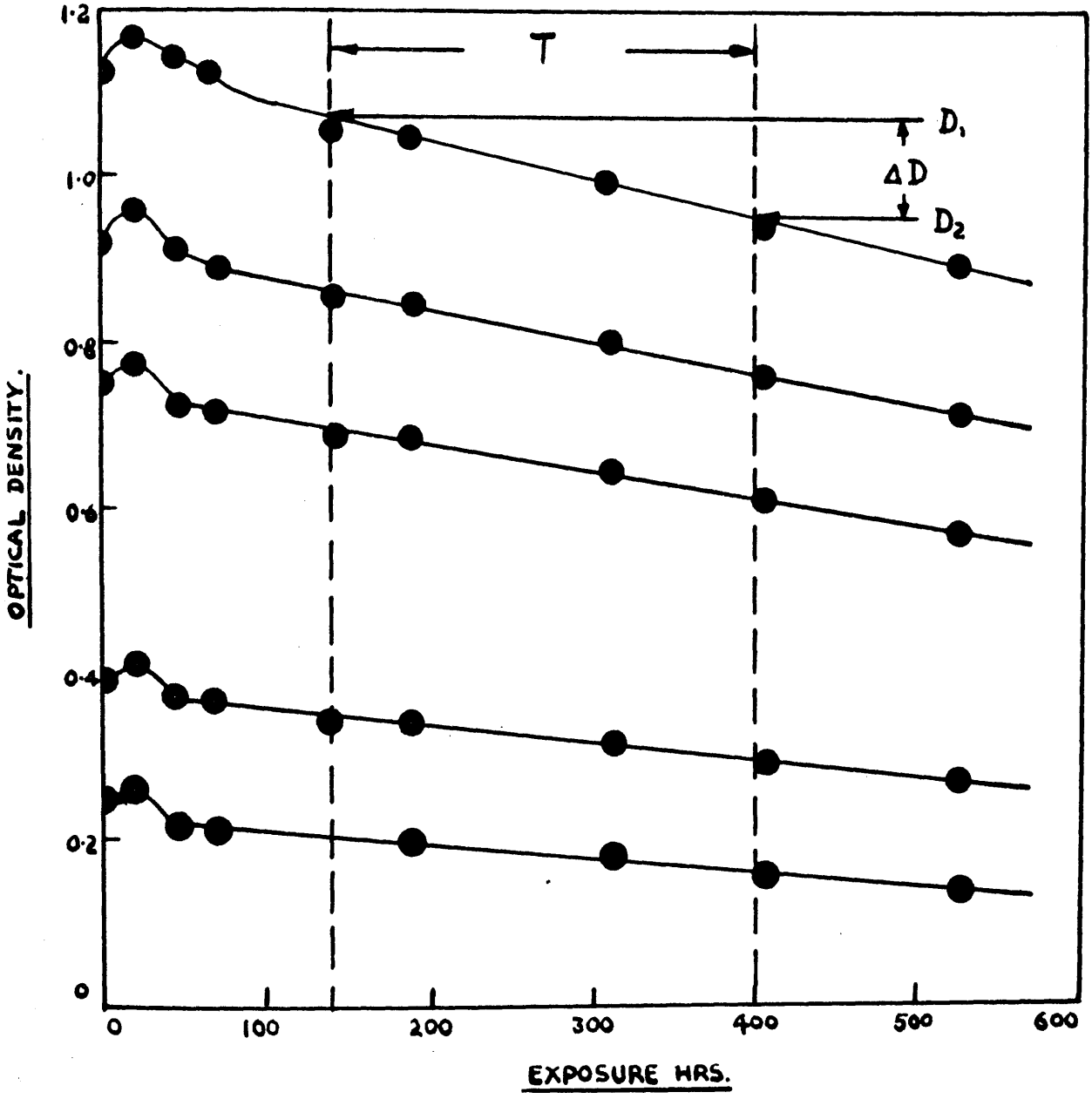


FIG. 3. CHARACTERISTIC FADING CURVES.

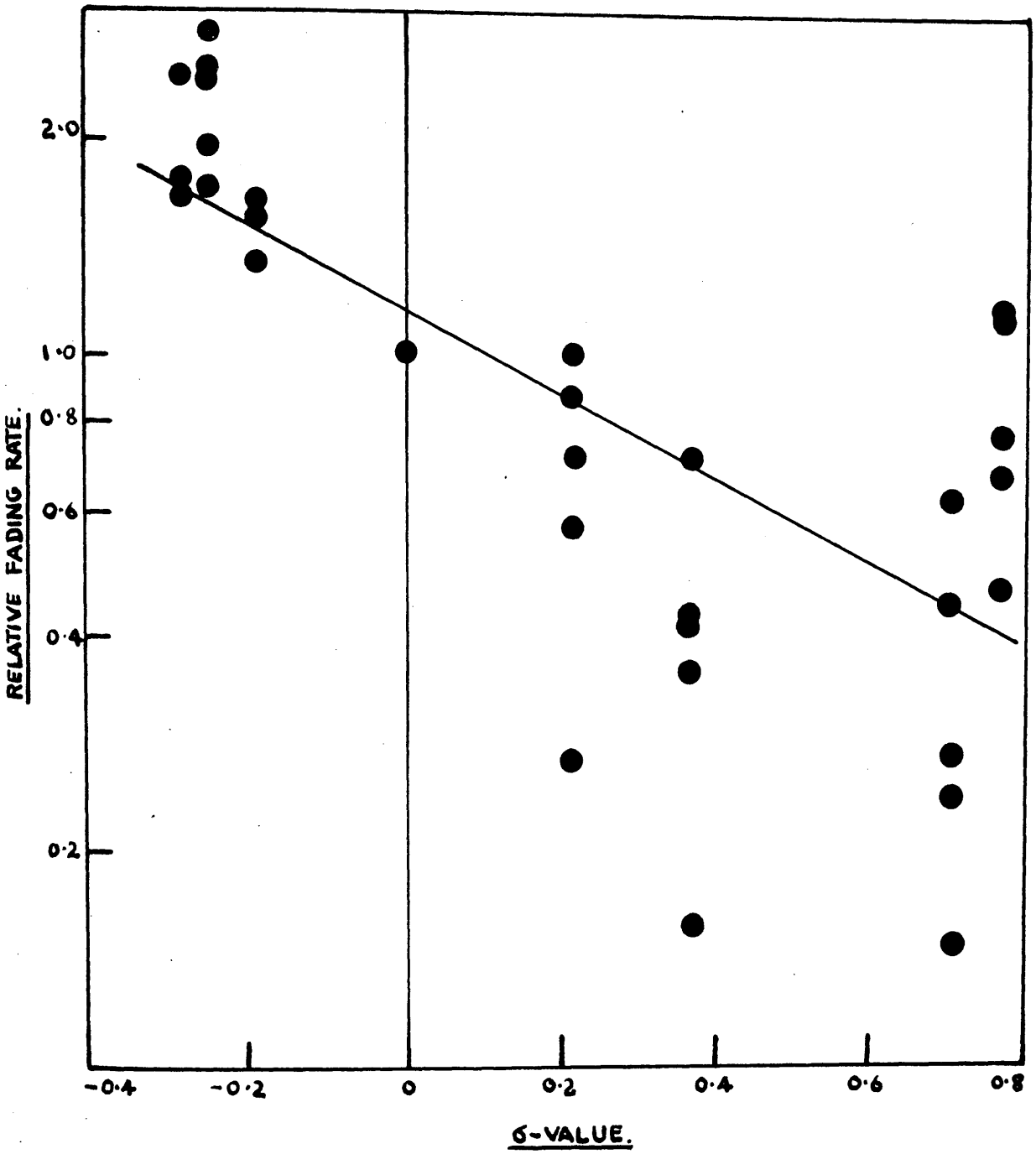


FIG. 4. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTATE: ALUMINIUM.

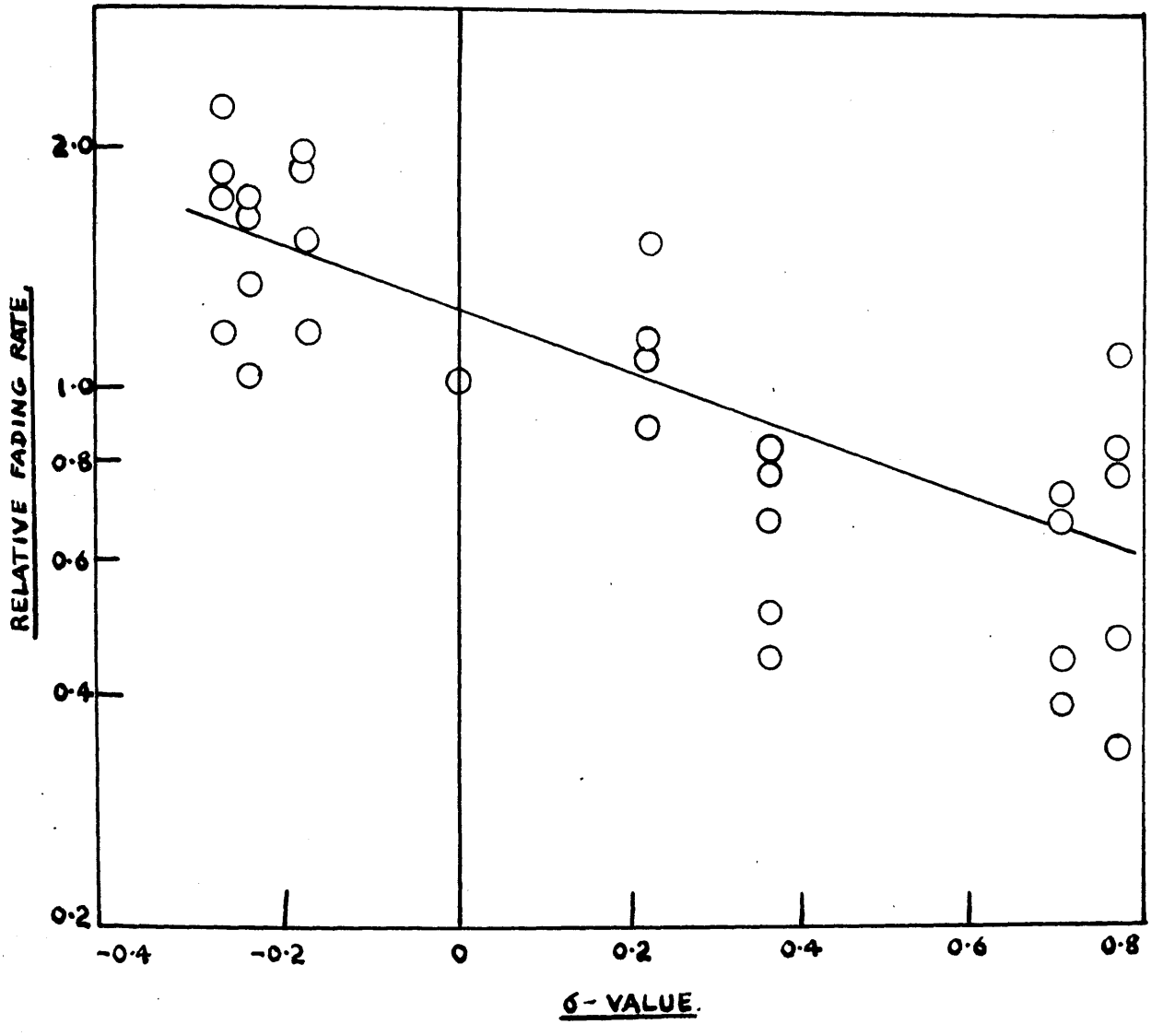


FIG. 5. RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: ASBESTOS.

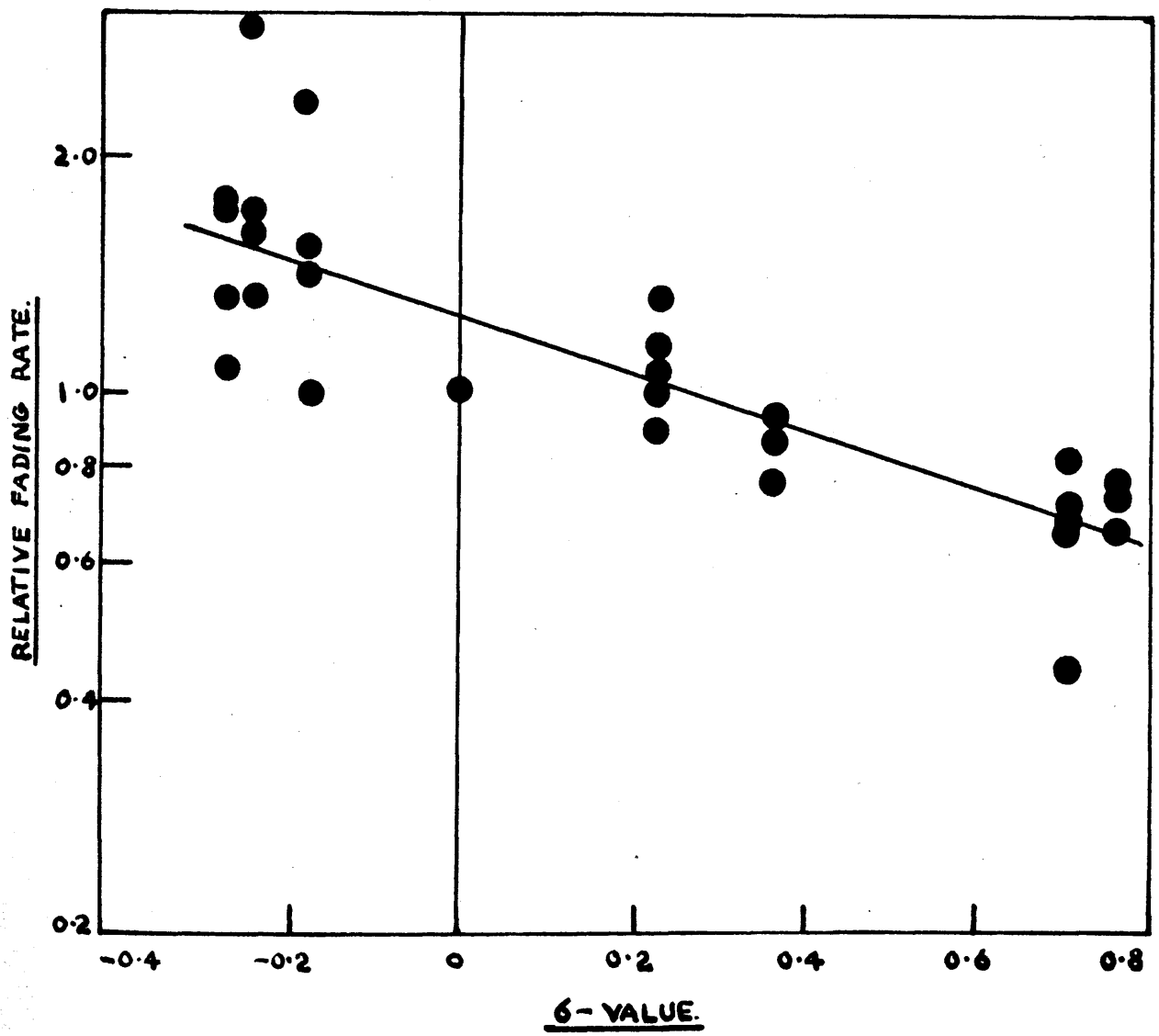


FIG. 6. RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: CELLULOSE POWDER.

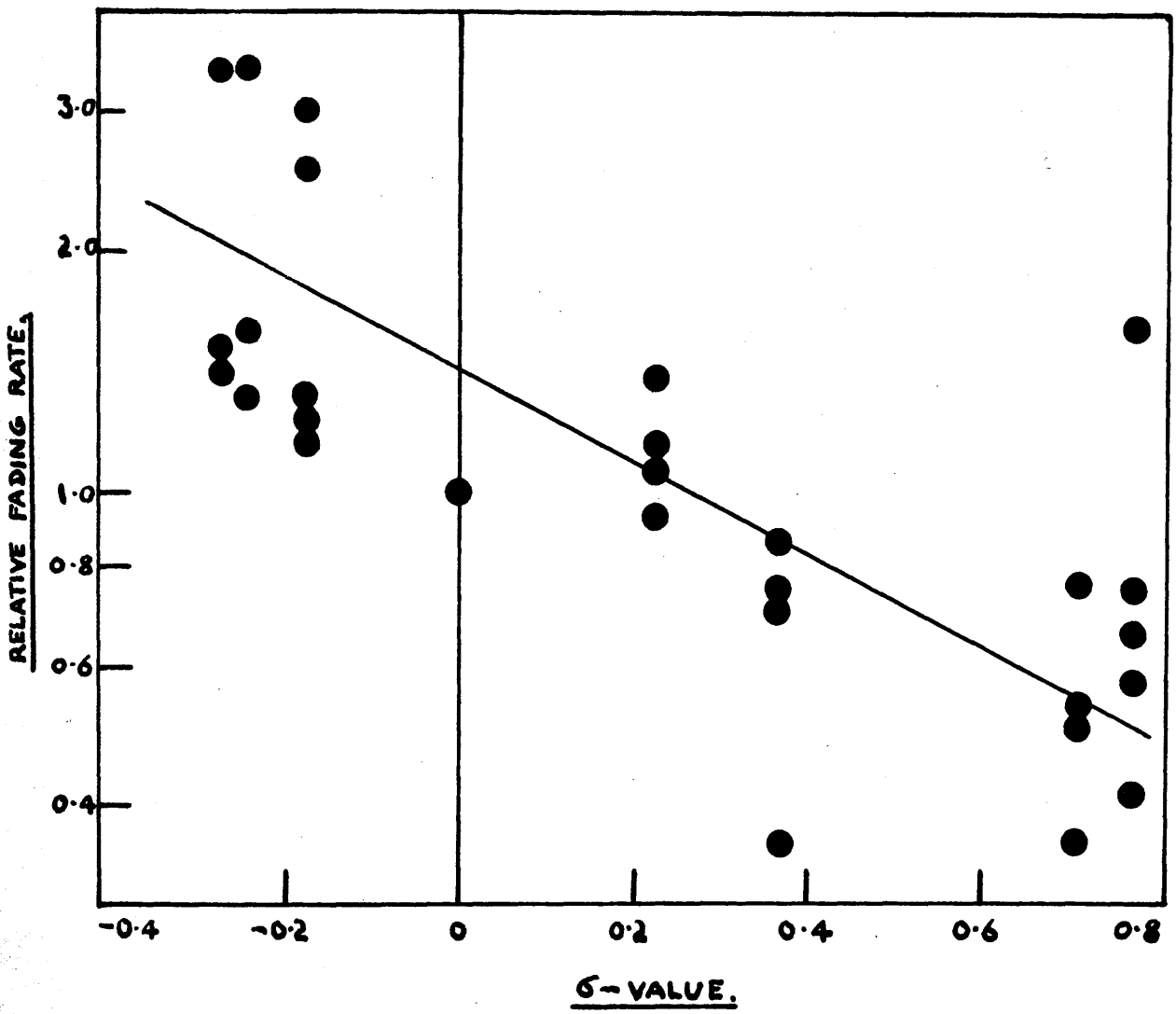


FIG. 7. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: COTTON.

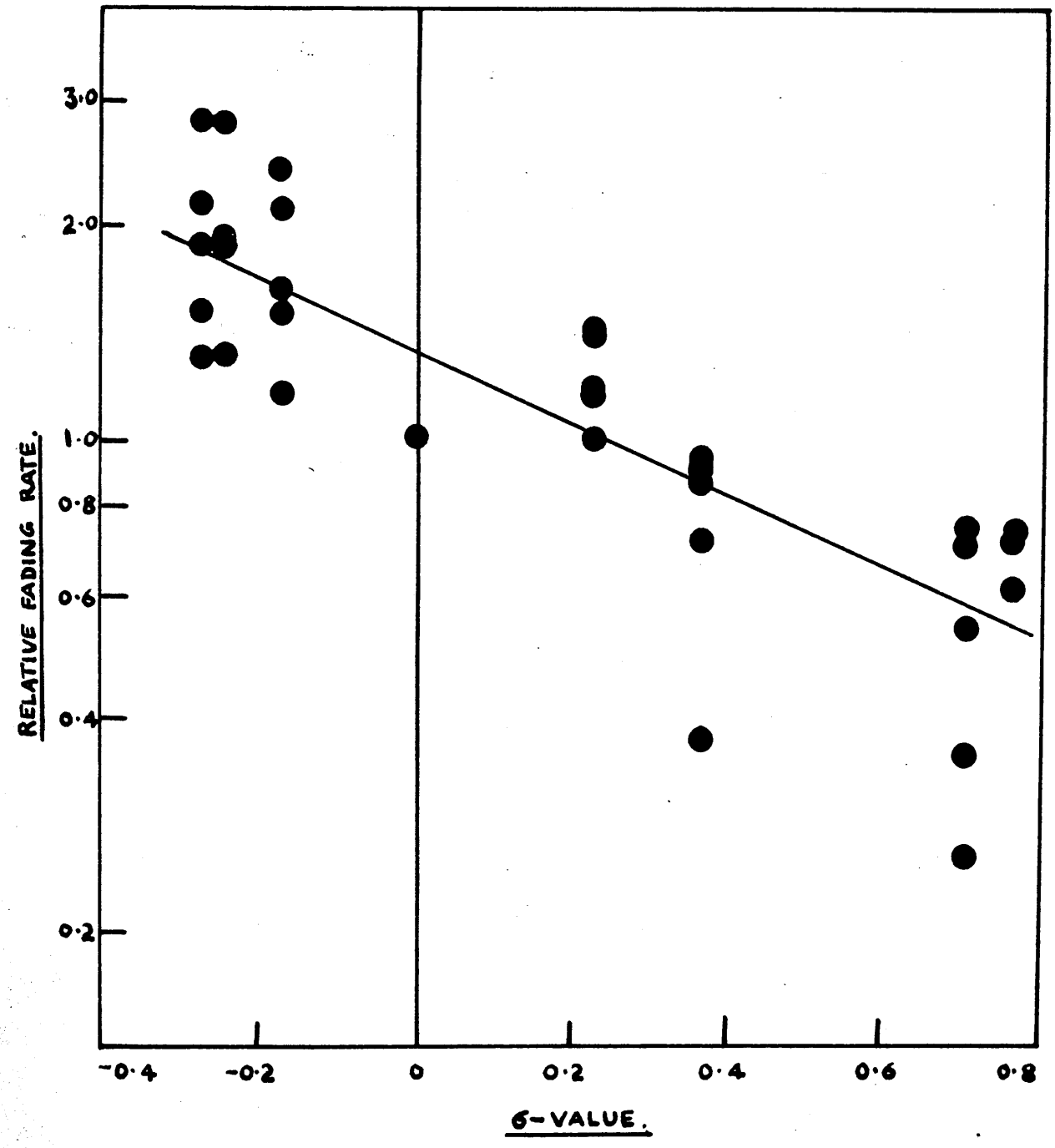


FIG. 8. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: PAPER.

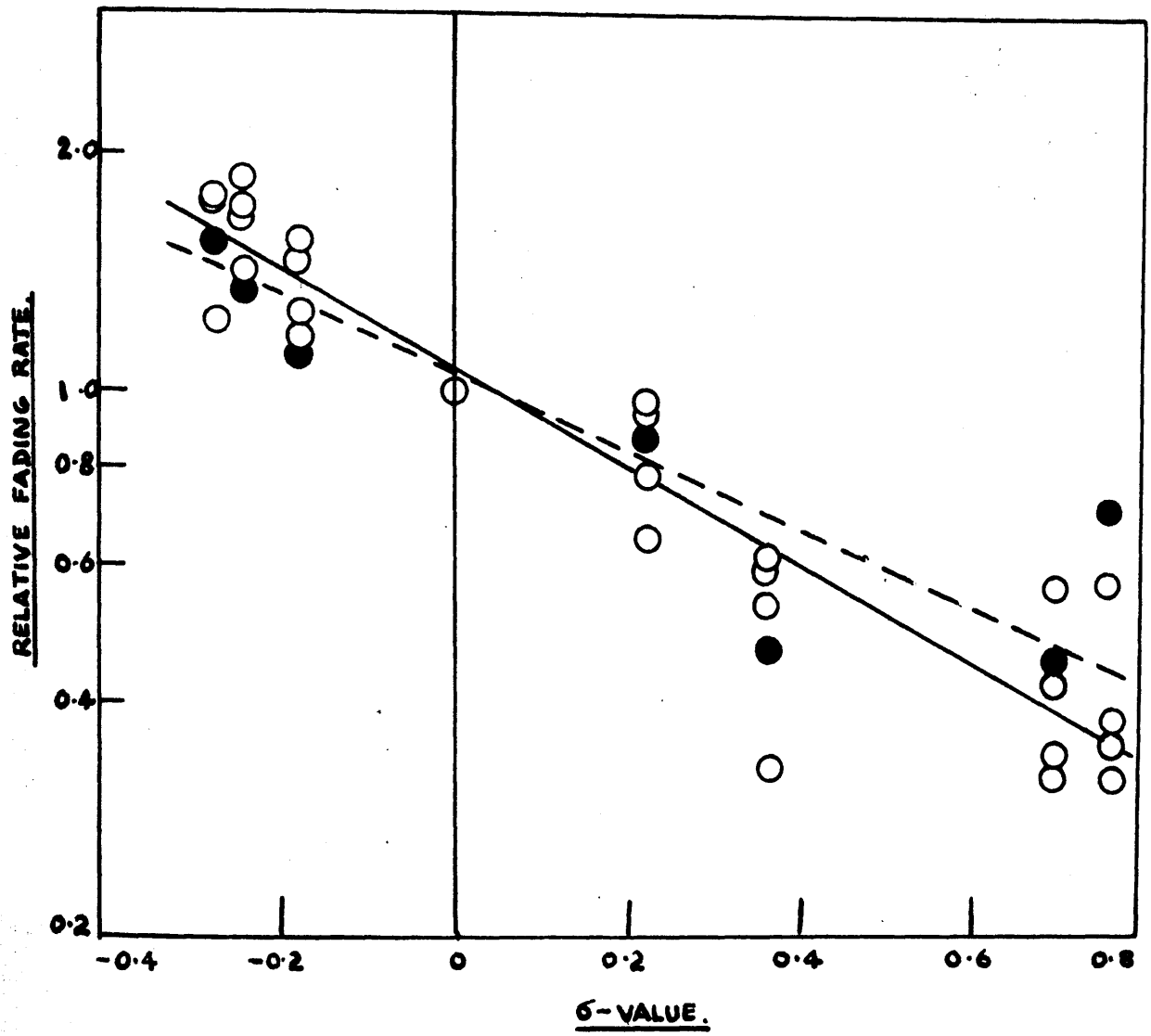


FIG. 9. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: "CELLOFAS A".
– –●– – FADED AT 3650 Å.

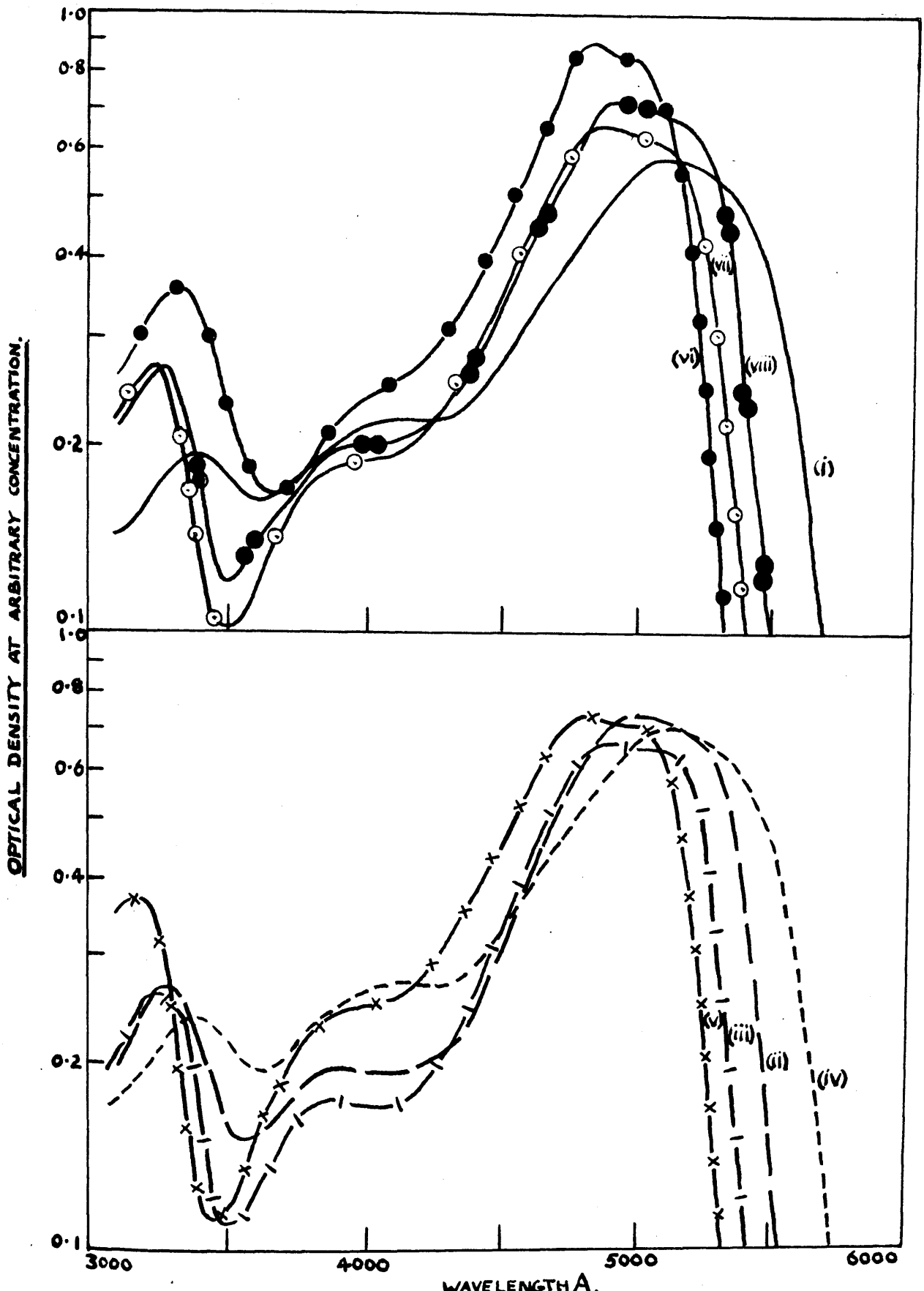


FIG. 10. LIGHT ABSORPTION CURVES FOR BENZENEAZO-R-ACID DYES IN WATER AND METHYETHYL CELLULOSE SOLUTION.

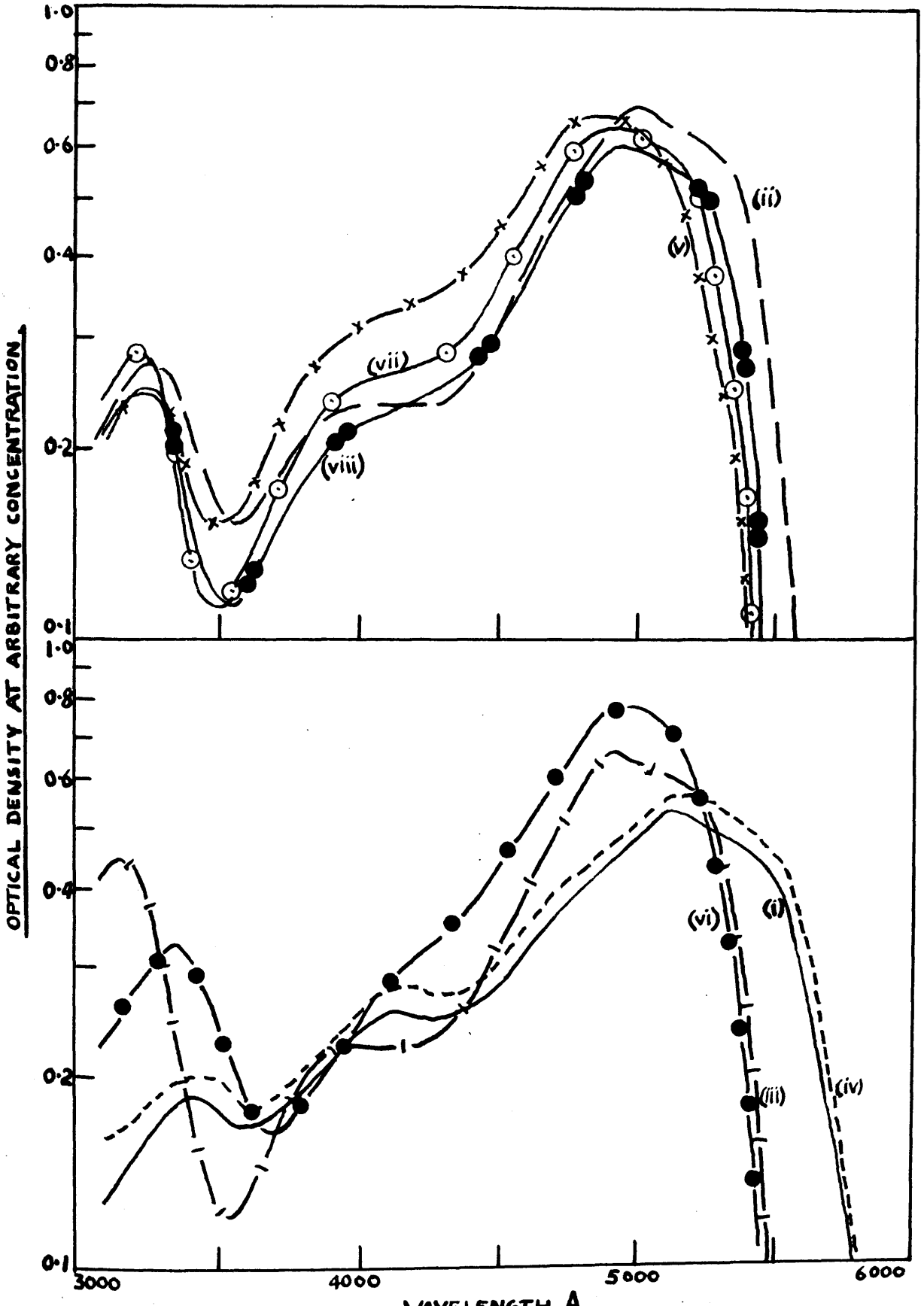


FIG. 11. LIGHT ABSORPTION CURVES FOR BENZENEAZO-R-ACID DYES IN "CELLOFAS A" FILM.

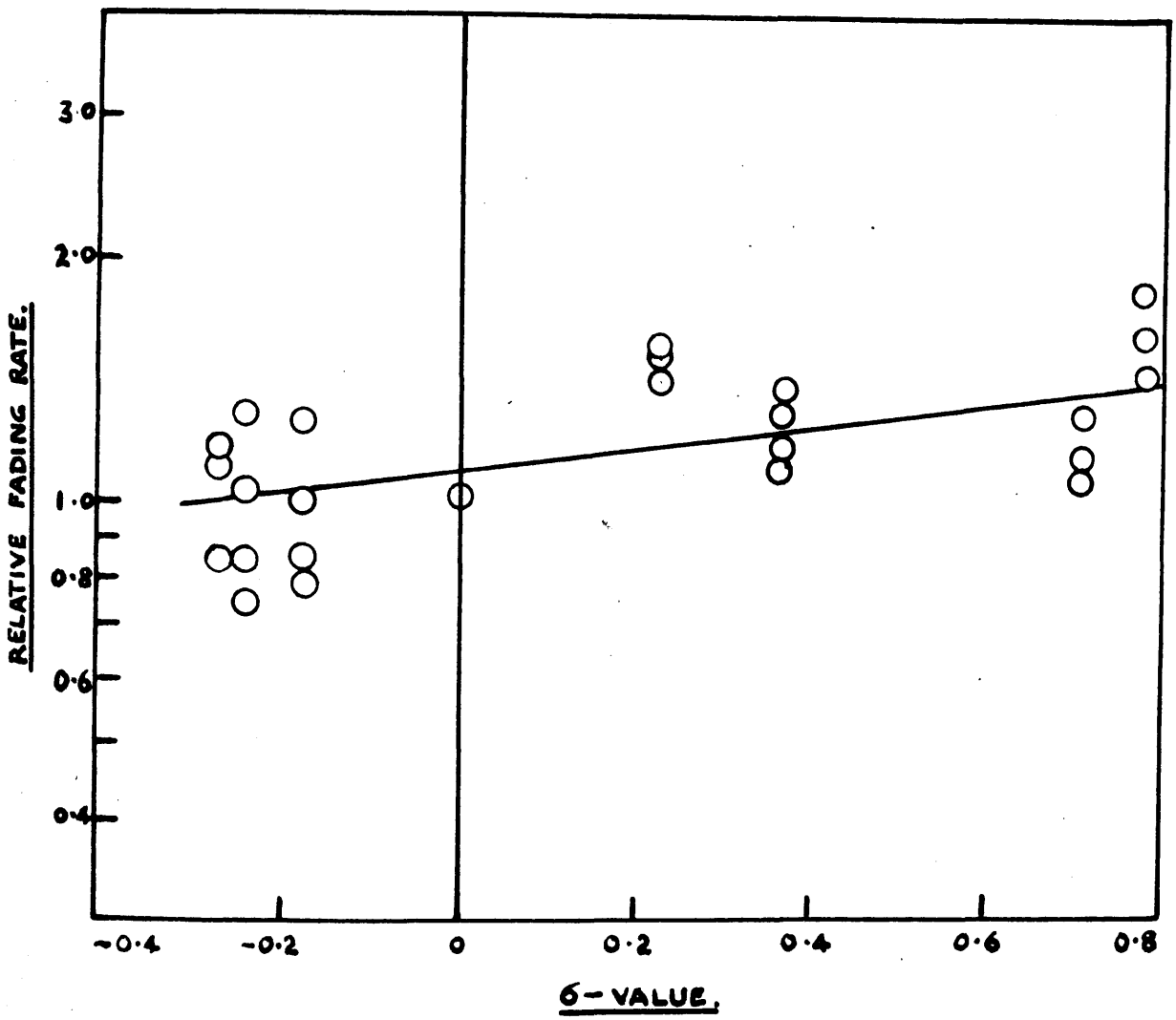


FIG. 12. RELATION BETWEEN RELATIVE FADING RATE AND δ-VALUE, SUBSTRATE: GELATINE.

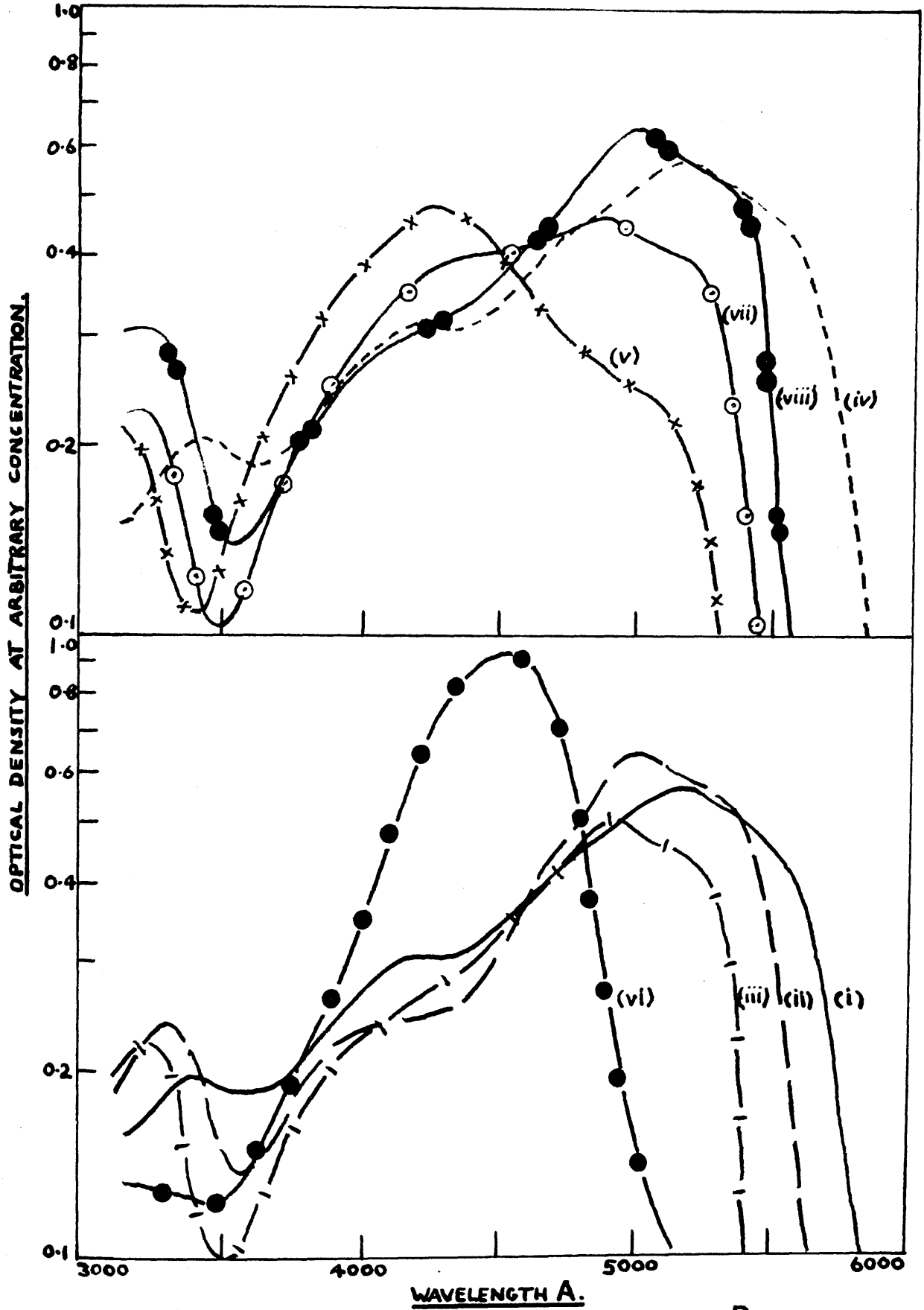


FIG. 13. LIGHT ABSORPTION CURVES FOR BENZENEAZO-R-ACID DYES IN GELATINE FILMS.

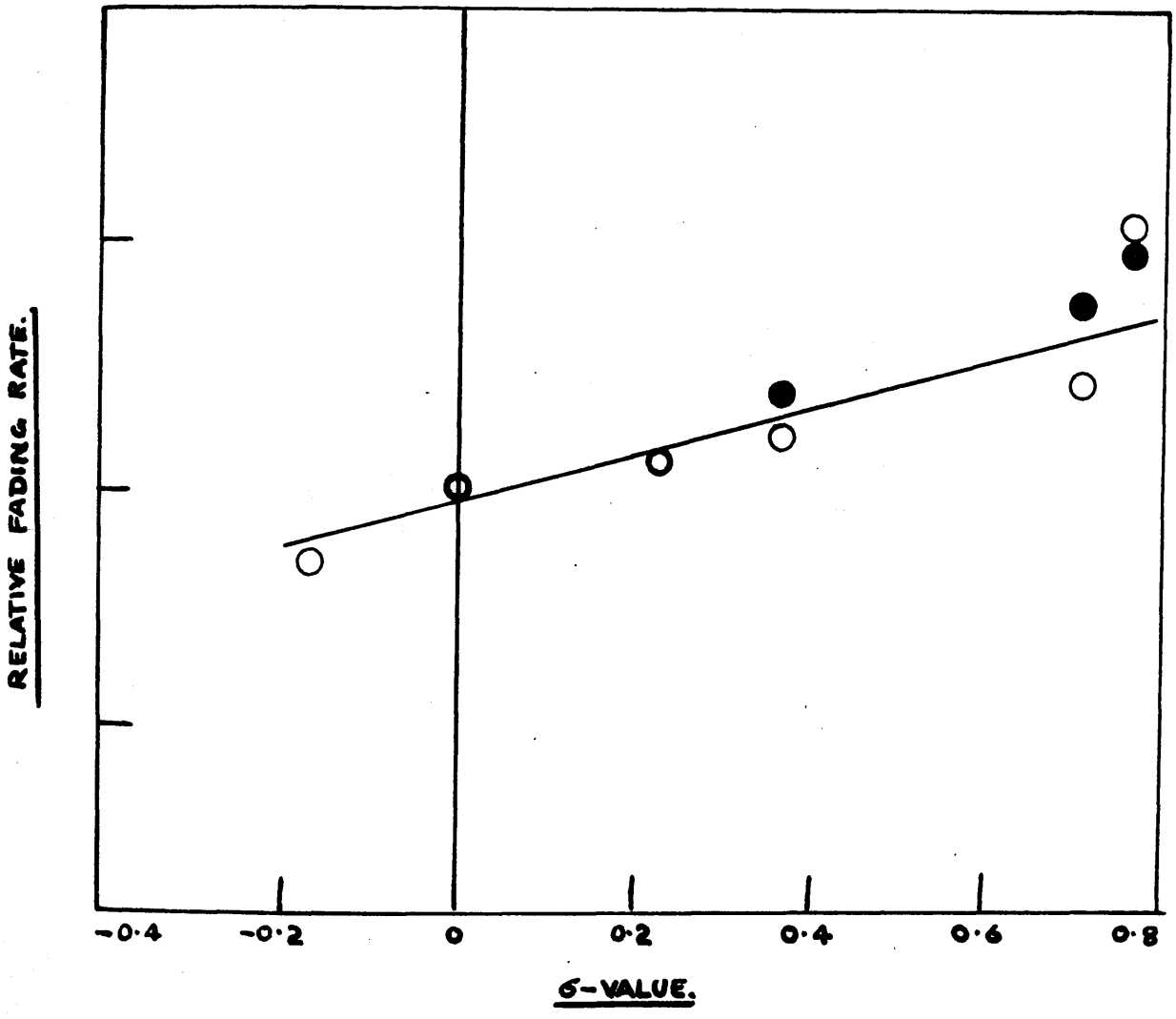


FIG. 14. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE : WOOL
● IN PYRUVIC ACID.

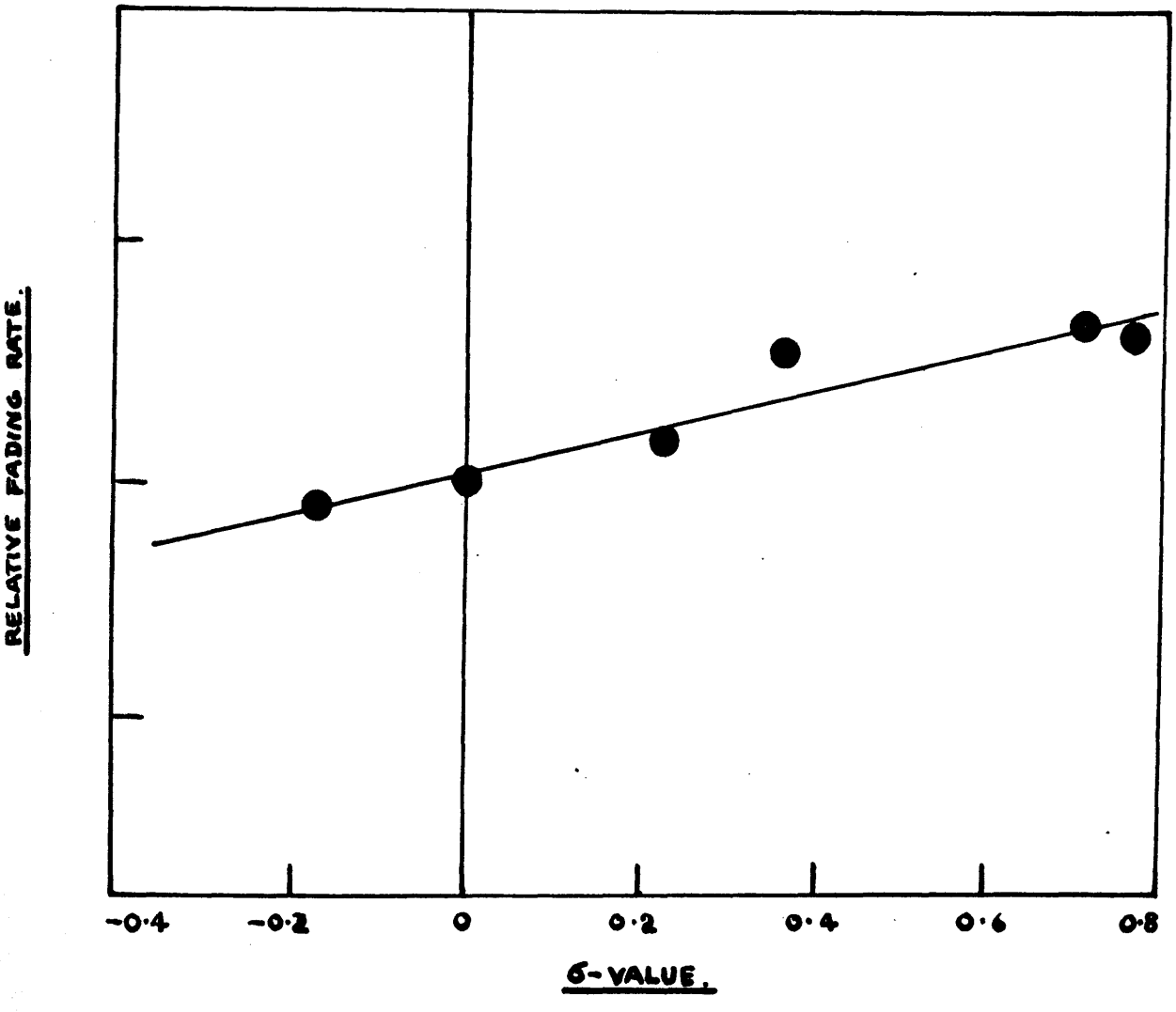


FIG. 15. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: SILK.

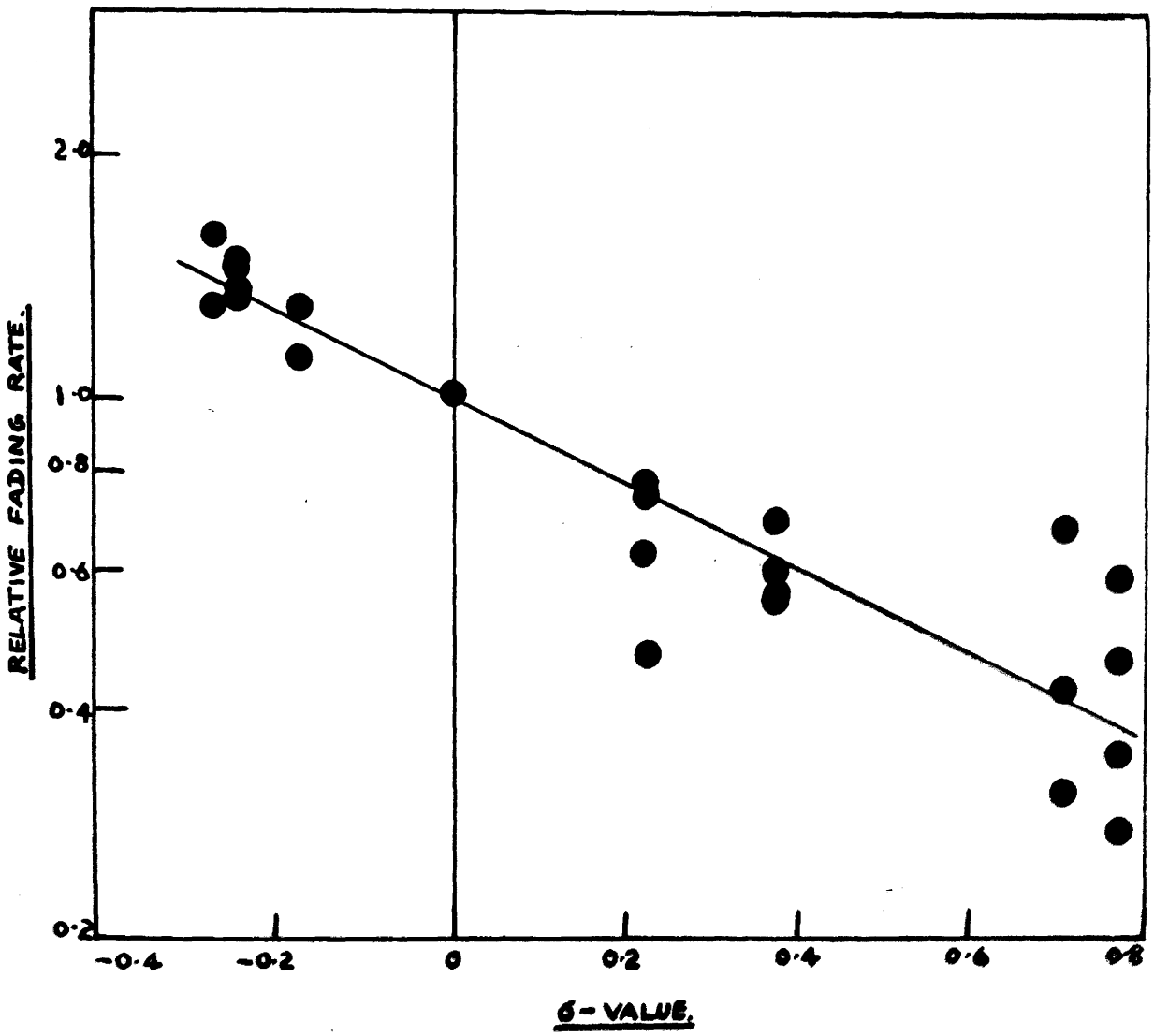


FIG. 16. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: NYLON.

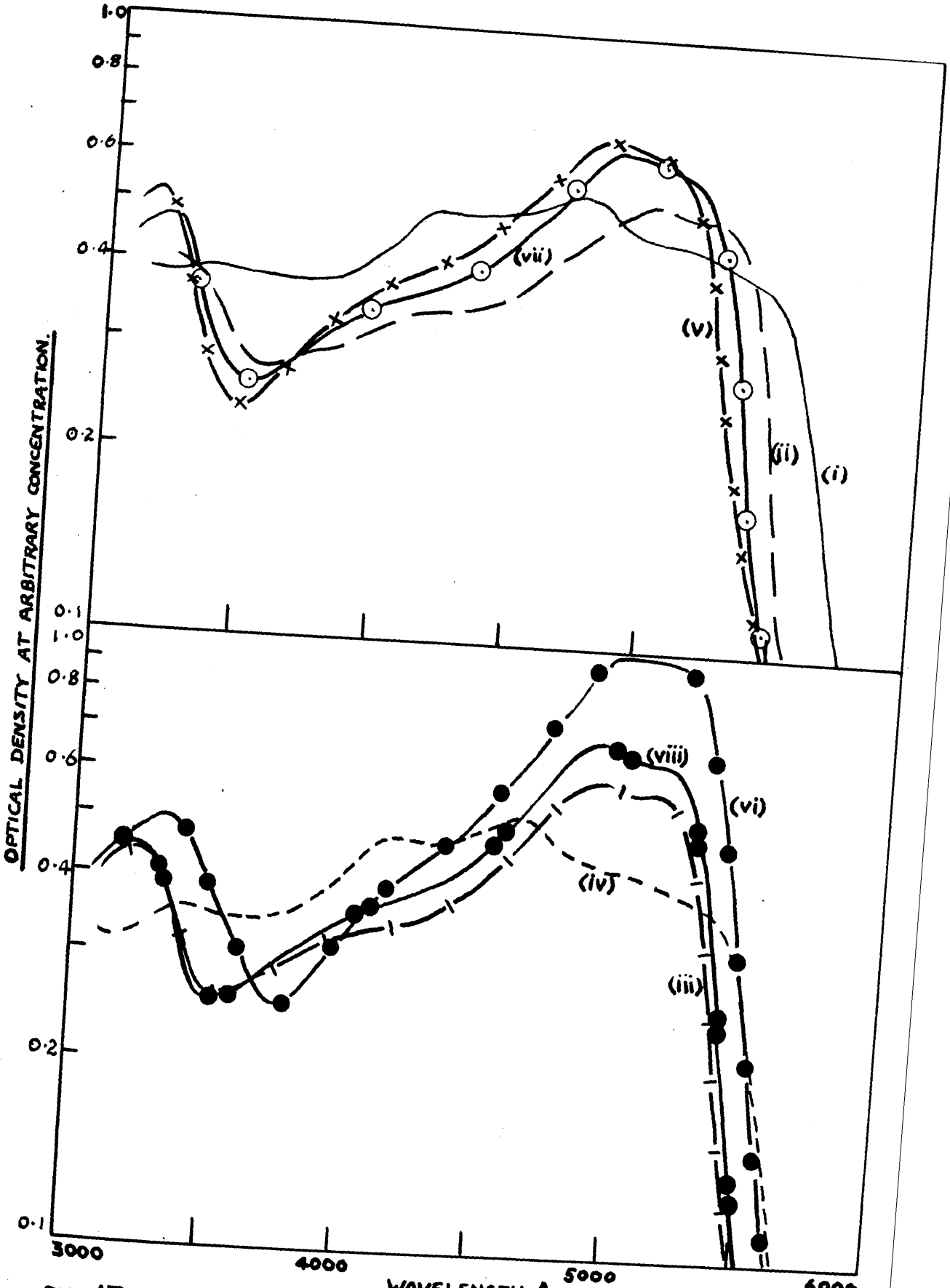


FIG. 17. LIGHT ABSORPTION CURVES FOR BENZENEAZO-R-ACID DYES IN NYLON FILM.

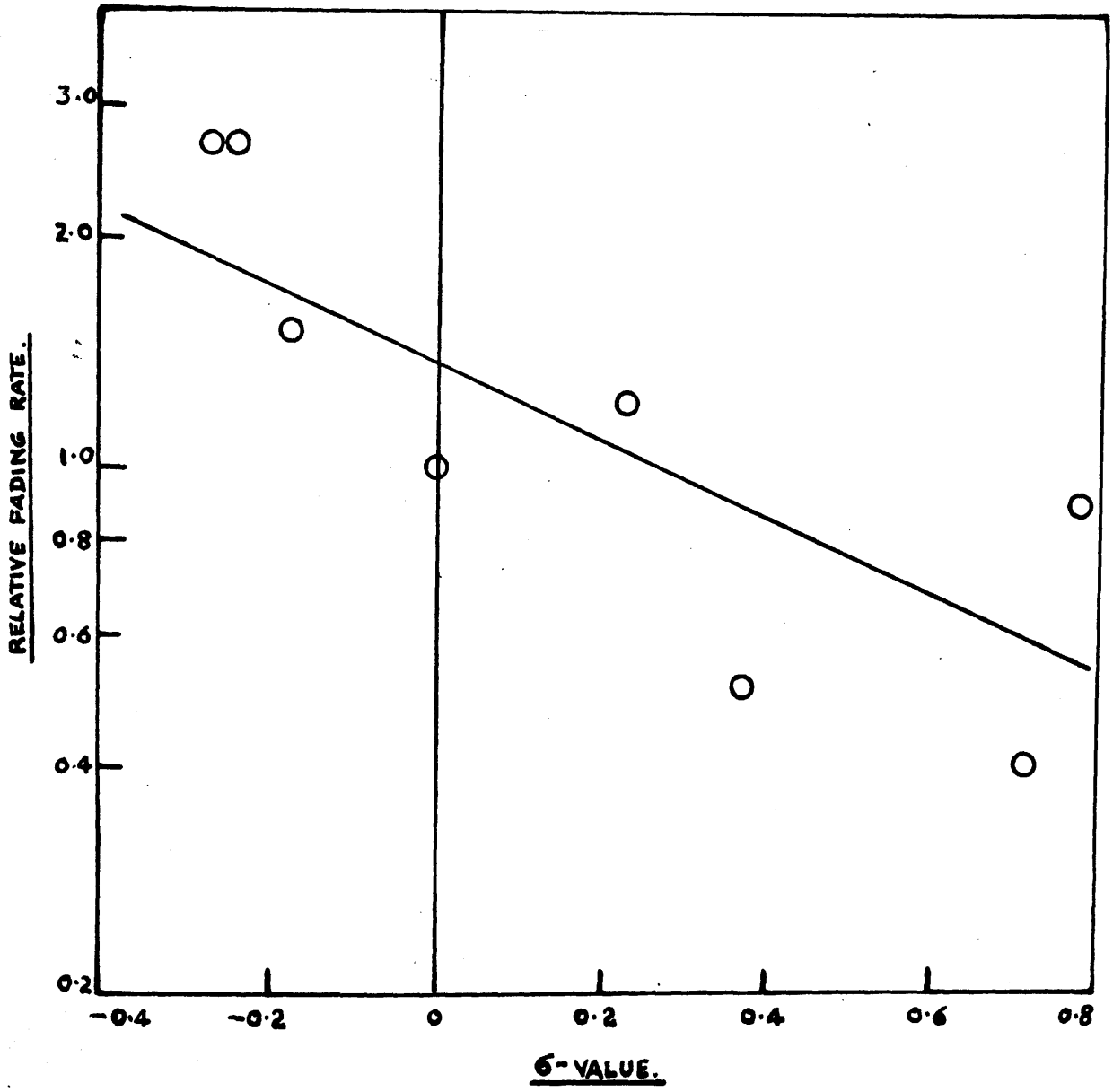


FIG. 18. RELATION BETWEEN RELATIVE FADING RATE AND σ-VALUE, SUBSTRATE: POLYGLYCINE.

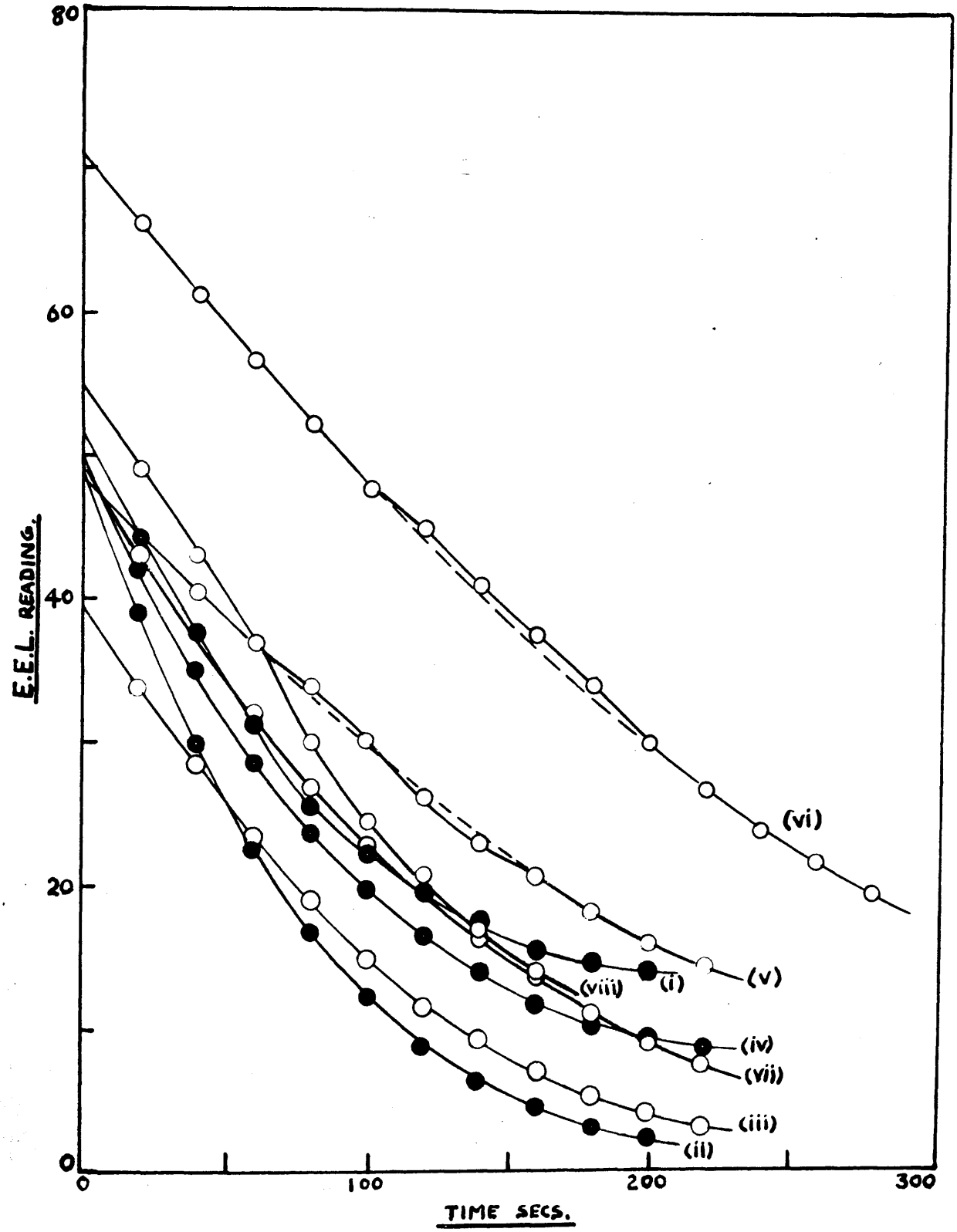


FIG. 19. OXIDATION OF R-ACID DYES IN ALKALINE SOLUTION.

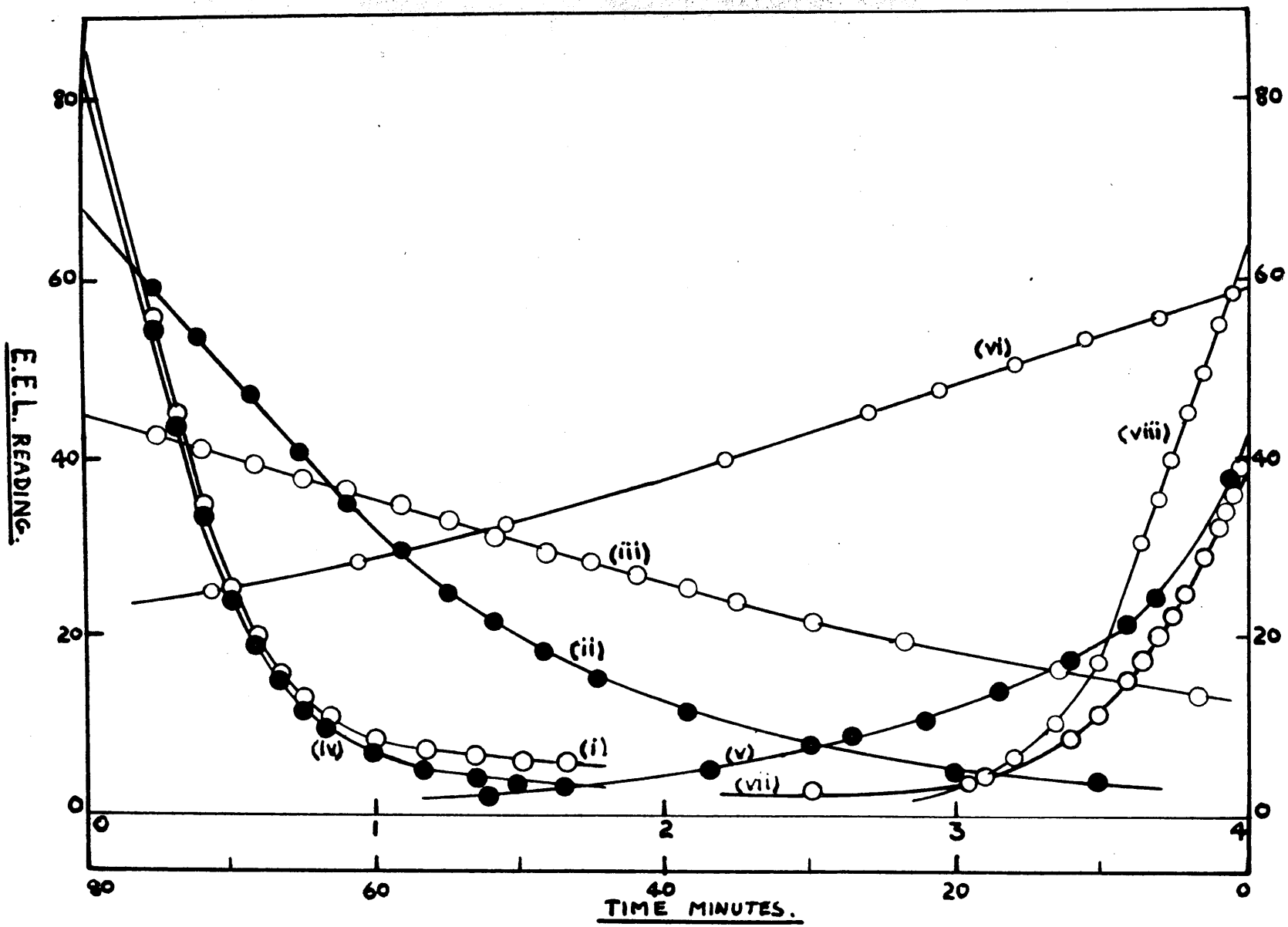


FIG. 20. OXIDATION OF R-ACID DYES IN ACID SOLUTION.

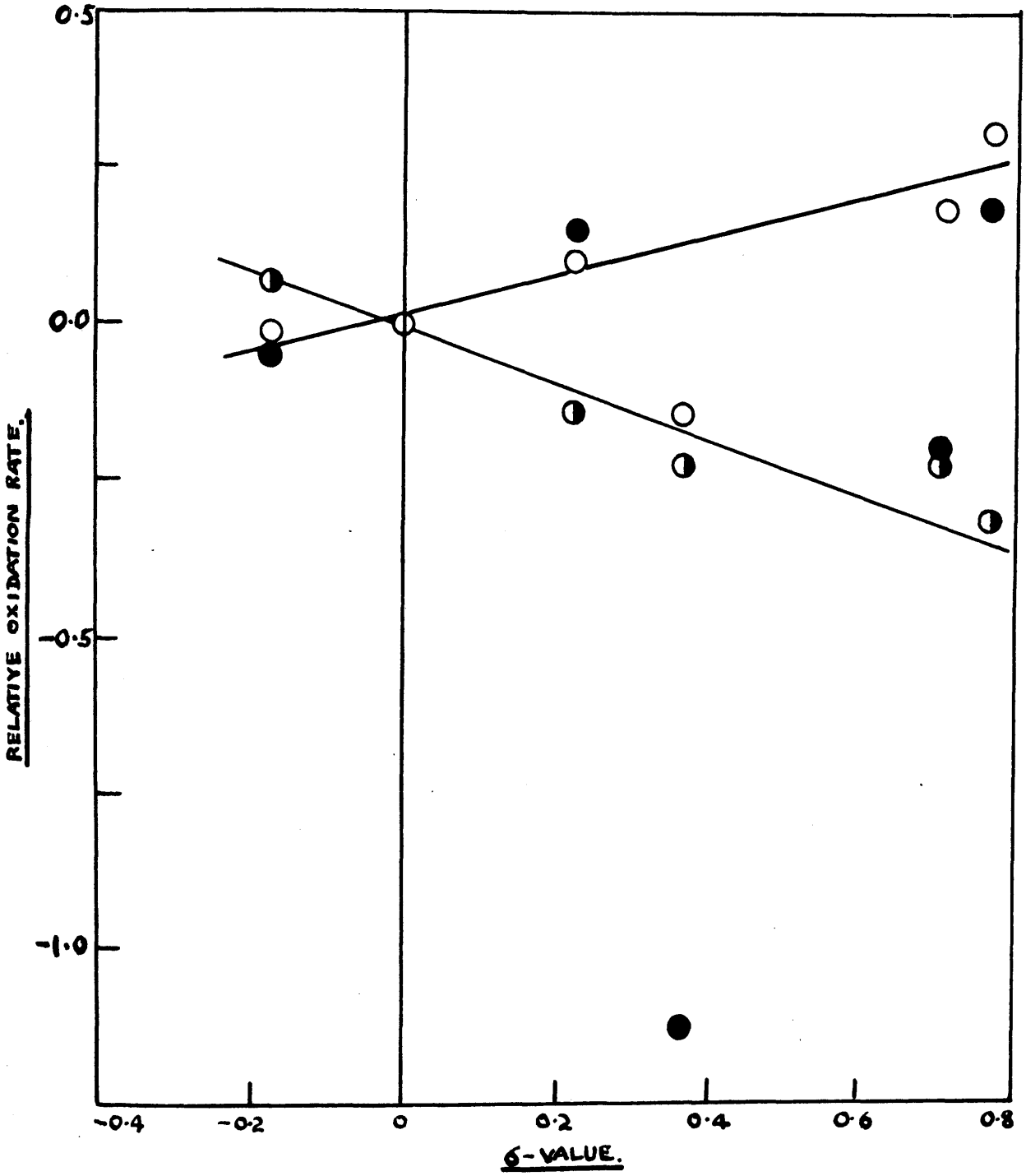


FIG. 21. RELATION BETWEEN RELATIVE OXIDATION RATE AND σ-VALUE, FOR R-ACID DYES.

○ P_H 3·92
● P_H 6·49
◑ P_H 9·00

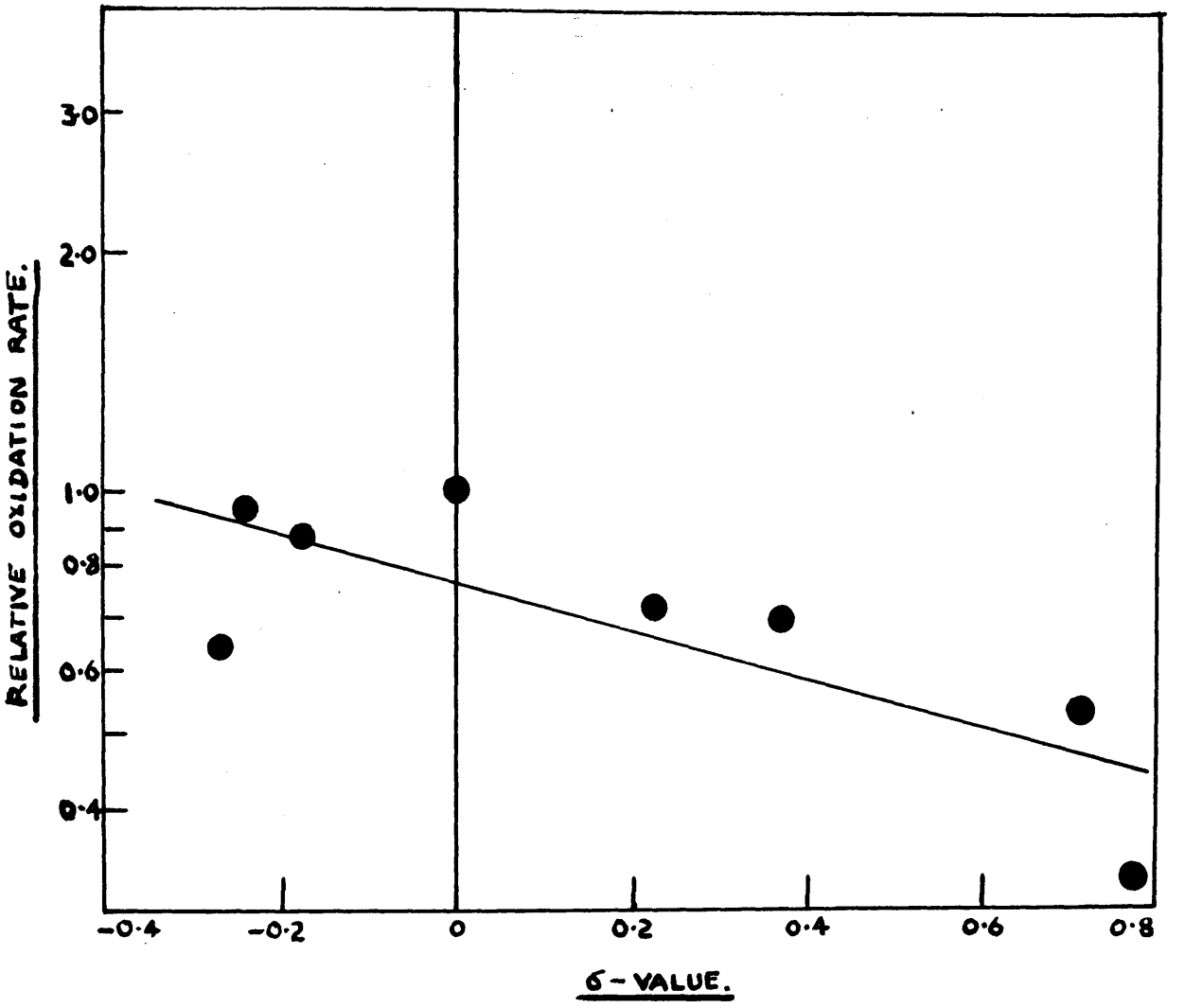


FIG. 22. RELATION BETWEEN RELATIVE OXIDATION RATE AND σ-VALUE FOR R-ACID DYES IN GELATINE. (H_2O_2 IN ALKALINE CONDITIONS).

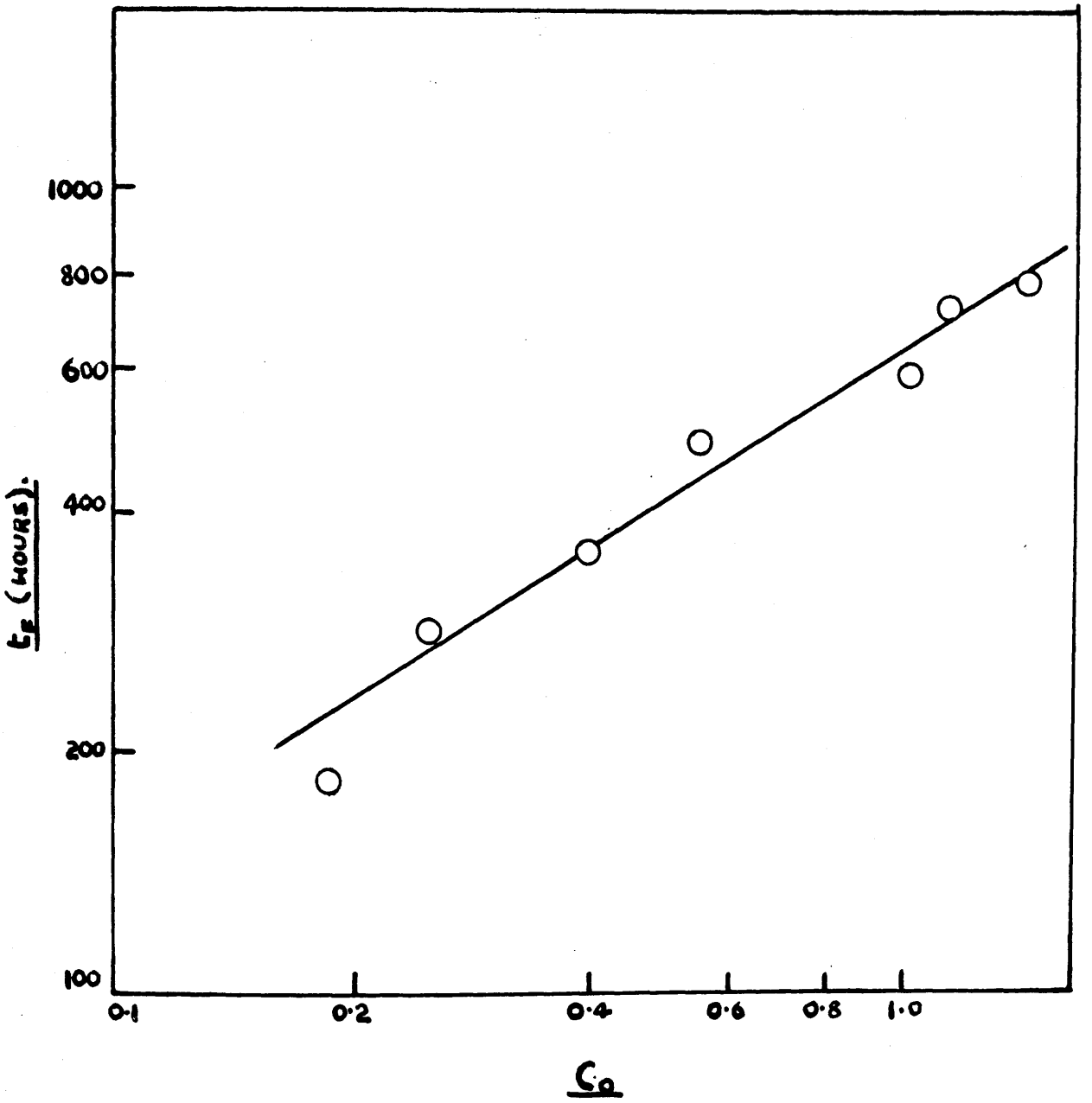


FIG. 23. MEROCYANINE DYE II PRECIPITATED IN GELATINE.

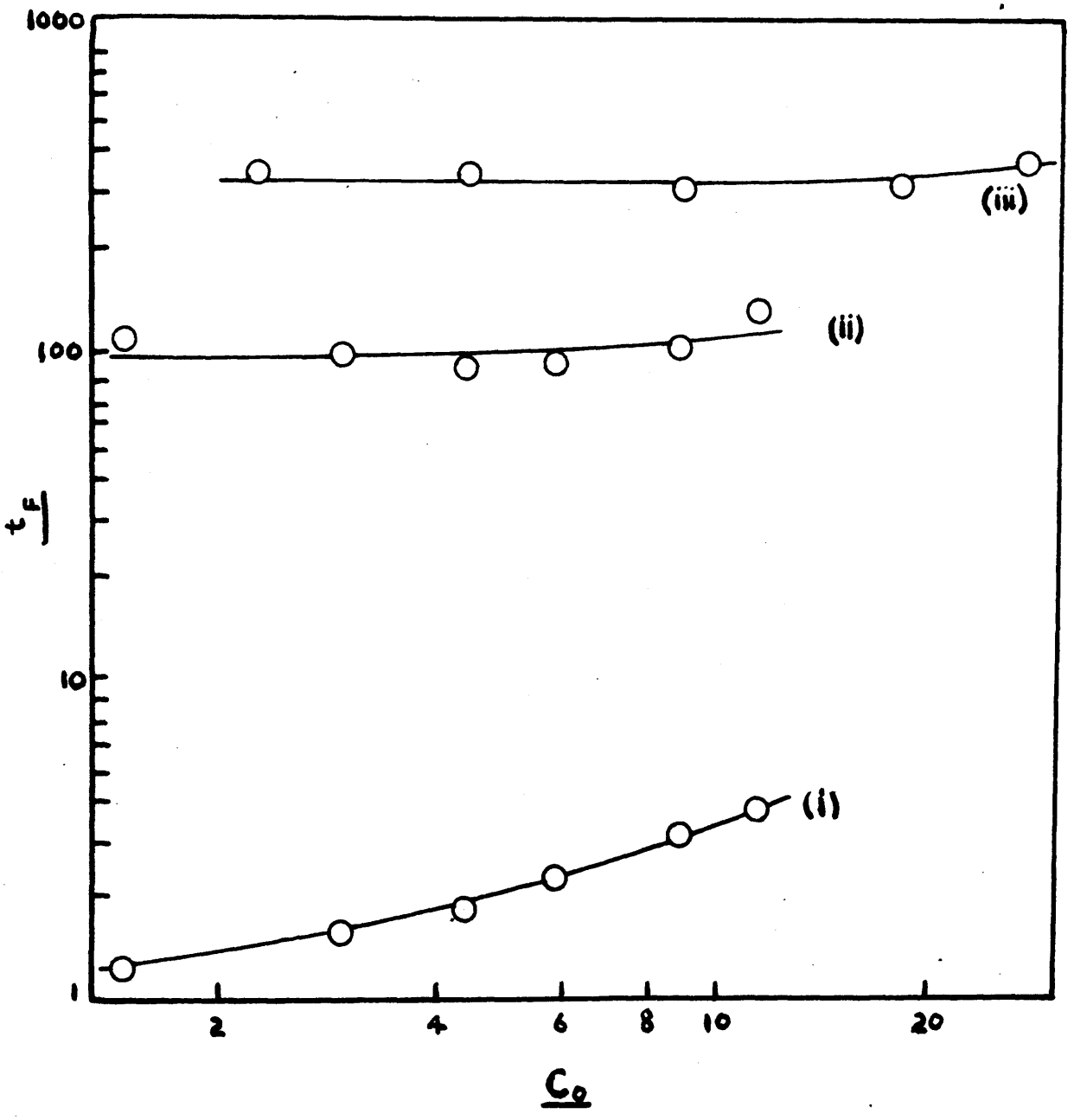


FIG. 24. MEROCYANINE DYE I. (i) IN COLLODION.
(ii) PRECIPITATED IN GELATINE.
(iii) DISPERSED IN GELATINE.

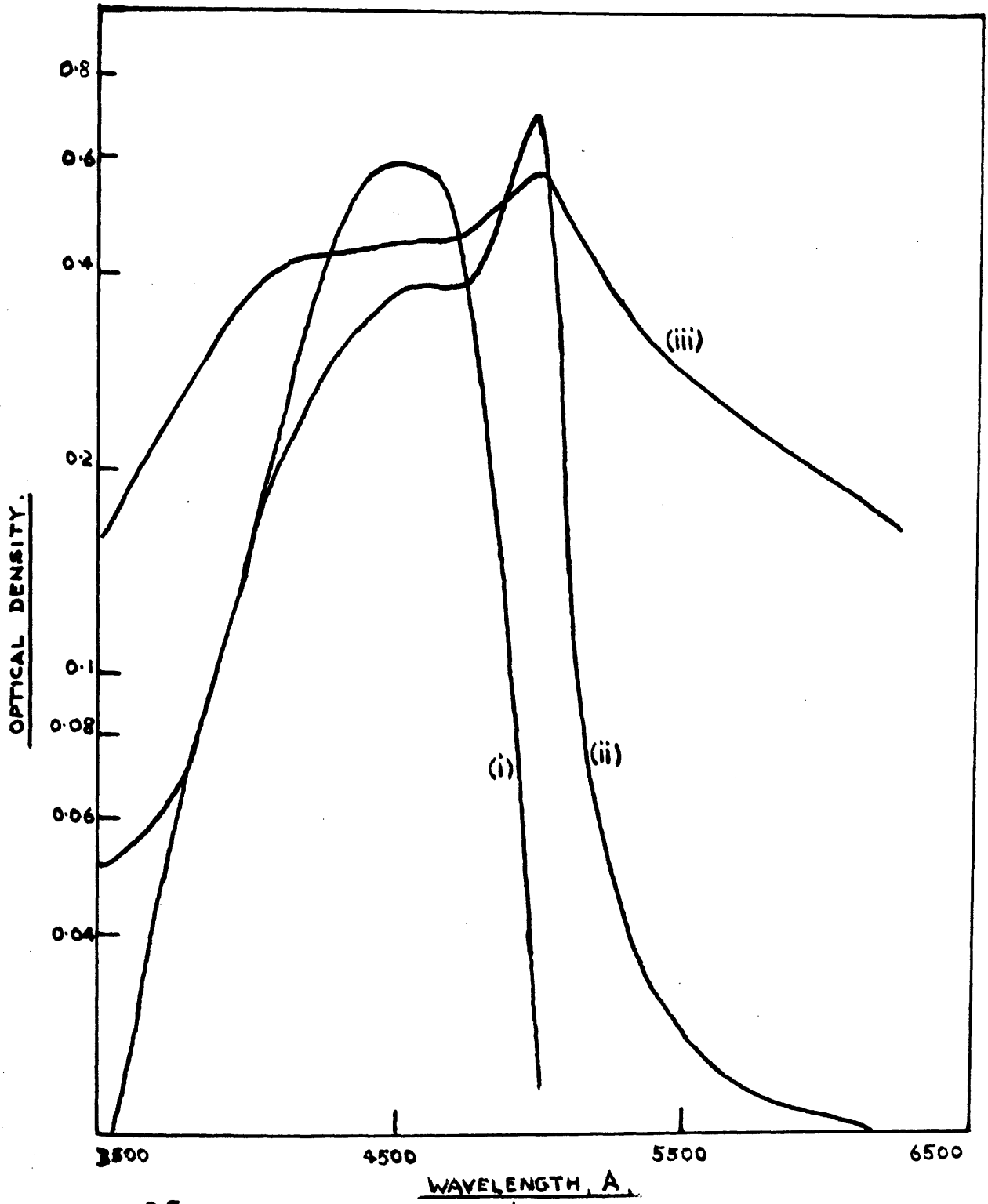
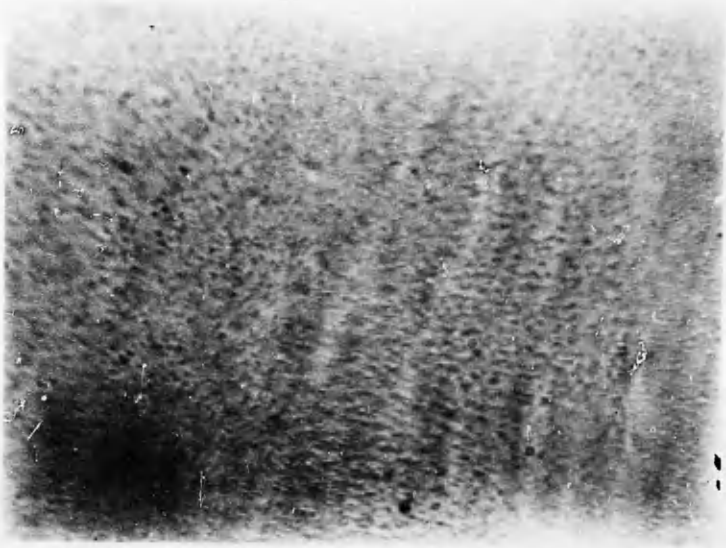
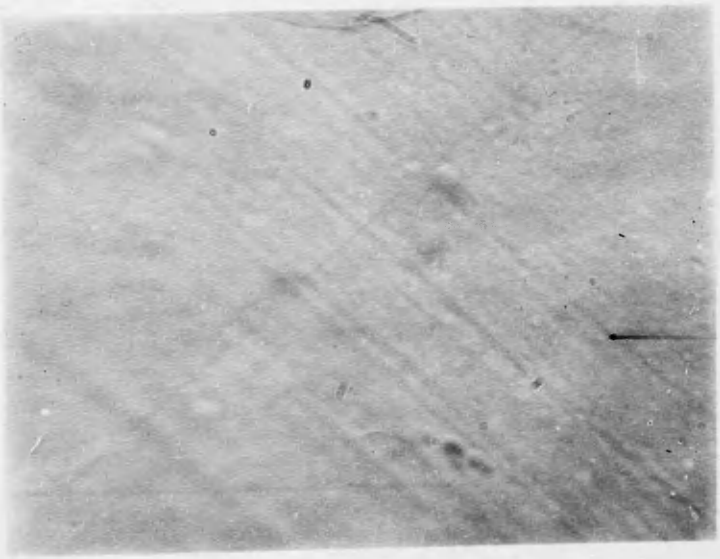


FIG. 25 MEROCYANINE DYE I (i) IN COLLODION.
(ii) PRECIPITATED IN GELATINE.
(iii) DISPERSED IN GELATINE.



SOAPED



UNSOAPED

FIG. 26

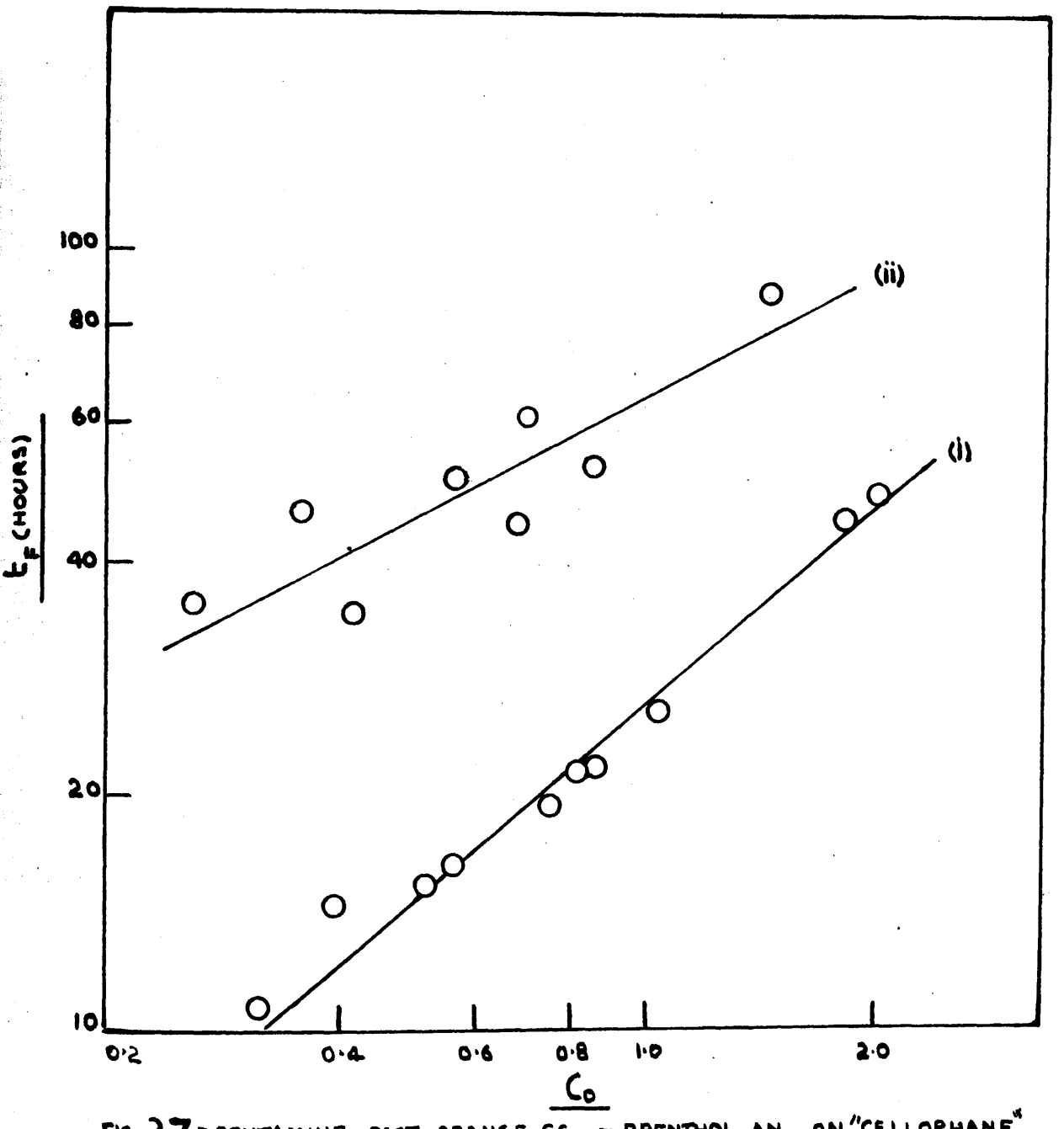


FIG. 27 BRENTAMINE FAST ORANGE GC. → BRENTHOL AN. ON "CELLOPHANE", (i) UNTREATED. (ii) SOAPED.

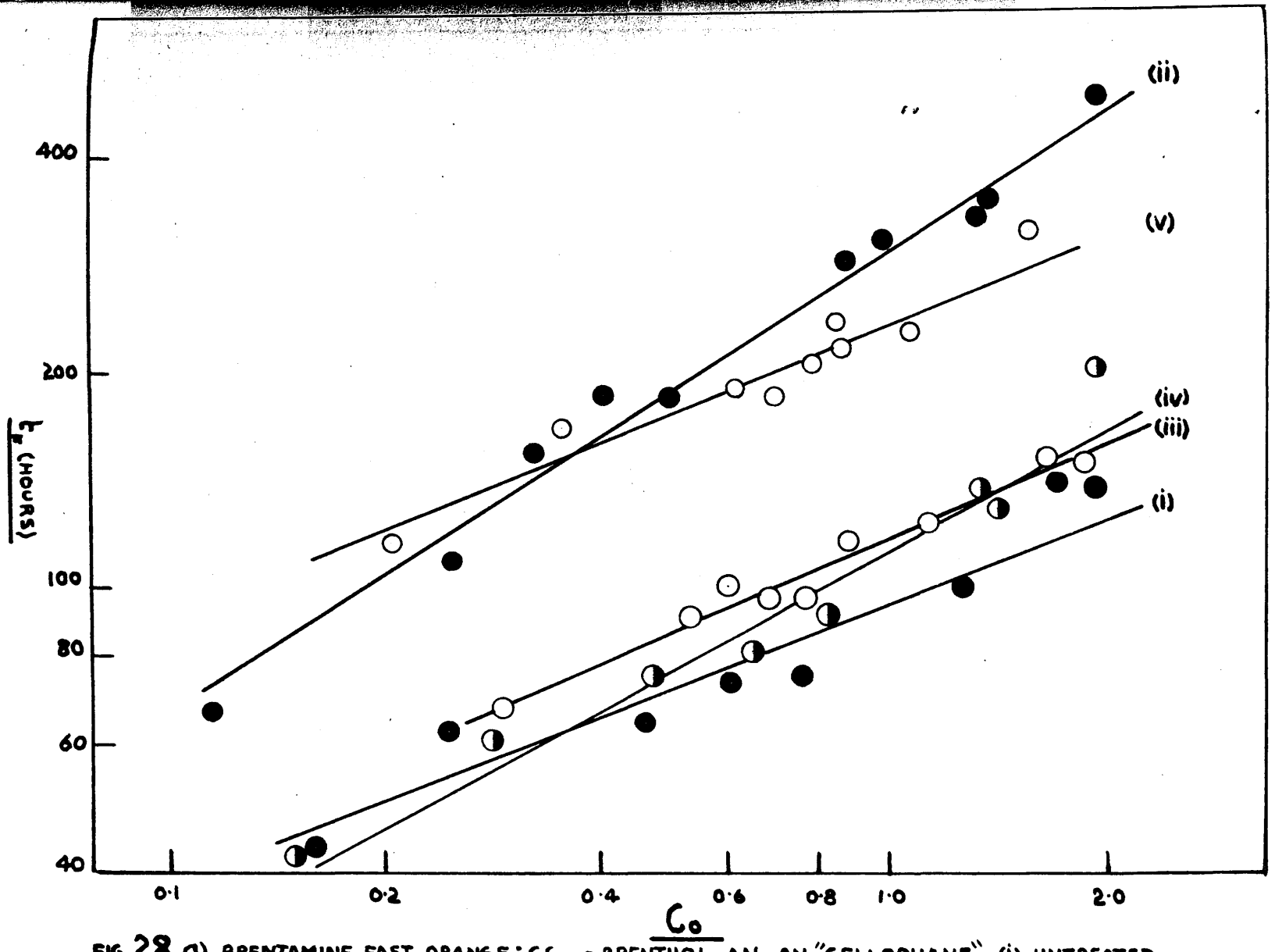


FIG. 28 a) BRENTAMINE FAST ORANGE GC. → BRENTHOL AN. ON "CELLOPHANE." (i) UNTREATED (ii) STEEPED (iii) SOAPED

(b) BRENTAMINE FAST ORANGE GC → BRENTHOL AS. ON "CELLOPHANE." (iv) UNTREATED (v) SOAPED

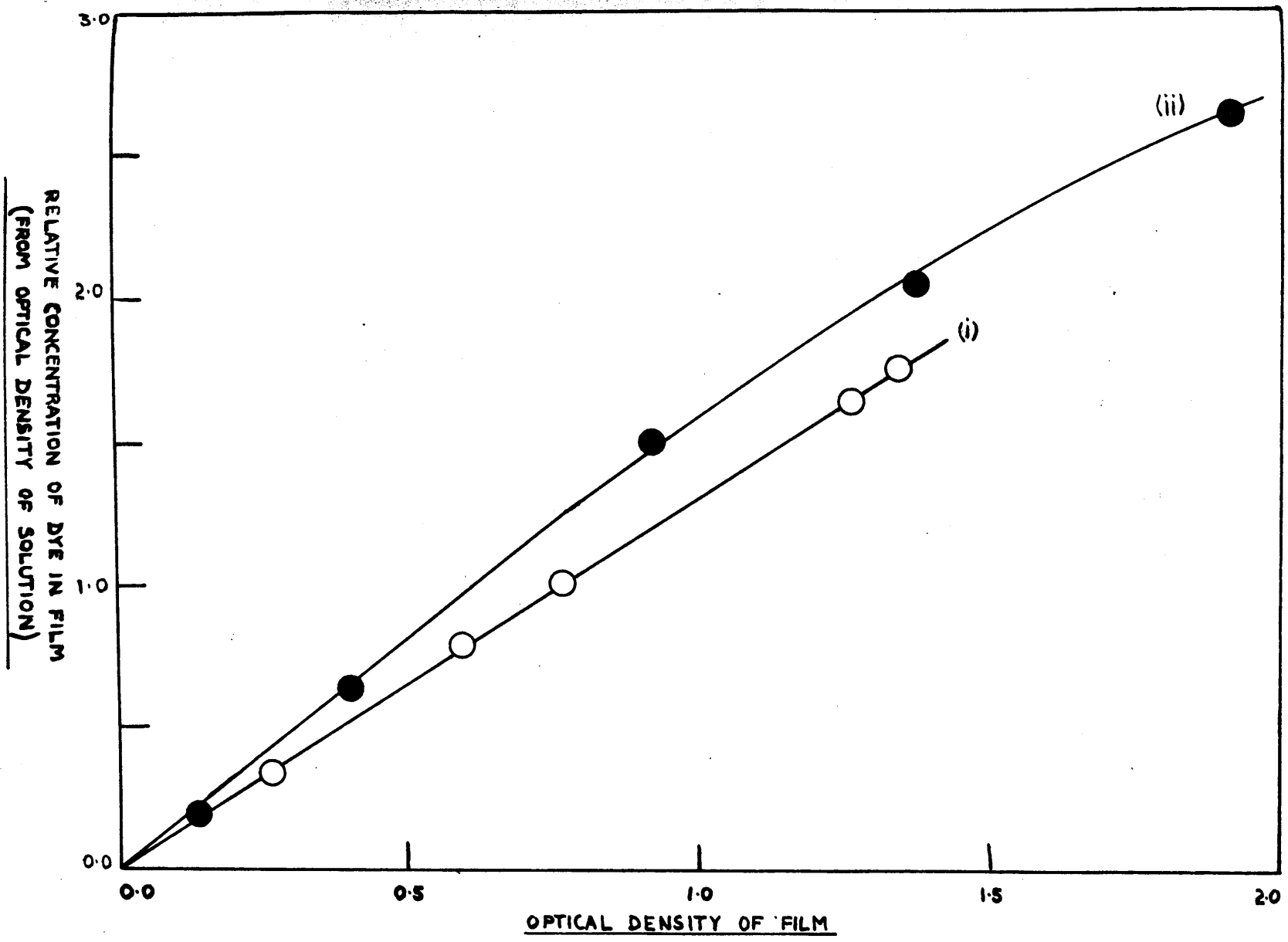


FIG. 29. BRENTAMINE FAST ORANGE GC. (i) UNSOAPED
(ii) SOAPED

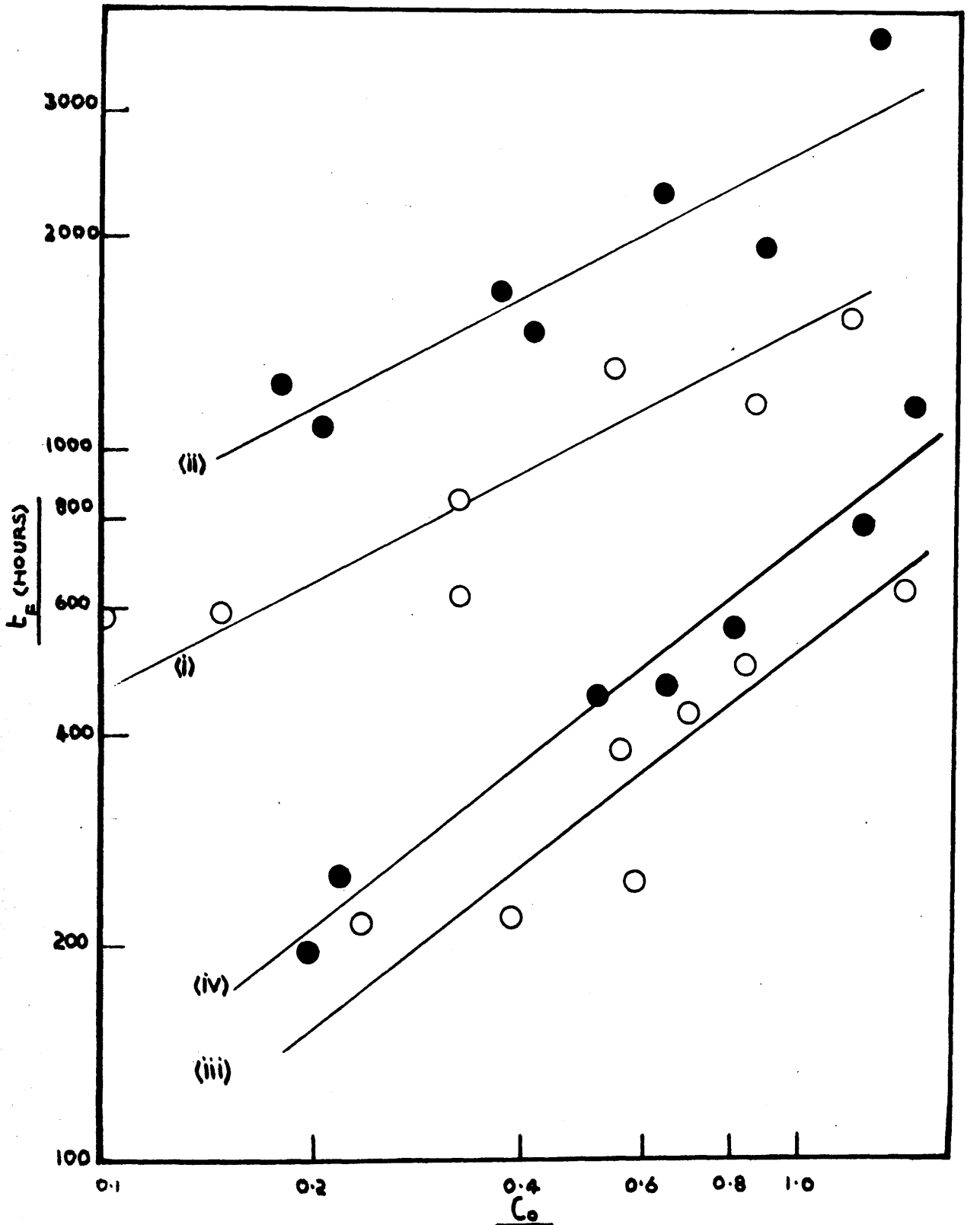


FIG. 30 VAT DYES ON NYLON. a) CALEDON YELLOW GN. (i) UNTREATED. (ii) TREATED.
b) CALEDON GREEN 7G. (iii) UNTREATED. (iv) TREATED.

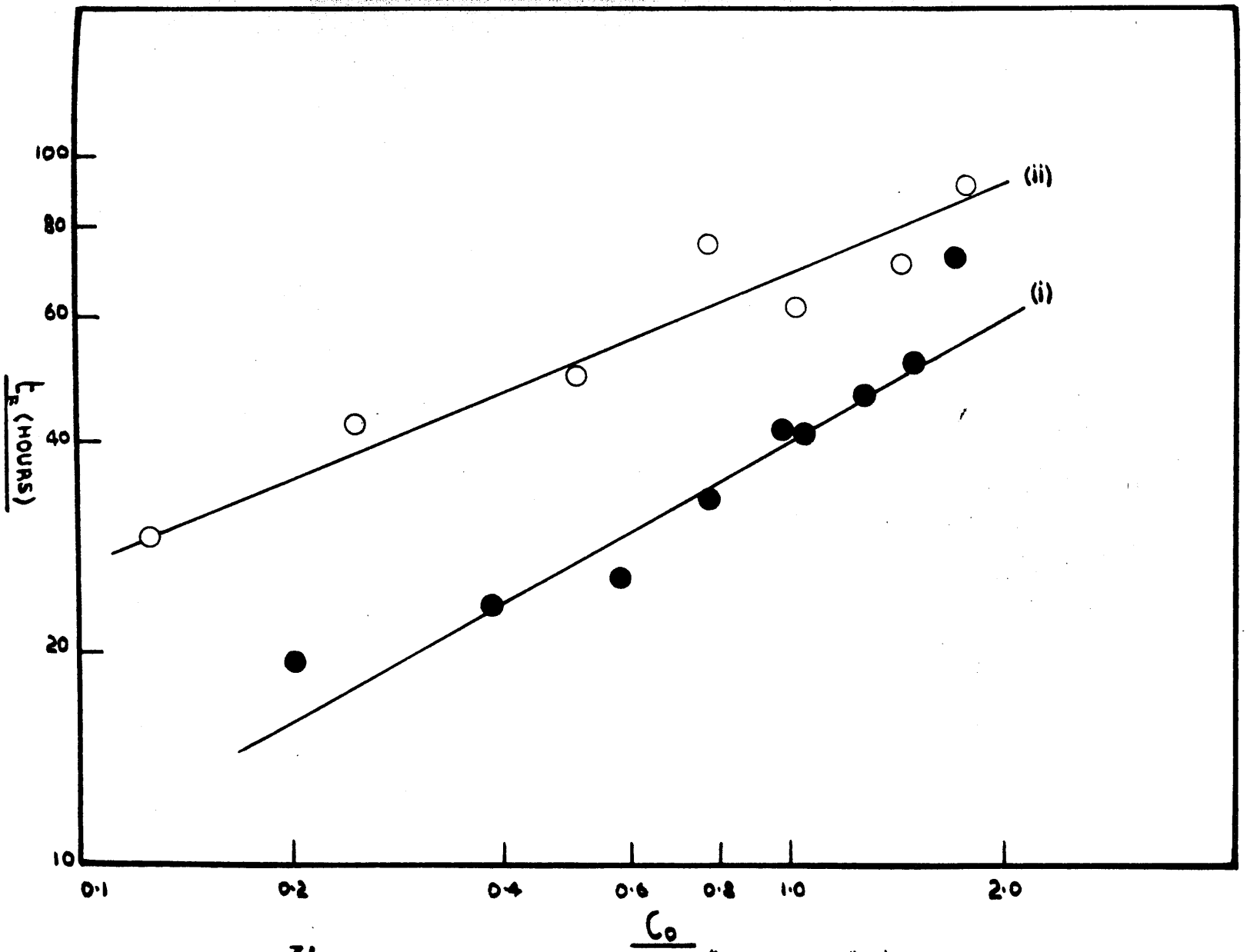


FIG. 31. CHLORAZOL SKY BLUE FFS. ON "CELLOPHANE" (i) NORMAL PORE SIZE. (ii) LARGE PORE SIZE.

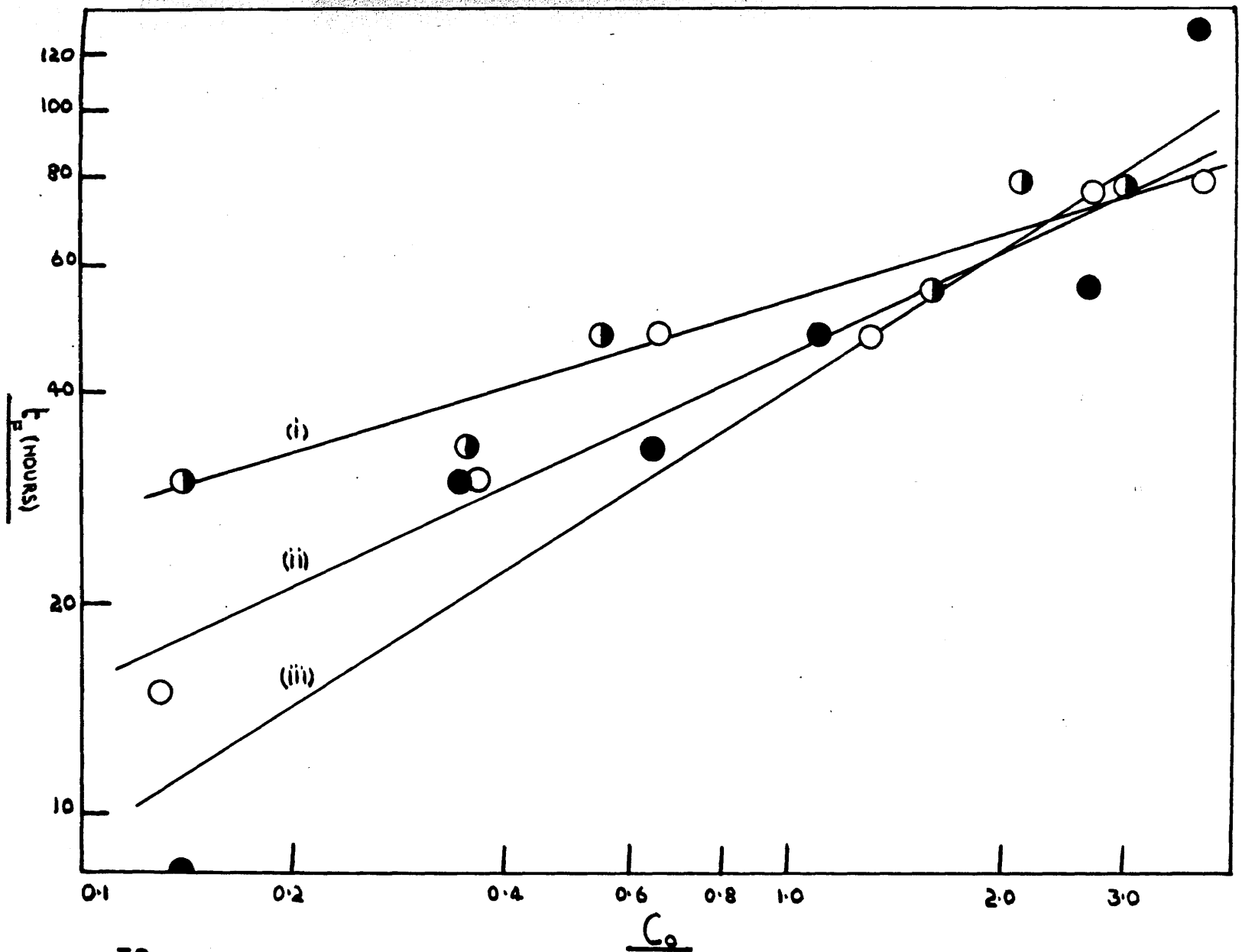


FIG. 32 CHLORAZOL FAST HELIO 2RKS ON VISCOSE OF VARIOUS PHYSICAL CHARACTERISTICS.
(i) STANDARD FIBRO. (ii) STRONG FIBRO. (iii) REDUCED IMBIBITION FIBRO.

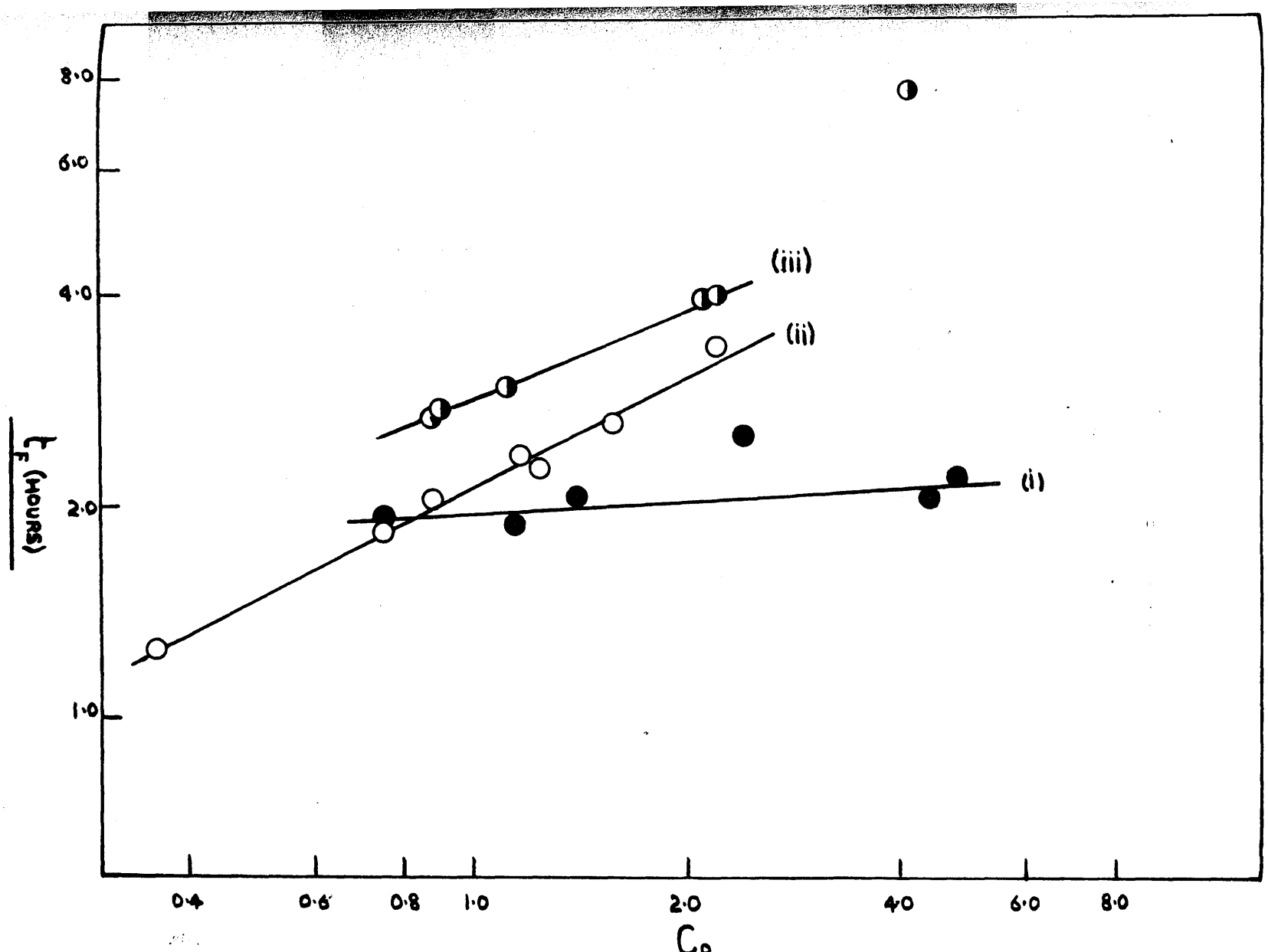


FIG 33. VICTORIA BLUE BO IN LITHOGRAPHIC VARNISH. (i) UNTREATED
(ii) PRECIPITATED EXACTLY WITH PHOSPHOMOLYBDIC ACID
(iii) PRECIPITATED WITH 25% XS. PHOSPHOMOLYBDIC ACID

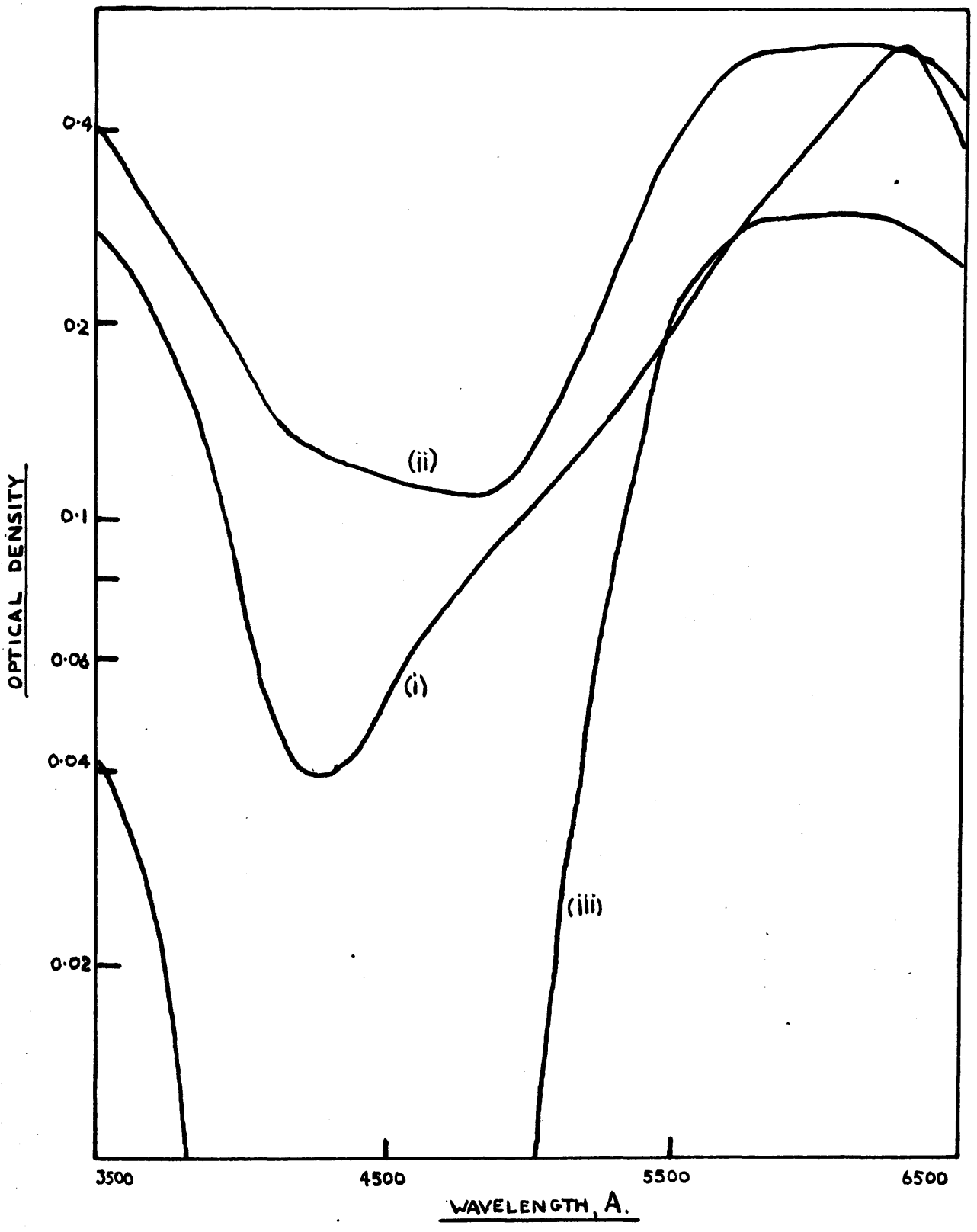


FIG 34 VICTORIA BLUE BO IN LITHOGRAPHIC VARNISH. (i) UNTREATED.
(ii) PRECIPITATED EXACTLY WITH PHOSPHOMOLYBDIC ACID.
(iii) PRECIPITATED WITH 25% XS. PHOSPHOMOLYBDIC ACID.

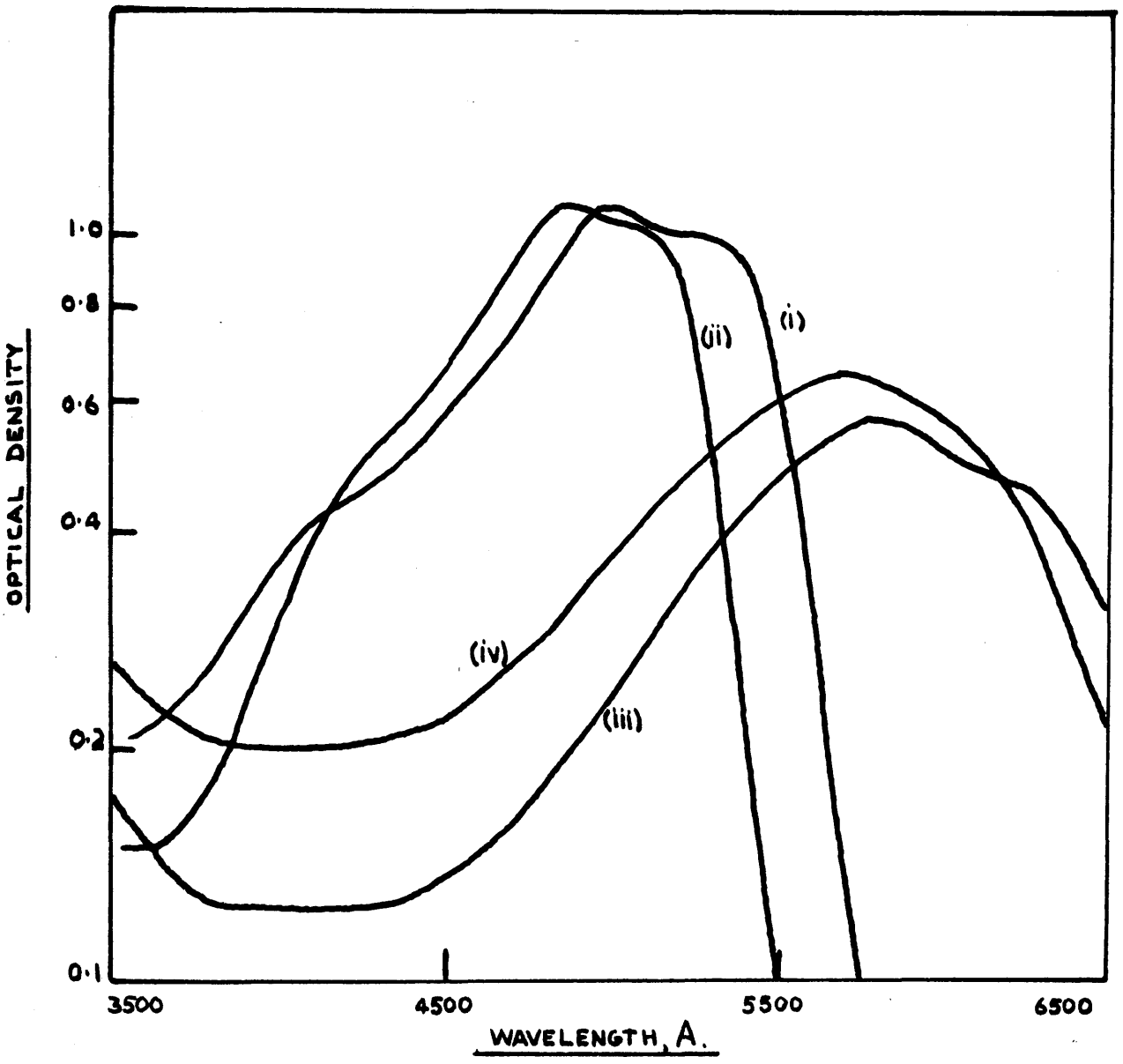


FIG 35. CHLORAZOL BRILLIANT ORANGE 3R. ON "CELLOPHANE" (i) UNTREATED.
(ii) AFTERTREATED WITH FIXANOL C.
CHLORAZOL COPPER BLUE BS. ON "CELLOPHANE" (iii) UNTREATED
(iv) AFTERTREATED WITH FIXANOL C

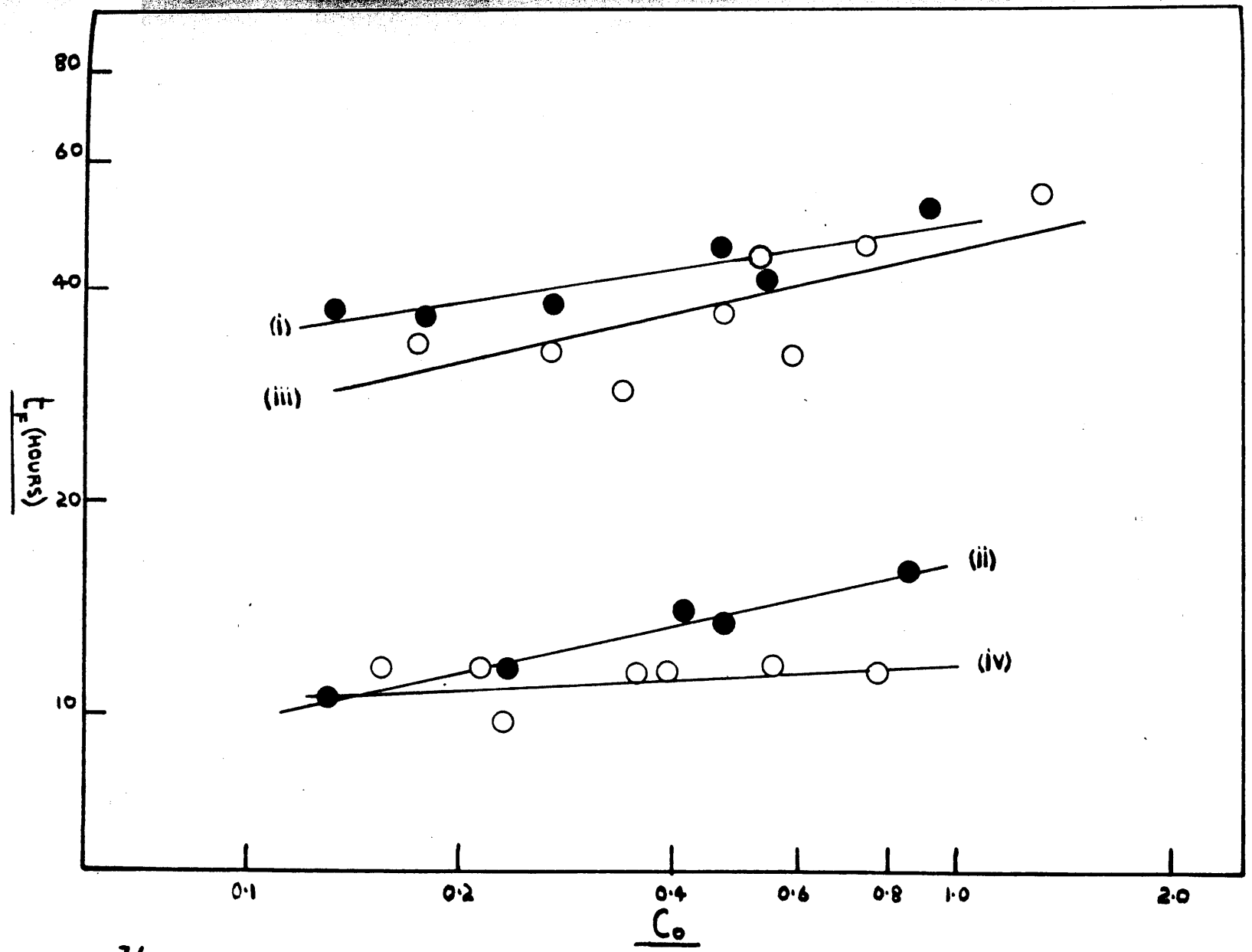


FIG 36 a) CHLORAZOL BRILLIANT ORANGE 3R. ON "CELLOPHANE." (i) UNTREATED.
(ii) AFTERTREATED WITH FIXANOL C.
b) CHLORAZOL COPPER BLUE BS. ON "CELLOPHANE". (iii) UNTREATED.
(iv) AFTERTREATED WITH FIXANOL C.

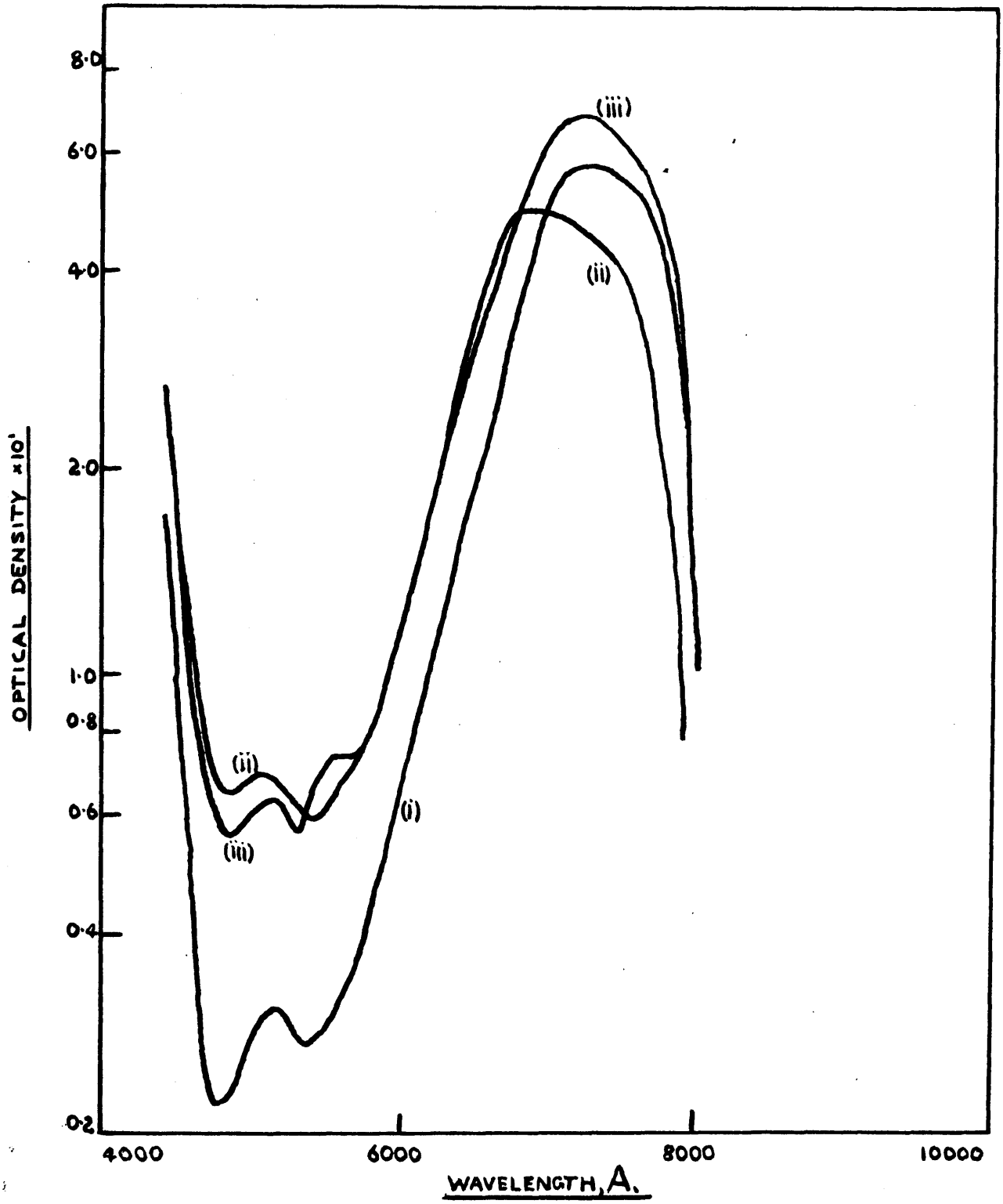


FIG 37. CHLORAZOL SKY BLUE FFS. ON "CELLOPANE."
(i) UNTREATED.
(ii) AFTERTREATED WITH FIXANOL C.
(iii) AFTERTREATED WITH METABOL O.

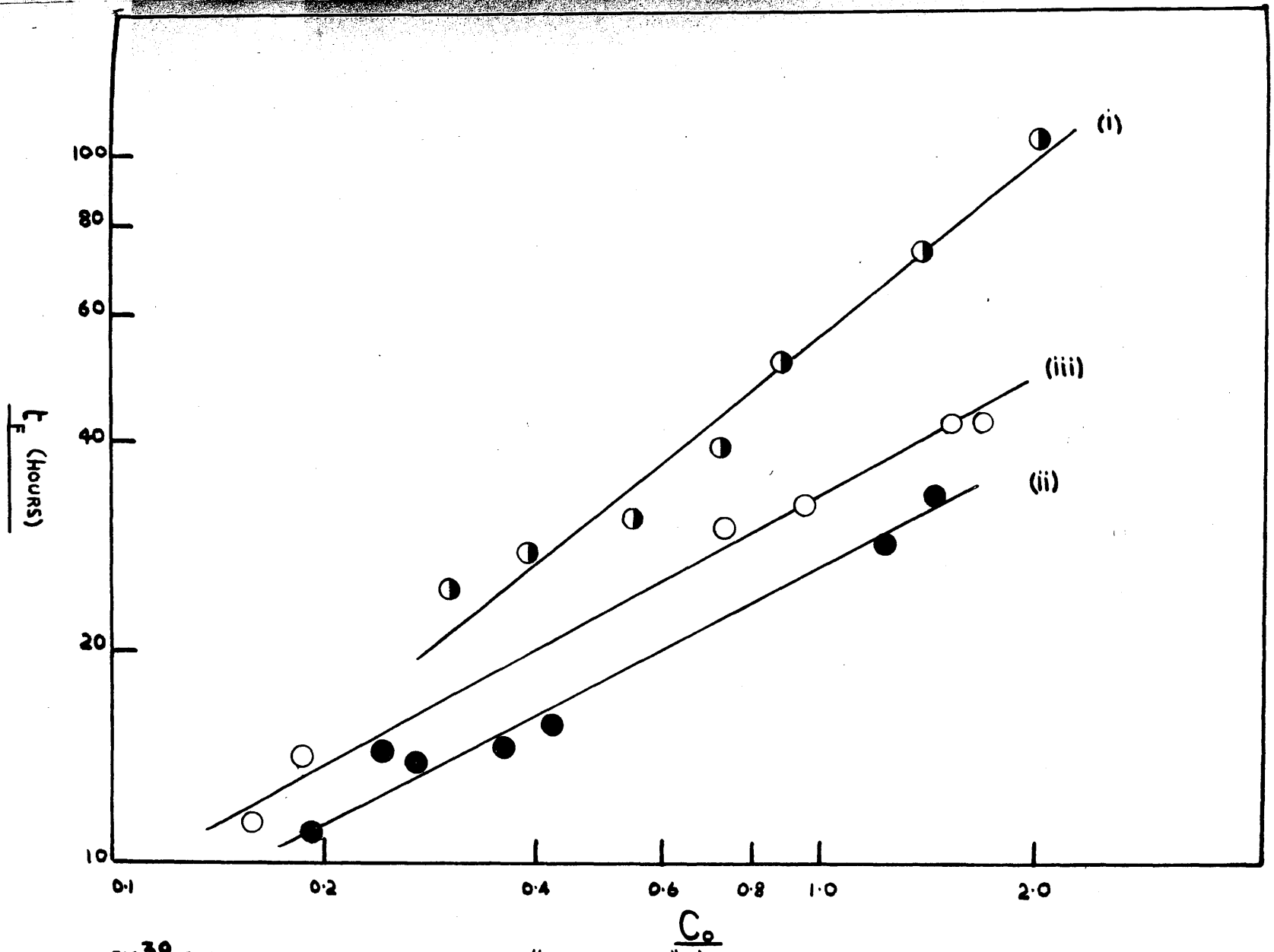


FIG 38 CHLORAZOL SKY BLUE FFS. ON "CELLOPHANE." (i) UNTREATED
(ii) AFTERTREATED WITH FIXANOL C.
(iii) AFTERTREATED WITH METABOL O.

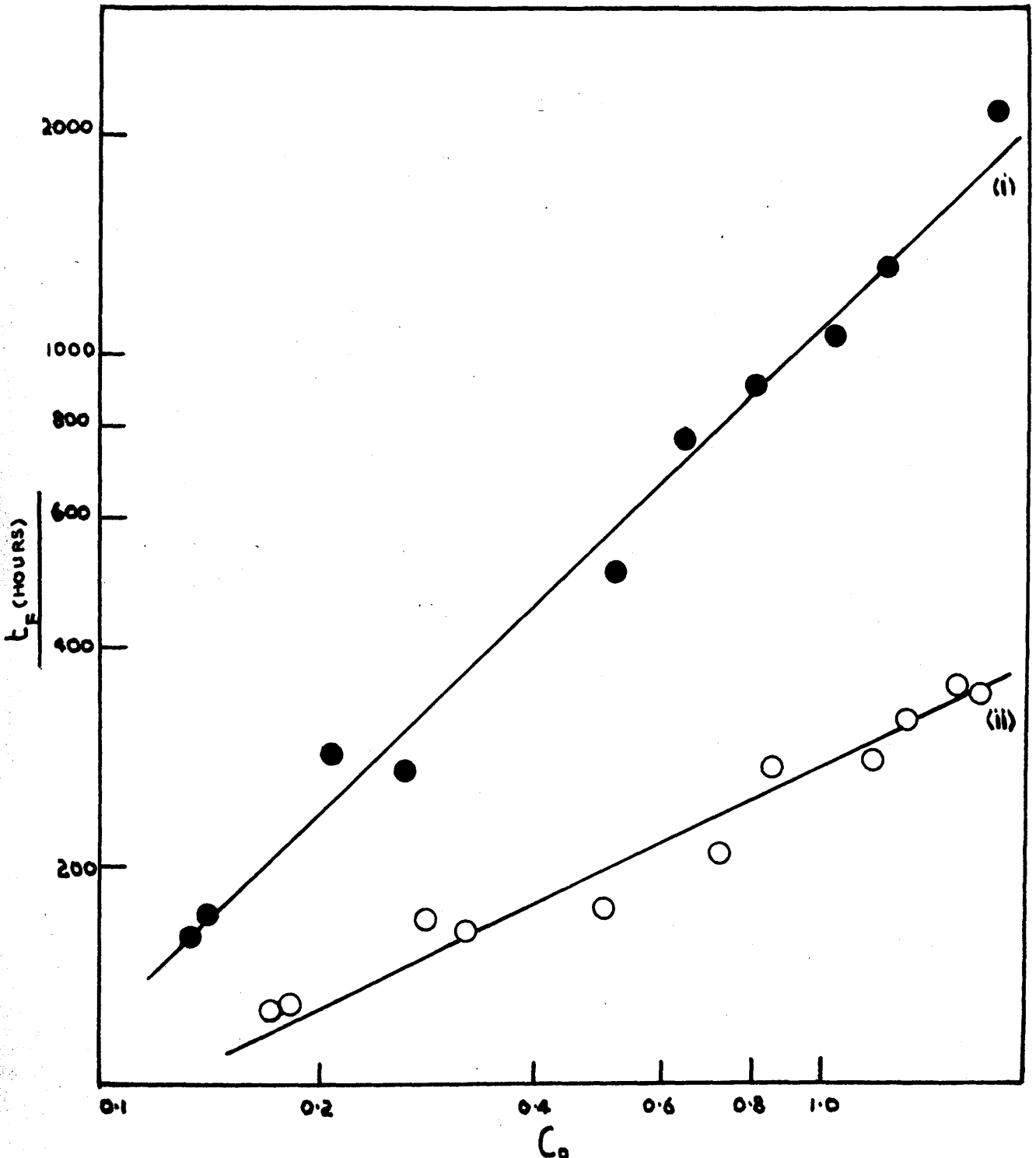


FIG. 39. DURINDONE BLUE 4BC. ON "CELLOPHANE." (i) UNTREATED.
(ii) SOAPED.

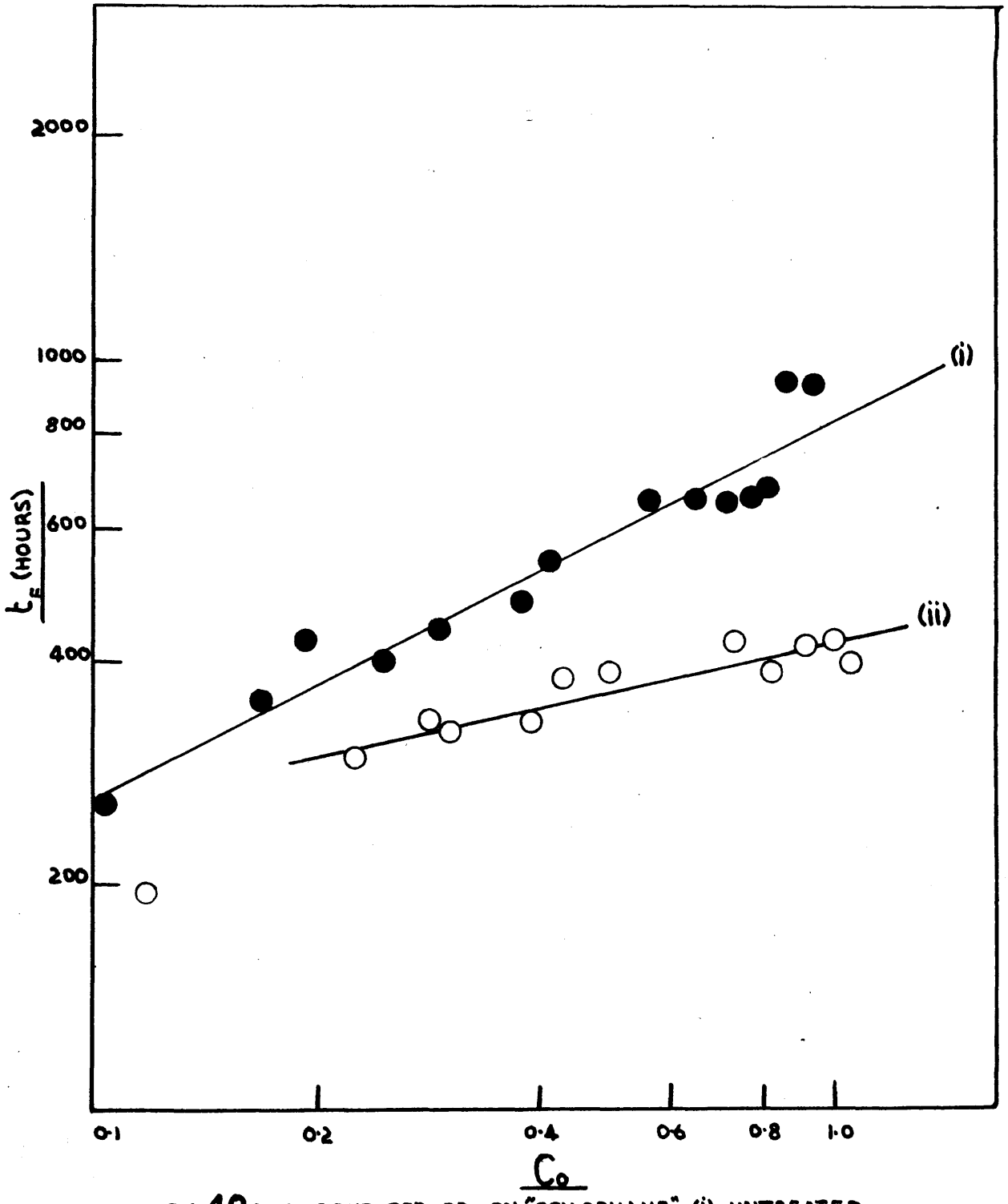


FIG. 40 DURINDONE RED 3B. ON "CELLOPHANE". (i) UNTREATED
(ii) SOAPED

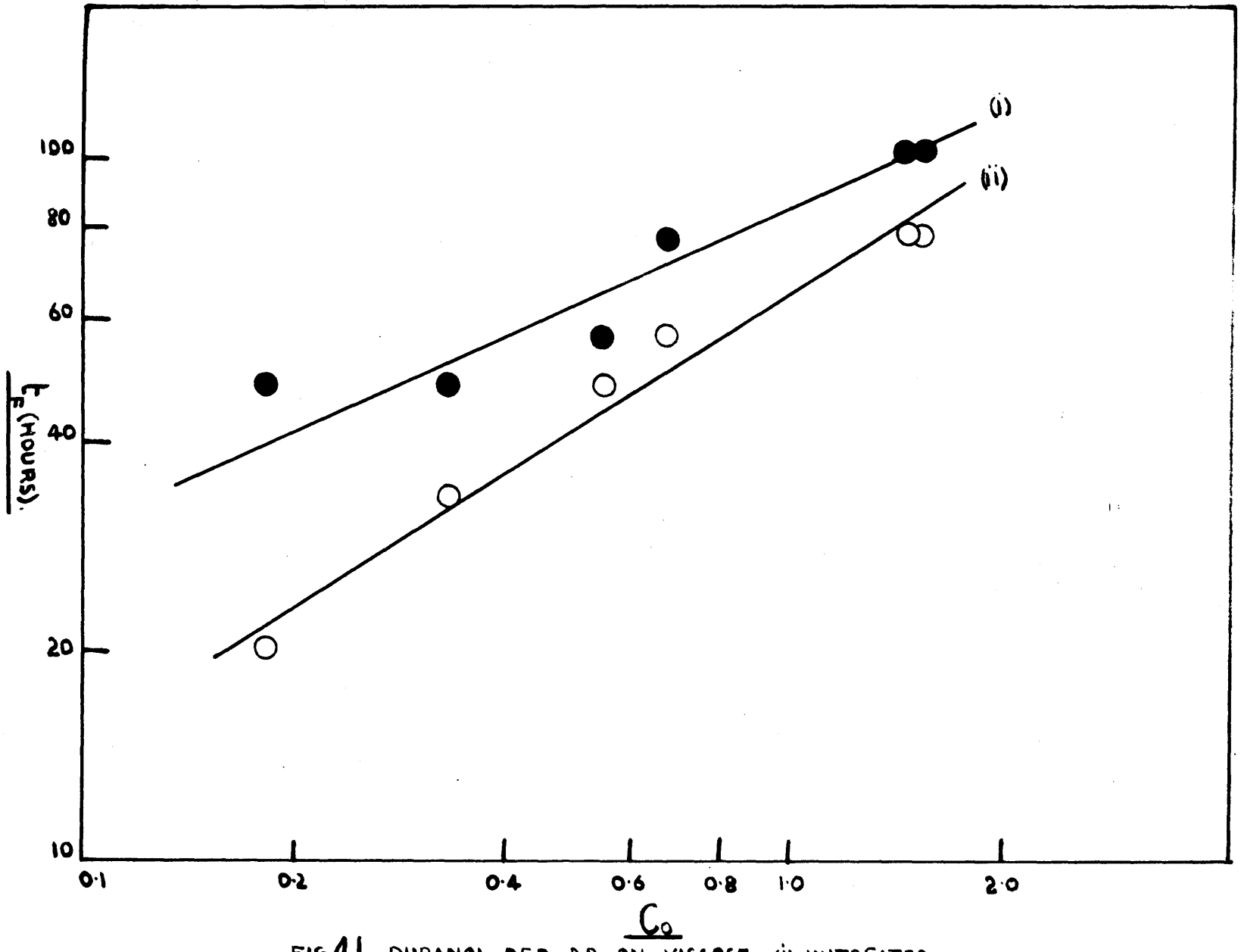


FIG. 41. DURANOL RED 2B. ON VISCOSE. (i) UNTREATED.
(ii) CREASE RESIST.

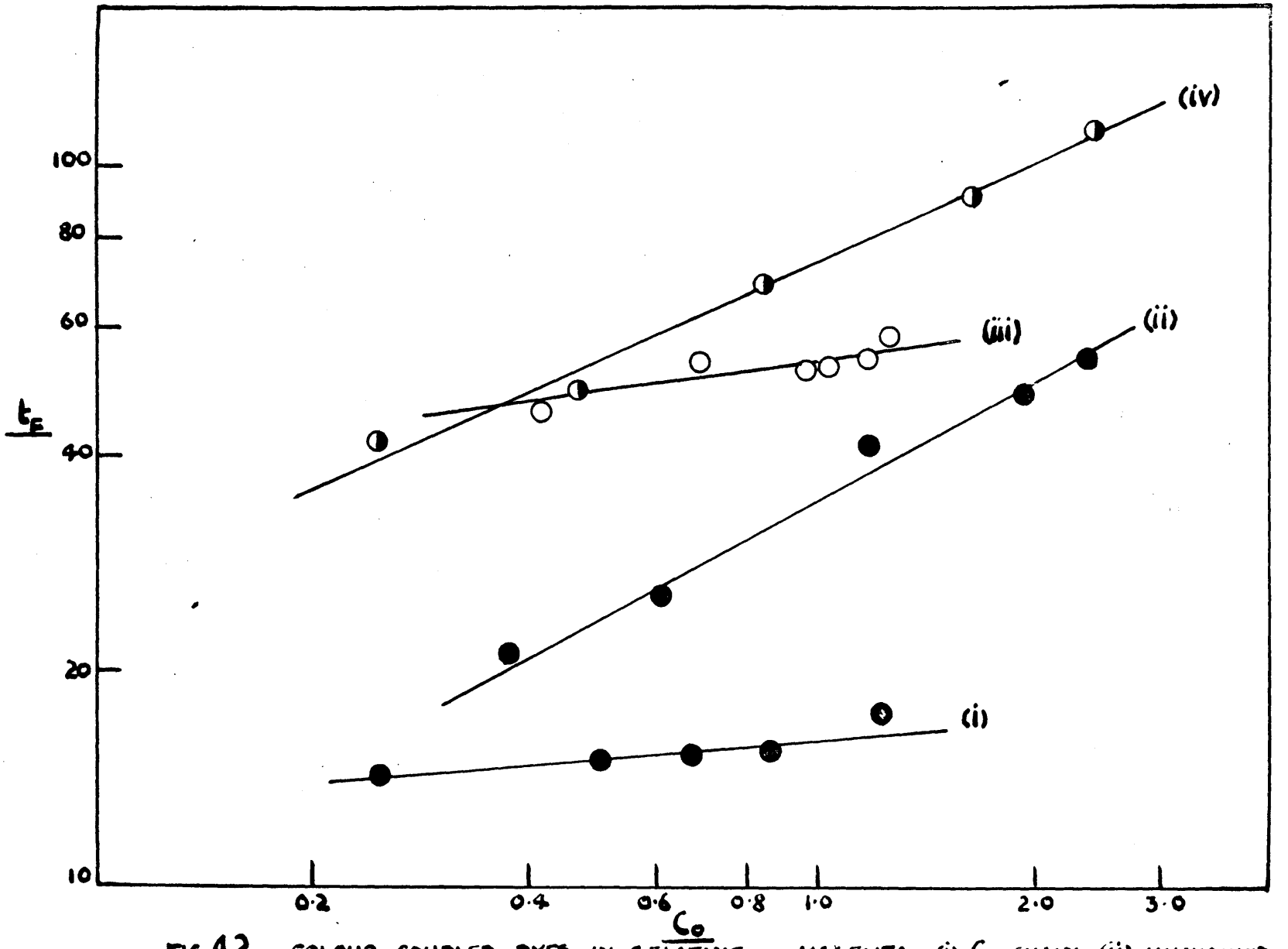


FIG. 42. COLOUR-COUPLED DYES IN GELATINE. MAGENTA. (i) C_{17} CHAIN. (ii) UNCHAINED.
CYAN. (iii) C_{17} CHAIN. (iv) UNCHAINED.

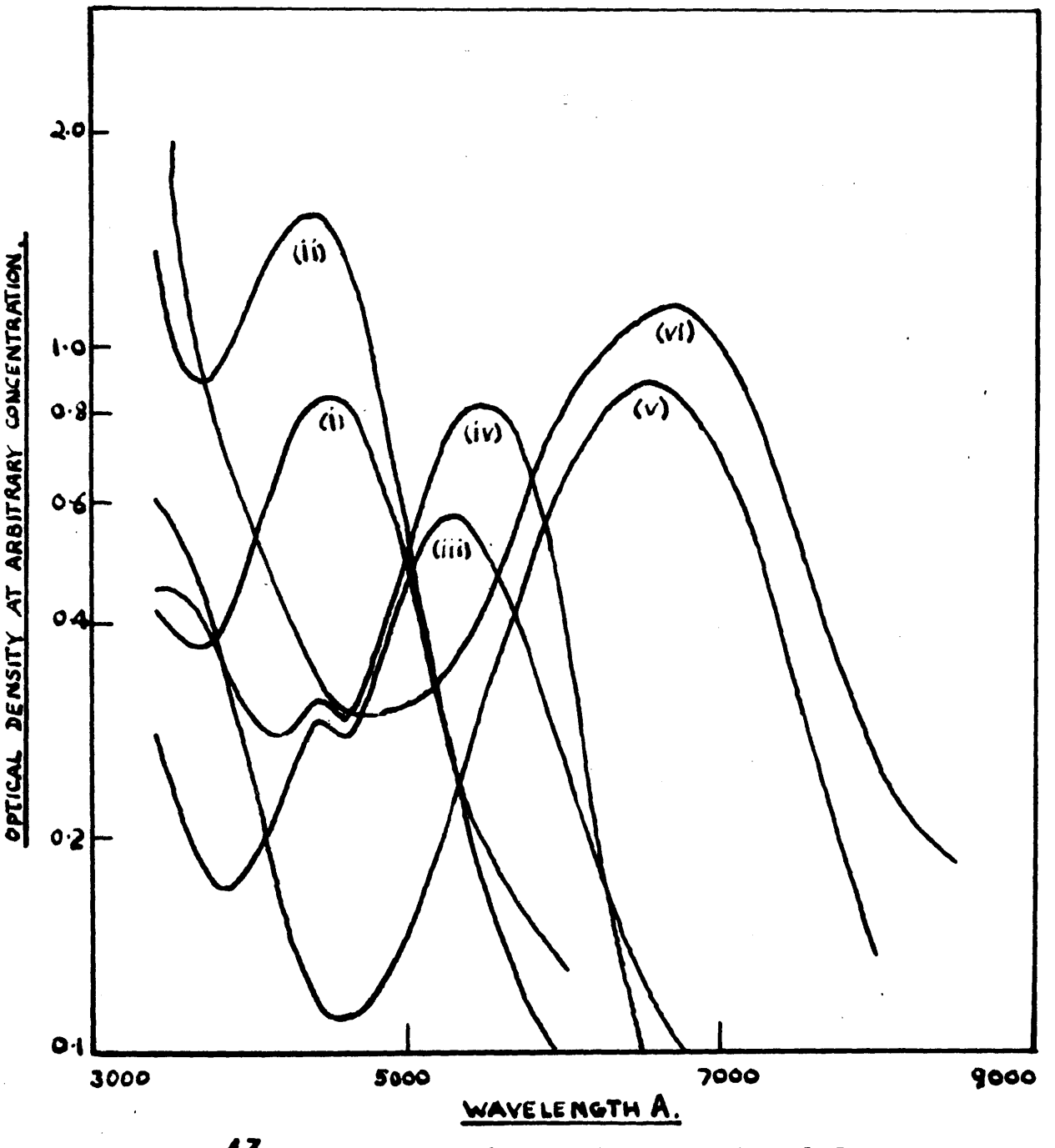


FIG.43. ABSORPTION CURVES FOR COLOUR-COUPLED DYES IN GELATINE. YELLOW. (i) NO CHAIN. (ii) C_{17} CHAIN.
MAGENTA. (iii) NO CHAIN. (iv) C_{17} CHAIN.
CYAN. (v) NO CHAIN. (vi) C_{17} CHAIN.

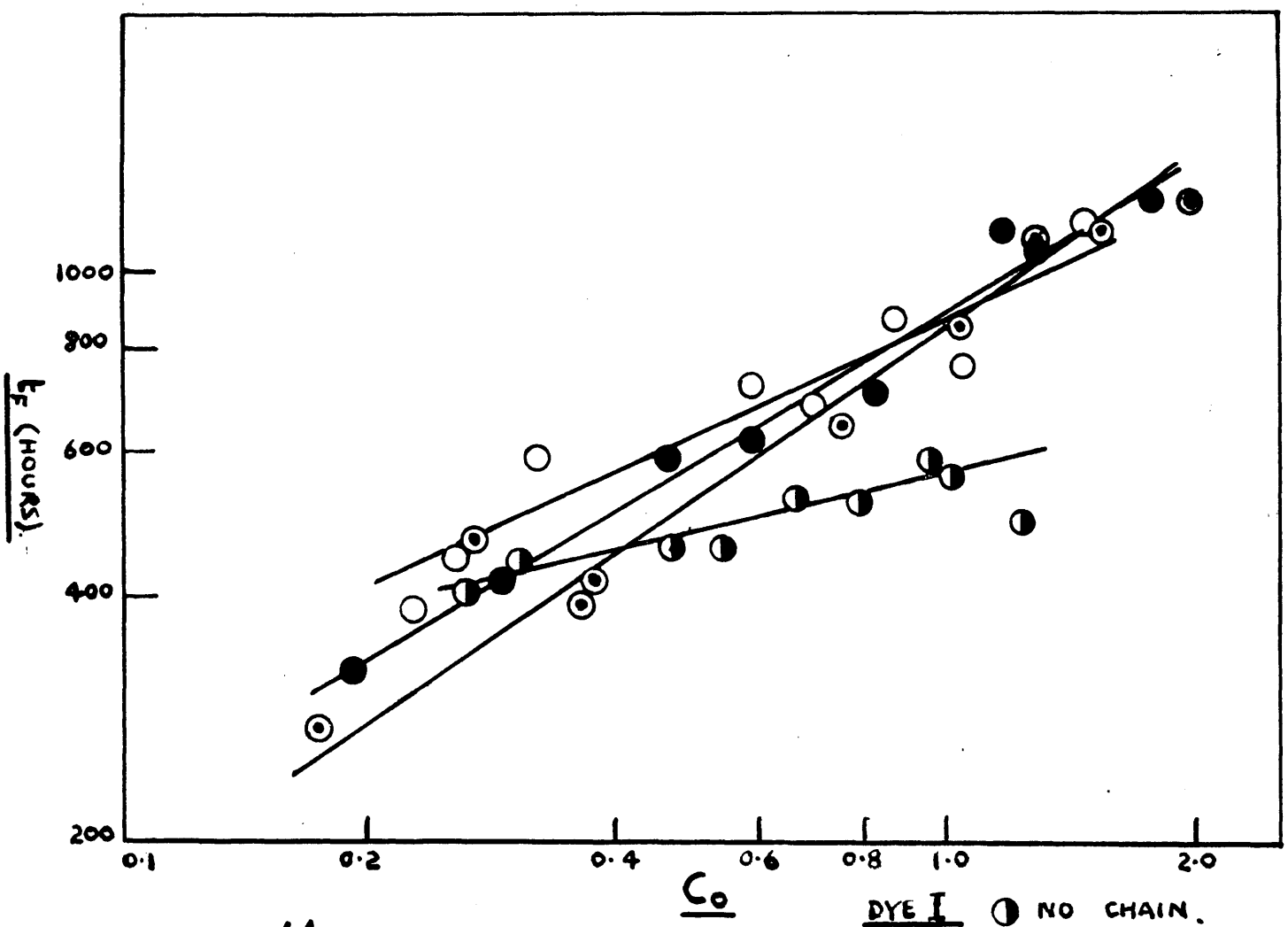


FIG. 44. ACID DYES IN GELATINE.

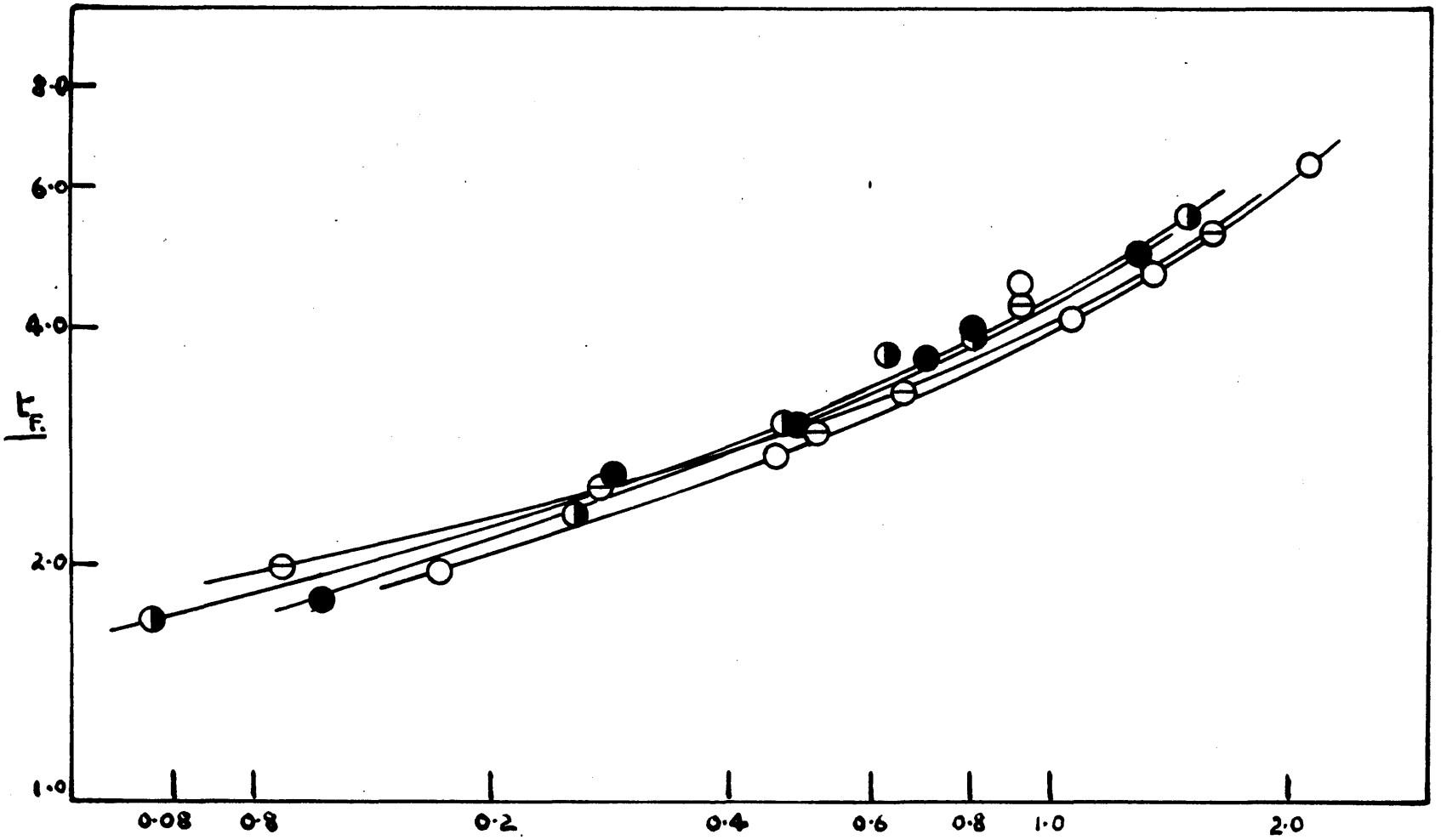


FIG. 45. MEROCYANINE DYE IN COLLODION.

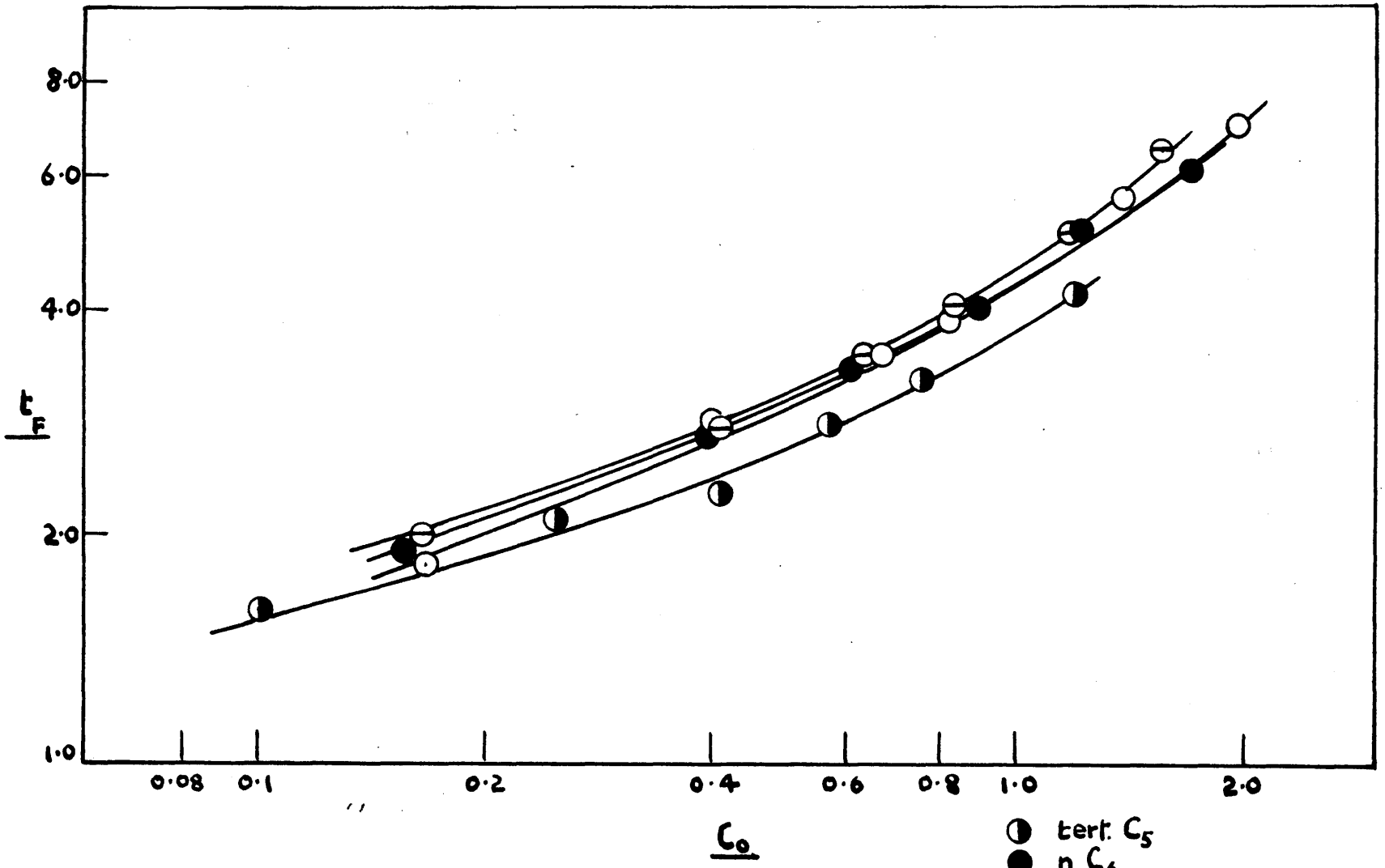


FIG. 46. MEROCYANINE DYE IN COLLODION.

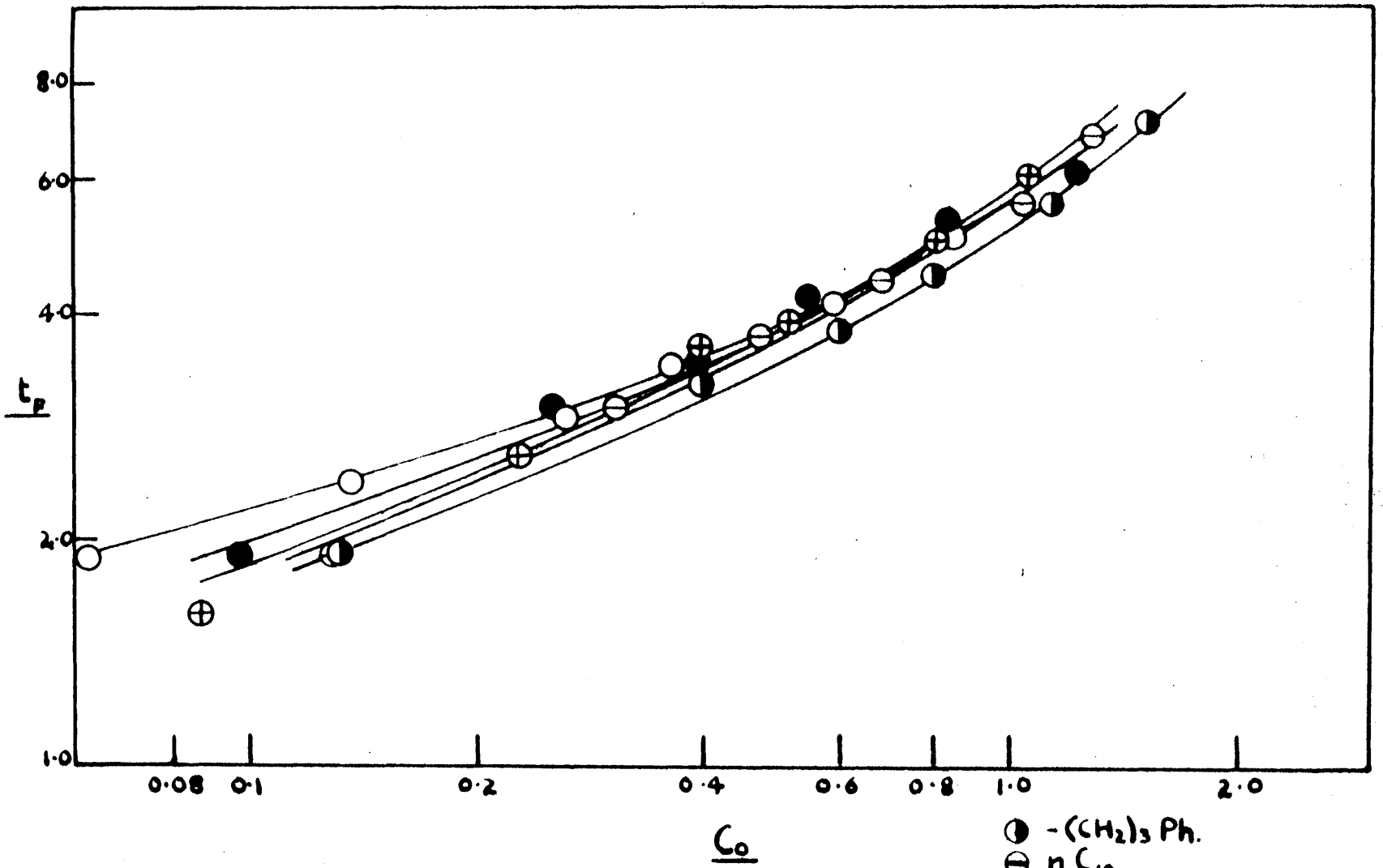


FIG. 47. MEROCYANINE DYE IN COLLODION.

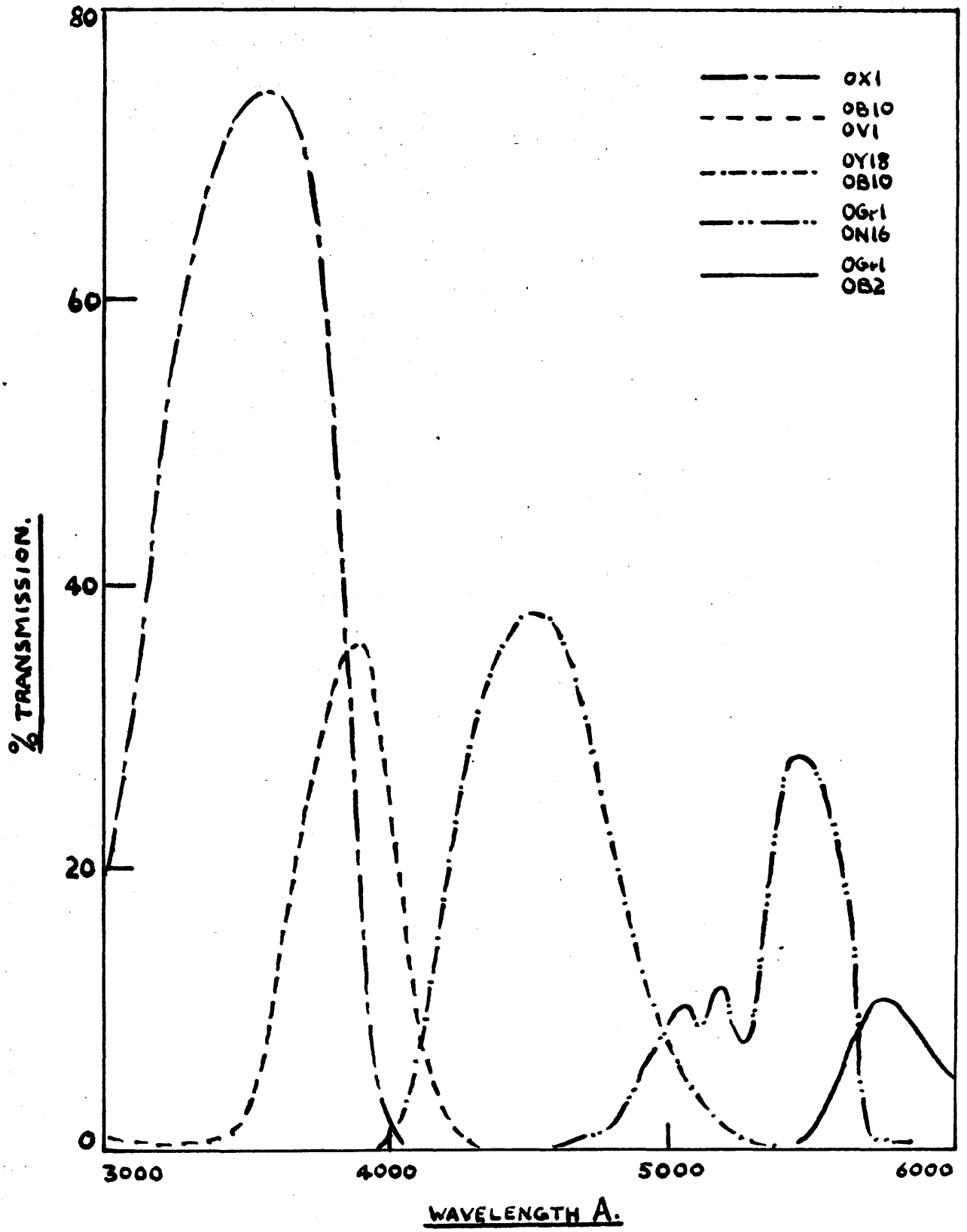
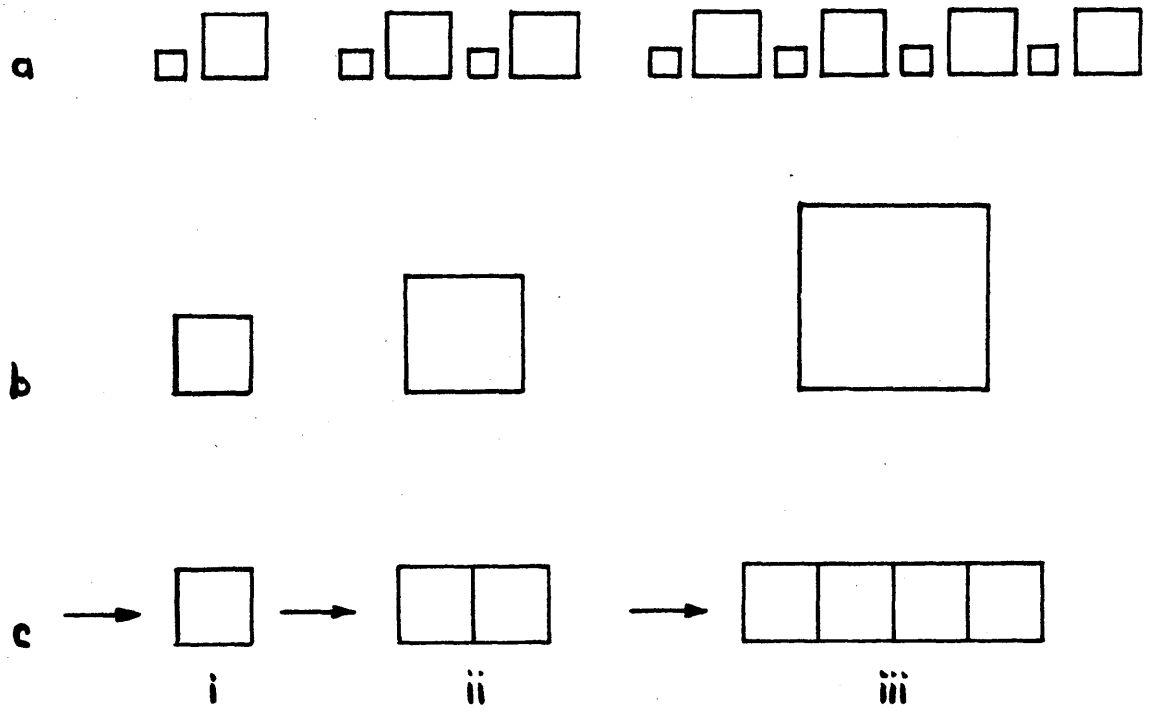


FIG. 48 TRANSMISSION CURVES OF FILTERS.



ILLUSTRATING TYPES OF GROWTH OF DYE PARTICLES.

RELATIVE TOTAL WEIGHT : (i):(ii):(iii) = 1:2:4.
ARROW SHOWS DIRECTION OF LIGHT IN (c).

FIG. 49.

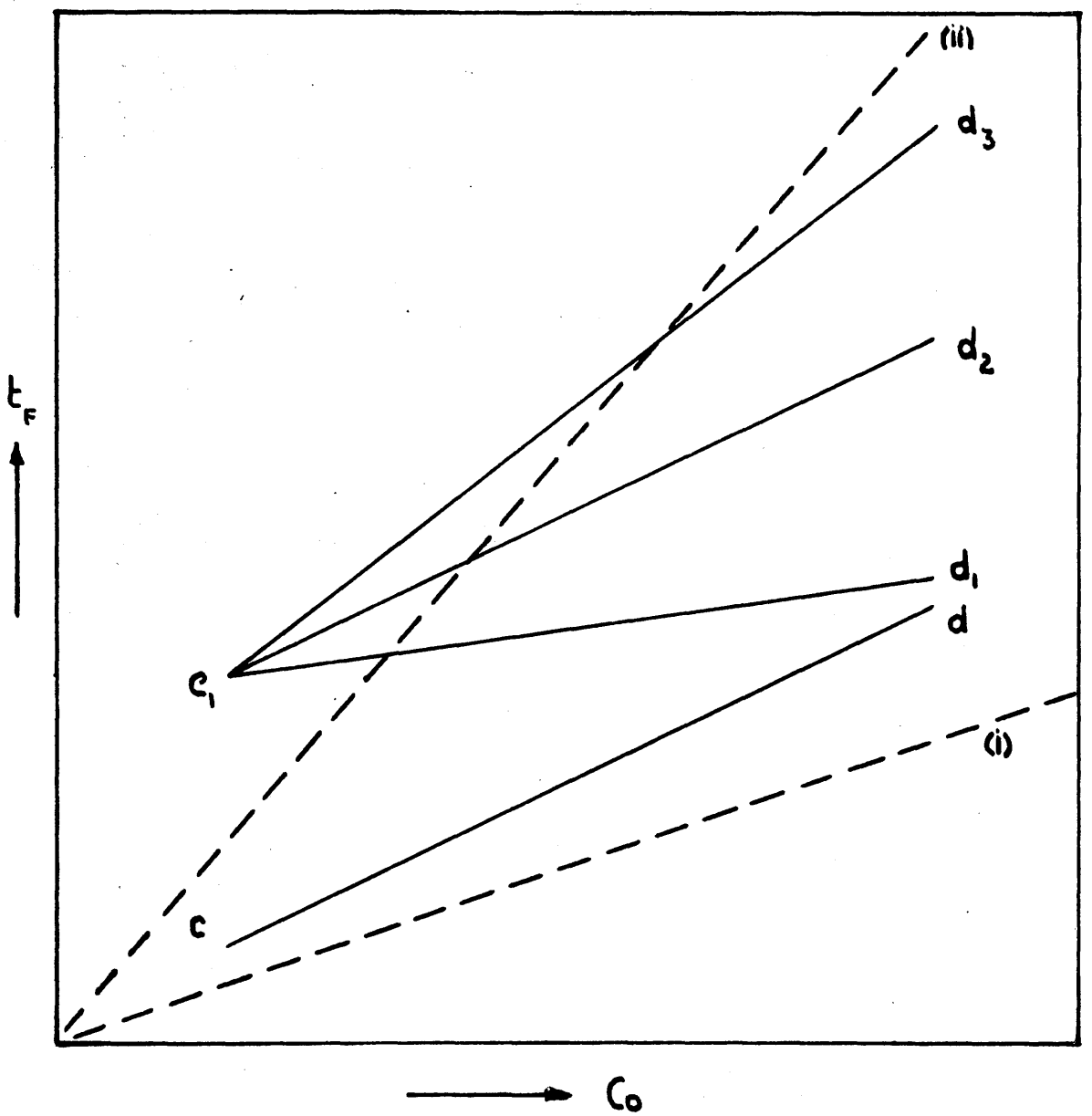


FIG., 50. CHARACTERISTIC FADING ORDER CURVES.

(i) THEORETICAL, FOR SYMMETRICAL GROWTH OF PARTICLES.
(ii) THEORETICAL, FOR "ZERO ORDER" UNSYMMETRICAL GROWTH.