THE OXIDATION OF AZO DYES AND ITS RELATION TO LIGHT FADING.

A THESIS

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INTRODUCTION.

The present research forms part of a series of investigations being undertaken in the Colour Chemistry Laboratory of the Royal Technical College upon various aspects of adsorption on surfaces. In particular, the present work was intended as part of a study of the photochemistry of dyes adsorbed on fibrous substrates.

The action of light on dyed fibres in air appears to involve an oxidation of the dye in many cases, and consequently, as a preliminary investigation, a study of the oxidation of dyes in solution by common oxidising agents was undertaken. This aspect of the work proved to be interesting enough to warrant a more intensive study than was originally proposed. The work on the photochemistry of surface-adsorbed dyes has therefore had to be confined to a series of measurements of relative light fastness, and their comparison with the results of the oxidation experiments in an attempt to elucidate the mechanism of the light fading process.

The fading of dyes in light is probably largely an oxidation process. Thus Hibbert (1) was able to isolate a small quantity of isatin from samples of indigo-dyed cotton cloth which had been faded by exposure to sunlight or to the light from a carbon arc. Haller and Ziersch (2) dyed cotton fabrics with simple azo dyes from β-naphthol and faded them both by means of ozonised oxygen and in the light of an arc. They were able to detect 1:2-naphthaquinone and phthalic and phthalonic/

phthalonic acids in aqueous and alcoholic extracts respectively of the light-faded patterns, and phthalic acid in alcoholic extracts of the patterns subjected to ozonised oxygen. These compounds represent successive stages in the oxidation of the β-naphthol component of the dyes. The atmosphere surrounding the patterns became enriched in nitrogen by the fading of the dyes. Peroxides were detected in the freshly exposed fabric, and Haller and Ziersch postulated the formation of azo dye peroxides as an intermediate stage in the complete breakdown of the molecule by light exposure.

Several investigators, e.g. Lasarev (3), have noted the dependence of light fading upon the presence of oxygen in the surrounding atmosphere. Scharwin and Pakschwer (4) found that, when dyed fabrics were exposed to sunlight or light from a quartz mercury vapour lamp in sealed tubes, fading took place in descending order of rapidity in presence of the following gases - oxygen, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, hydrogen, nitrogen. A similar observation was made by Egerton (5) in connection with the study of the photochemical degradation of cotton in presence of tendering vat dyes. It has also been shown by Egerton (6) that when certain yellow and orange vat dyes dispersed within a textile material, or supported on an inert base, are irradiated in the neighbourhood of undyed cotton not in contact with the dye, relatively rapid photochemical degradation of the undyed cotton/

cotton occurs. This effect is observed only in moist, oxygen-containing atmosphere, and Egerton explained it by the photochemical oxidation of water to hydrogen peroxide, sensitised by the dye, and by the subsequent photochemical oxidation of the neighbouring undyed cotton by the volatile hydrogen peroxide. Whether hydrogen peroxide is formed on photosensitisation of azo dyes is doubtful. Ashton, Clibbens and Probert (7) found that the photochemical oxidation of cotton by the air is sensitised by sulphur and basic dyes, as well as by vat dyes. The only direct dye, amongst the ones studied, to accelerate the photochemical oxidation was the thiazole dye Primuline. The evidence suggested not only that the direct azo dyes had no sensitising action, but also that the introduction of an azo group into the molecule diminished or destroyed the activity of the thiazole dyes.

It does not seem to have been proved conclusively that fading of dyed fabrics in light does not occur at all in absence of oxygen. This would be difficult to determine because traces of air may be retained tenaciously by the fibre. The fibre molecules themselves may also be a source of oxygen.

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LITERATURE REVIEW.

(i) General.

The following is a review of the work previously reported on the subject.

Decomposition of azo dyes by mineral acids:

The decomposition of azo dyes by mineral acids has been studied by various investigators. Wallach and Kiepenheuer (8) found that m-dinitrophenol is formed by the action of nitric acid (sp. gr. 1.2) on 4-hydroxyazobenzene. Bohn and Heumann (9) also obtained m-dinitrophenol by the action of cold fuming or warm concentrated nitric acid on the same. By the action of nitric acid (sp. gr. 1.42) on benzeneazo naphthols, Meldola and Morgan (10) obtained dinitro derivatives of the naphthol components. As a result of the examination of the behaviour of a series of various types of azo compounds with ten to twenty times their weight of cold red fuming nitric acid, Schmidt (11) found that the decomposition occurs with varying ease according to the constitution of the azo compound, but the products are normally the nitrate of the diazo compound used in making the azo compound and a nitro derivative of the coupling component. The influence of the constitution of the azo compound and the concentration and temperature of nitric acid on the course of the reaction in the case of hydroxyazo compounds was also studied by Charrier and Ferreri (12).

Finally/

Finally, examination of the behaviour of a series of typical azo derivatives of β-naphthol with cold fuming nitric acid by Rowe and Levin (13) demonstrated that fission may or may not be accompanied by nitration of the diazo residue according to the constitution of the latter. This reaction and the products to which it gives rise are now so well understood that cold fuming nitric acid is a valuable supplementary reagent for use in the determination of the constitution of certain monoazo compounds, e.g. those containing nitro groups which present difficulty when examined by the more generally employed reduction methods.

The decomposition of azo compounds by means of other mineral acids has been studied by various investigators, including Zinin (14), Schmitt (15), Jacobson (16), Witt (17), Wallach (18), Wallach and Kolliker (19), Bucherer and Hanusch (20) and Limpricht (21), but the nature of the reactions involved are not so well known and are less clearly understood.

In so far as the authors quoted above referred to the nature of these decompositions of azo compounds with hydrochloric acid, they regarded the reaction as primarily reduction, followed by oxidation and chlorination of some of the fission products by liberated chlorine.

Zincke (quoted by Haller and Ziersch (2)) oxidised o-aminoazo compounds to N-arylphenols and naphthotriazoles with chromic acid.

Rowe and Dangerfield (22) studied the action of various strengths/

strengths of sulphuric acid on azo compounds and they came to the conclusion that when azo compounds are heated with aqueous sulphuric acid, they are decomposed with greater or less ease according to their constitution. Fission of the azo group occurs with re-formation of the first component base and substantially without reduction of a nitro group when one is present. Consequently this provides a supplementary method for obtaining the first component base from azo compounds that may sometimes be helpful in determining the constitution of the latter. The reaction conditions are so stringent with insoluble azo compounds, however, that neither the coupling component nor an identifiable derivative of it can be isolated. Although arylamides of β-hydroxynaphthoic acid readily undergo hydrolysis of the arylamide group under similar conditions, that is not so with their insoluble azo derivatives, which merely break down at the azo group except when they are derived from β-hydroxynaphthoic *m*-nitroanilide, in which case hydrolysis of the arylamide group occurs to a greater extent than fission of the azo group. Water-soluble azo dyes are decomposed more easily and even prolonged boiling with water may be sufficient. The decomposition products of Orange I and Orange II are the first component base, ammonia and α-naphthaquinone or β-hydroxy-α-naphthaquinone respectively. Disazo acid dyes of/

of the Sulphoncyanine or Coomassie Navy Blue types are decomposed in separate stages, initially with formation of the first component base and a monoazo compound, which is not an aminoazo compound, followed by fission of the remaining azo group. It was not possible to determine definitely whether the fission of azo compounds by hot aqueous sulphuric acid is due to hydrolysis or reduction of the azo groups, but all the evidence obtained favours the former as the more probable reaction. Whether the reaction is ever direct hydrolysis of the azo group or not, in many cases a preliminary rearrangement of the azo compound may well occur with the formation of a quinoneimine derivative, which is then hydrolysed as suggested by Bucherer and Hanusch (20) as in the course of the reaction in the decomposition of Orange II by boiling dilute hydrochloric acid.

Decomposition of azo dyes by alkali:

Rowe and Ueno (23) showed that when cotton dyed with insoluble azo colours is subjected to the Kier-boiling test recommended in 1928 by the German Fastness Commission, in addition to undergoing the physical changes of aggregation and migration, the colouring matter is liable to be attacked chemically. Thus, in the case of a 3.46% dyeing of Para Red, for example, rather more than one-quarter of the nitro azo colouring matter was destroyed and about one-tenth of it was proved/

proved to be converted into 4-aminobenzeneazo-β-naphthol by the reducing action of cellulose in presence of caustic soda.

Decomposition of azo dyes by heat, light, oxidising agents, etc.

Desai and Venkataraman (24) found that when artificial ghee (a mixture of hydrogenated vegetable oils) coloured with benzeneazo-β-naphthol was heated, aniline was obtained.

Charrier and Crippa (24a) oxidised *o*-aminoazo compounds to N-arylphenols and naphthotriazoles with hydrogen peroxide.

Karczag (25) studied the decolourising effect of two drops of hydrogen peroxide on 2 c.c. lots of 0.005% solutions of some 34 organic pigments of known chemical composition in the presence of one drop of ferrous sulphate, ferric sulphate, copper sulphate, ferrous ammonium sulphate, nickel sulphate, manganous sulphate, cobalt nitrate, ferric chloride, platinum chloride or "ferroammonium sulphate." The general summary of the results indicates that the iron compounds oxidise all the dyes in the cold without exception, and with no regard to their chemical constitution or reaction. The structural influence of the dye is a factor in the time taken for decolourisation. Linton, Holder and Bigelow (26) oxidised *p*-nitro-*p*'-hydroxyazobenzene, *p*-hydroxyazobenzene and *p*-aminoazobenzene with 30% hydrogen peroxide and found that in the case of the first two compounds, prolonged treatment (25 hours) disrupts both benzene rings and results in their complete oxidation to carbon dioxide, water/

water and nitrogen or oxides of nitrogen. Oxidation of the third compound was not complete after six days.

Seyewetz and Chaix (27) studied the decolourising (oxidising) action of sodium hypochlorite on 2% aqueous solutions or suspensions of a number of representative azo dyes in the presence of hydrochloric acid at 0-5°C. They came to the following conclusions:-

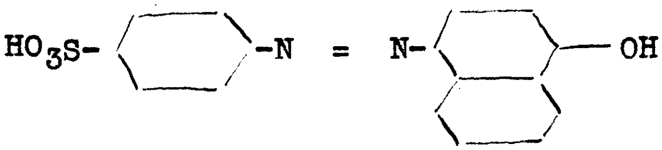
(1) Azo compounds which do not contain the auxochromic groups, like azobenzene and azotoluene, resist the oxidising action of sodium hypochlorite in acid media in the cold.

(2) All other azo compounds which they examined were decomposed at the azo group nearest to the auxochrome group, affording the original diazonium compound together with an oxidation or chlorination product of the amine or phenol residue.

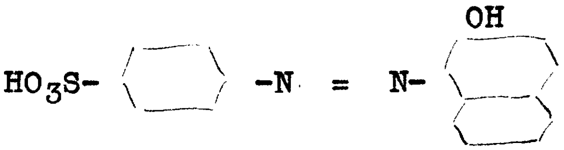
(3) In the case of amino azo compounds, if the amine coupled is primary, like amino azobenzene, it forms the quinone and chloranil, but if the amine is tertiary, as in Orange III, $NaO_3S-C_6H_4-N = N-C_6H_4-N(CH_3)_2$, there is on the other hand, liberation of aliphatic alkylated amine. The reaction is less simple with the diphenylamine in the case of Orange IV, $NaO_3S-C_6H_4-N = N-C_6H_4NH\ C_6H_5$; the amine gives complex products of oxidation without the formation of quinones but with production of a small quantity of diphenyl. In the case of a m-diamine as/

as in Chrysoidine, $C_6H_5-N = N-C_6H_3-(NH_2)_2$, one gets an aminoquinone or a triazoic derivative.

(4) With the oxyazo compounds, a mono-phenolic residue gives rise to chloranil as in Tropeoline Y, $HO_3S-C_6H_4N = N-C_6H_4-OH$. It probably forms a chlorohydroxy quinone in the case of a dihydricphenol as in Chrysoine, $HO_3S-C_6H_4-N = N-C_6H_3-(OH)_2$. If the oxidation is carried out with a residue of α-naphthol as in Orange I,

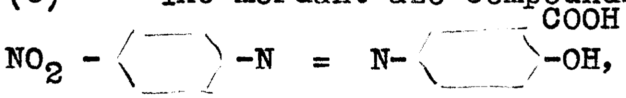


α-naphthaquinone is obtained and with a residue of β-naphthol as in Orange II,



dihydroxy-β-naphthaquinone is obtained. When the phenol residue contains one or more sulphonic groups, it forms mono or polysulphonic quinones.

(5) The mordant azo compounds such as Anthracene Yellow RN,

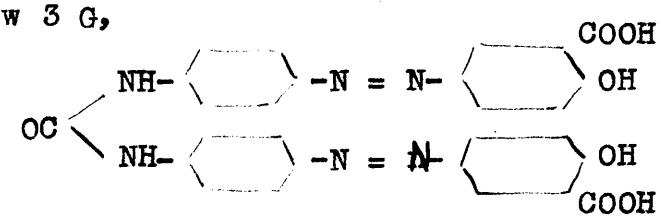


which contain a nitro group in the molecule of the diazotised amine and a carboxyl group in the coupled phenol, give the general reaction. The diazonium compound of p-nitroaniline is obtained along with carboxylic trichloroquinone.

(6) The polyazo derivatives of diazotised aminoazo compounds regenerate/

regenerate the diazo compounds used in their preparation and the residue of amines or phenols which are coupled to them give rise to the oxidation products analogous to those obtained from monoazo compounds.

(7) The tertiary polyazo compounds such as Diamine Fast Yellow 3 G,



give the general reaction of azo compounds, but at the same time carbon dioxide is evolved and the two nitrogen atoms of urea unite.

(8) The polyazo compounds from diamines behave like monoazo compounds. There is regeneration of the tetrazo derivative of the original diamine and the formation of oxidation products analogous to those already pointed out in the case of monoazo compounds.

(9) The pyrazolone dyes split into diazo compound and pyrazolone, the latter resisting the oxidation.

All the hitherto described methods made use of such reagents which not only oxidised the dye but also formed substitution products. They cannot, therefore, be strictly compared with the reaction mechanism in the photochemical oxidation, where oxygen is the active oxidising agent and the question of a side oxidation followed by nitration or chlorination of the decomposition products does not arise.

Petriew/

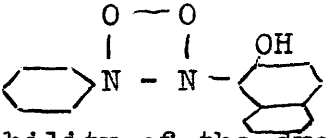
Petriew (28) oxidised azobenzene at 150-200°C. with chromic oxide in a bomb and obtained azoxybenzene. Angeli (29) got the same substance by allowing 30% hydrogen peroxide to react with azobenzene in glacial acetic acid at room temperature for a long time. Lauth (30) observed a further change in the initial products by treatment of azo dyes with lead peroxide and sulphuric acid. He got a diazonium salt and quinone. Fichter (31) followed the electrochemical oxidation of azobenzene following on the work of Heilpern (32). An apparently large number of oxidation decomposition products were identified, e.g. p-p'-dihydroxyazobenzene, diphenyl disazophenol, phenol and acetic acid. The formation of azoxybenzene was taken to be the first stage of oxidation although this substance could not be identified in the reaction mixture. Both the first named decomposition products appeared to be stable to the influence of anodic oxygen by their capacity to form quinoneazine and this lower activity was believed to be due to the high molecular weights.

Haller and Ziersch (33) carried out work on the photochemical oxidation of simple monoazo dyes. On refluxing benzeneazo-β-naphthol with glacial acetic acid and hydrogen peroxide for two hours in a water bath, they obtained phthalic acid, phthalonic acid and a phenolic high molecular compound. In/

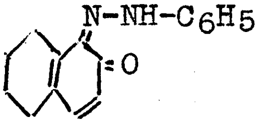
In the next experiment, they used ozone as the oxidising medium. Ozonised oxygen (12%) was bubbled through a solution of the dye in glacial acetic acid to which some water was added. Bleaching was complete in eight hours. Substances like those in the last experiment were obtained.

Haller and Ziersch then studied the decomposition products of dyeings when exposed to photochemical oxidation and came to the conclusion that the process was comparable to chemical oxidation. Eight azo-β-naphthol combinations dyed on cotton were exposed to a Fadeometer. After exposure, the dyeing was covered with water, three drops of acetic acid added, followed by 1 c.c. of 1% potassium iodide solution and finally a freshly prepared cold solution of starch. Liberation of iodine after one hour indicated the formation of a dyestuff peroxide. The exposed undyed cotton did not give this reaction. The formation of the peroxide was confirmed by the test recommended by Haller (34). On treating with a mixture of equal parts of freshly prepared N/10 solution of ferric chloride and N/10 solution of potassium ferricyanide for about five minutes, the formation of Prussian Blue occurs on the exposed pattern owing to the reduction of ferricyanide to ferrocyanide. This singular reaction was observed by Kassner (35) in the action of hydrogen peroxide on alkaline potassium ferricyanide solution. The separation/

separation of Prussian Blue occurred with all the eight dyes examined, and the iodine reaction was generally positive excepting in three cases where it was doubtful. If the peroxide test was not carried out immediately after the exposure, the test became more and more indistinct as time elapsed. The Prussian Blue test is not very confirmative since phenol and naphthaquinone are also known to react with such iron salts. On the other hand, the observed separation of iodine shows that either hydrogen peroxide or dye peroxides have formed on exposure to light. Since such peroxides of azo dyes have not been synthesized, one has still to assume their constitution. Perhaps the following constitution for benzeneazo-β-naphthol peroxide may be assumed:

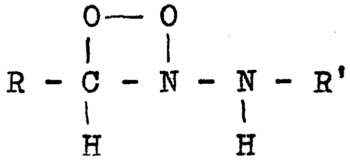


The insolubility of the dye in alkali is expected, as the quinone structure is probably predominant. Liebermann (36) writes the compound as

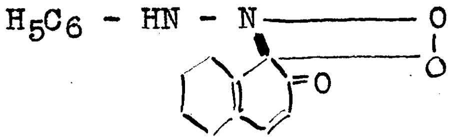


It can also be considered as the naphthaquinone-phenylhydrazone. The structure of the peroxide formed in the oxidation is given as being similar to that given by Busch and Dietz (37) for/

for the peroxides formed on auto-oxidation of phenylhydrazones in hydrocarbon solvents. These workers give the peroxides the following structure:-



They liberate iodine from hydroidic acid. The naphthaquinone phenylhydrazone peroxide can be formulated analogously:



On further oxidation fission occurs, probably between the naphthalene ring and the azo group, because β-naphthaquinone is detected by various tests. Owing to the extremely small quantity of β-naphthaquinone, identification through melting point was not feasible. The formation of β-naphthaquinone by the auto-oxidation of the azo dyes by light is comparable to the chemical oxidation of 1-amino-2-naphthol with dichromate or ferric chloride to β-naphthaquinone. Extraction of the pattern with alcohol in a Soxhlet apparatus gave unaltered dye and phthalic and phthalonic acids, these latter being formed by further oxidation of the β-naphthaquinone. The extracted patterns were dirty yellow and contained phenolic decomposition products difficult to identify. They dissolved in alkali with a reddish-brown colour, and the solution coupled with diazotised

p/

p-nitroaniline. All the results were confirmed by the examination of the exposed dyeings under the microscope.

A comparison of the speed of the reaction with dissolved dye and dyed material indicates that the cellulose exerts a catalytic influence on the degradation of the dyestuff. They also worked out the loss of strength which the individual dyeing undergoes after exposure on both sides of the sample. The exposure was always for 100 bleach hours. It was found thus that azo dyes show no accelerating action on tendering of cotton by light.

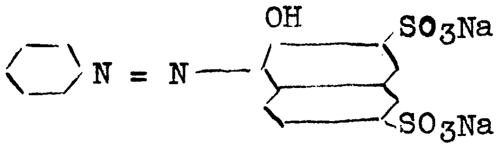
This work confirms that of Ashton, Clibbens and Probert (loc. cit.) who found that azo dyes do not tender cellulose on irradiation, except when they contain a nucleus, e.g. a thiazole ring, which is known to accelerate tendering independently. Even then, the activity of such a nucleus is reduced by the presence of the azo group.

Scharwin and Pakschwer (38) studied the oxidation of organic dyes and cellulose under the influence of light. Different organic dyes on cotton or paper were sealed in glass tubes with the gases, oxygen, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, hydrogen or nitrogen, and exposed to sunlight or to light from a quartz mercury lamp. The speed of bleaching decreased in the order of the gases named/

named. Carbon dioxide was detected with barium hydroxide.

To correlate the structure of monoazo dyes with their fastness to light, Kienle, Stearns and Van der Meulen (39) carried out the following experiments.

Twenty-five highly purified monoazo dyes were used. These dyes were obtained by introducing various groups, like hydroxyl, methoxy, phenyl, methyl, chlorine, carboxyl, sulphonic and nitro groups in the <u>ortho</u>-, <u>meta</u>- and <u>para</u>-positions in the benzene ring of the parent dye,



These were faded in aqueous solutions, as wool dyeings and as gelatin film dyeings, using a Fadeometer. Relative dye concentrations were determined spectrophotometrically. Fading in the solutions was random, i.e. of poor reproducibility, very slow at first, then very rapid, suggesting an induction period followed by a different reaction mechanism, rendering reaction rate calculations impossible. Fading on wool or gelatin was quite reproducible with the order of reaction between one and two. Rates were calculated on the approximate assumption of first order kinetics. The position <u>ortho</u>- to the azo group is most sensitive to the effect of substituents. The smallest rate (maximum fastness to light) occurs with <u>o</u>-carboxyl and high rates/

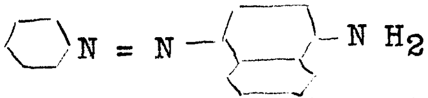
rates with *o*-chloro- and *o*-nitro groups. The rates of the *meta*- and *para*- compounds analysed by Hammett's method, follow the usual linear relation with substituent constants, with Hammett's reaction constant 0.18 for wool dyeings and 0.22 for gelatin dyeings. Such low values indicate that the substituent is a less important factor in fading than it is in the ionisation of the correspondingly substituted benzoic acid.

No attempt is made to suggest a mechanism of the fading reaction, however, apart from the statements that it involves destruction of the azo link and that: "It is to be expected that this benzene side-chain reaction will be influenced by substituent groups in the same way as many other reactions ..."

Blaisdell (40) has made qualitative observations on the photochemistry of azobenzene and 4-amino-4'-nitroazobenzene solutions in *iso*propyl alcohol and *iso*-octane in the presence of various amounts of oxygen. The fading reaction, according to this author, consists in the addition of hydrogen, extracted from the solvent, to the azo linkage to form, first, a substituted hydrazine and later substituted anilines. In the presence of oxygen, there is a photo-sensitised oxidation of the solvent. In *iso*propyl alcohol as solvent, the fading of the dye is completely inhibited by one atmosphere of oxygen, but after exhaustion of the oxygen, the dye fades very rapidly. In the presence/

presence of a large excess of oxygen, the dye eventually fades slowly. The rate of oxygen consumption increases during the exposure and continues to increase after complete destruction of the dye. In this case, the oxidation products contain aliphatic acids and carbon dioxide in addition to acetone. The number of carbonyl groups produced is in excess of equivalence to the molecular oxygen consumed.

Using a carbon arc cinema projector as a light source, Atherton and Seltzer (41) studied the fastness of a series of simple monoazo dyes in cellulose acetate film. The dyes were derived from the parent dye:



and their light fastness was characterised in terms of their destruction efficiency constants. In defining this quantity, account was taken of the specific absorbing powers of the dyes for the heterchromatic light used to fade them. The following general conclusions emerged:-

(1) The destruction efficiency values obtained for the series of <u>meta</u>- and <u>para</u>- substituted dyes studied lie in the reverse order to the dissociation constant of the corresponding substituted benzoic acids.

(2) Assuming the formation of an azoxy derivative as the initial step in the fading reaction, the above order is to be expected from consideration of the electrophilic nature of the/

the substituent.

(3) A comparison between the results obtained and other work in this field shows that studies of the initial fading rates exhibit less variation from a rational relation to Hammett's "σ" value, than results obtained from long period fading.

The action of light on azo dyes was studied by Seyewetz and Mounier (42) leading to the following conclusions:-

(a) Decolourisation of azo dyes by ultra violet light is apparently due to an oxidation, as it is increased in the presence of oxidising agents and decreased in the presence of reducing agents.

(b) The oxidation products obtained by the action of hydrogen peroxide give various colour reactions comparable to those given by the decomposition products of the dyes under the action of ultra violet light.

(c) The decomposition products of azo dyes under the action of ultra violet light act as stabilizers towards the same dyes.

(d) The decomposition products obtained by the action of ultra violet light are apparently the same as those obtained by the action of oxidising agents on the same dyes.

<u>Oxidation of dyes in general</u>:

Lasarev (43) studied the influence of pressure on the bleaching/

bleaching of cyanine, pinachrome and lepidicyanine in collodion membranes. With constant energy absorption, the rate of bleaching varied linearly with the pressure (concentration of oxygen). As the curves when extended did not pass through the origin, he inferred that the bleaching process should have a measurable velocity in vacuo, an inference which was confirmed by experiment. In these experiments, the pressure of oxygen did not exceed one atmosphere. With a view to testing the applicability of his theory to higher pressures, Lasarev (44) repeated his experiments with cyanine, using however a receptacle in which the pressure could be raised to over 100 atmospheres. The results showed that at high pressures, the rate of photochemical decomposition of the dye does not increase in direct proportion to the concentration of oxygen, but tends to a certain limit where the decomposition is independent of pressure. To explain this, Lasarev offers the following hypothesis.

In each unit of time, light liberates electrons from a small number only of neutral molecules of the dye, thus forming ions which unite with the oxygen to form the bleached substance. To effect this union, the ions must come into collision with the oxygen molecules. At low pressures it may be assumed that the number of ions produced is larger than the number of ions colliding with the oxygen molecules within a given time. With increasing/

increasing pressure, the number of colliding ions gradually increases, until the pressure reaches a certain value when the number of colliding ions equals the total number of ions produced. A further rise in pressure merely causes the oxygen molecules to collide more frequently with the neutral molecules of the dye, but there being no further increase in the number of ions, the reaction becomes stationary and independent of pressure.

The influence of oxygen on the velocity of the photochemical process in dyestuffs was further studied by Lasarev (45) at a pressure of 150 atmospheres. He found that the velocity of bleaching V is given by the equation

$$V = \beta(1 - e^{-K_1 C_1})$$

where β and K_1 are constants and C_1 is the concentration of oxygen. From the data obtained, it is shown that the fundamental law of the bleaching of dyes must have the form:

$$-\frac{dC}{dt} = \alpha_0 (1 - e^{-KC}) - (1 - e^{-K_1 C_1})$$

where C is the concentration of the dye and α_0, K and K_1 are constants. The mechanism of photochemical reactions in dyes, which is represented by this equation, is discussed in the light of the modern theory of the structure of the atom.

Karczag (46) studied the decolourisation of several dyes by hydrogen peroxide alone. The compounds could be separated into/

into a decolourisable and a non-decolourisable class as distinct from the action of hydrogen peroxide in the presence of metallic salts when all the dyes are decolourised. The reaction is considered as an intramolecular change in the colour-producing radical. The dyes which are decolourised belong almost without exception to the triphenylmethane series. However, only those members of this series which have the benzene radical free or combined together through a carbon atom are attacked. A ring union between two benzene rings leads to resistance to decolourisation. Derivatives of fluorescein and eosine, azo, pyrazolone, benzidine and nitro dyes are resistant. The condensation of the benzene ring contributes to resistivity as shown by the relatively higher stability of the anthracene dyes. Among the heterocyclic (tricyclic) compounds, those which contain oxygen or an oxygen and a nitrogen atom in the central ring are decolourisable as are the derivatives of pyronine and oxazine. Those dyes of the same type which have one or two nitrogen atoms or a nitrogen and a sulphur atom are resistant, e.g., the derivatives of quinoline, acridine, phenazine and phenothiazine.

Karczag's observation that azo dyes are resistant to the action of hydrogen peroxide is not in agreement with the present work in which it is found that soluble azo dyes do ~~get~~ become oxidised/

oxidised by neutral peroxide.

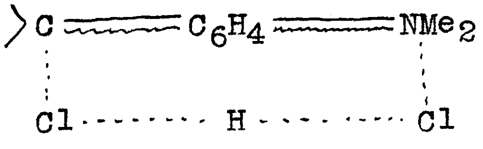
Krause and Polanski (47) studied the oxidation of aqueous solutions of organic dyes with hydrogen peroxide in the presence of rontgenographically amorphous ortho-ferric hydroxide as a catalyst. Certain dyes (e.g., indigo carmine, malachite green and alizarine black) are easily oxidised. It is assumed that hydrogen peroxide and ferric hydroxide combine, forming a ferric peroxide which dehydrogenates the dye. This action is inhibited by adding sufficient sulphuric acid to convert ferric hydroxide into ferric ions which have no catalytic effect on the system. The speed of oxidation is greater in the presence of ferrous ions, but stops as soon as the ferrous ions are oxidised to ferric.

Fading.

Haller and Ziersch (33) studied the decomposition products of dyeings when exposed to photochemical oxidation and came to the conclusion that the process was comparable to chemical oxidation. Since the photolytic oxidation of cellulose is accompanied by evolution of carbon dioxide and since cotton dyed with simple azo dyes yields more carbon dioxide upon radiation than undyed, Haller and Ziersch (33), (48), concluded that fading was an oxidative process. The production of carbon dioxide is greater when the samples are exposed while in an atmosphere rich in oxygen. Oxidation of/

of such dyes with hydrogen peroxide breaks the double bond of the -N = N- group, and the colour reactions of the exposed dye samples indicate a similar splitting on the fibre.

Gebhard (49) regards the influence of light as two-fold, firstly it produces ionisation of labile bonds, and then saturation. The first is very rapid and the second a relatively slow process. He considers a "bridge union," of the colour-producing elements of dyes. The characteristic properties of the chromophore depend on its unsaturated nature, i.e. on its ability to yield ionised valencies for the bridge formation; the greater the ionisation, the deeper is the colour, but when the ionised valence becomes unity, in other words - becomes saturated, the bridge is broken and the compound becomes colourless. The auxochrome, likewise, under the influence of light tends to pass over into the saturated state, but in the case of the chromophore saturation is accompanied with disappearance of colour, while in the effort of the auxochrome to saturate itself, ionised valencies are produced, making possible the appearance of colour. Illumination, therefore, produces bleaching only when the intensity of absorption of the chromophore exceeds that of the auxochrome, and vice versa. The bridge union in which, e.g. Cl exists in malachite green:



$$\begin{array}{ccccc} \rangle C & = & C_6H_4 & = & NMe_2 \\ \vdots & & & & \vdots \\ Cl & \cdots & H & \cdots & Cl \end{array}$$

explains, likewise, why this element cannot be detected with silver/

silver nitrate. As the primary process is not a chemical reaction but merely a change in the valences, the dye recovers its original colour in the dark, but if in the presence of air the peroxide-like oxygen has had time to combine with sufficient firmness with the activated amino group, the process is not reversible in the dark. The influence on the sensitiveness to light of amino, hydroxyl, sulphonic and carboxyl groups in various positions in azo dyes, and the behaviour of nitro compounds is discussed from the point of view given above.

Since tests with hydrogen peroxide do not always give concordant results, it has been denied by Gebhard (50) that oxidation is always involved. The method proposed by Bancroft, Elsenhast and Grant (51) is, therefore, criticised. It is well known that oxidations in light may be wholly different from those in the dark, even when the same oxidising agent is used. New Blue R solution to which sufficient hydrogen peroxide is added, is bleached in the dark. In the light, however, the more strongly coloured New Blue R - peroxide is formed. Greater differences are found when different oxidising agents are employed in the two cases. In the dark, atomic oxygen from the oxidising agent is the most important factor, while in the light, this is not the case. In the absence of hydrogen peroxide, the oxygen split off adds on to the dye to form a peroxide/

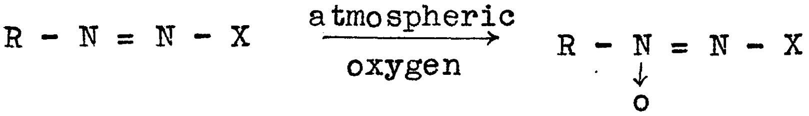
peroxide, while in the presence of hydrogen peroxide, OH^+ and OOH^- are formed. These ions are very reactive and by oxidation can destroy the whole dye. The reactivity of dyes depends upon their unsaturated nature. "Ionised" valencies determine the point of attack (49). In the light, however, the reactivity of a dye does not depend solely upon the "ionised" valence, but in as great, if not greater, degree upon the ability of many groups to pass from a lower to a higher stage of oxidation. These groups may react directly with oxygen, or may so influence the valence distribution in the atom, that the point of attack of oxygen is shifted. In the first case, the reaction in the light will correspond in general to that in the dark, while in the second case, it will be wholly different. Gebhard illustrated this behaviour graphically by the nitrophenols, methylene blue and methylene green. Light of different wavelengths may cause the oxidation to proceed in different ways. Since oxidation in the light is a slow process, and that caused by hydrogen peroxide and persulphates is rapid, steric hindrance may cause groups in the <u>ortho</u>- position to those reacting with oxygen to check the reaction in the light, while in the dark they may not have the same effect.

Perrin (52) regards the fading of dyes as associated with/

with fluorescence in either the visible or the invisible regions of the spectrum.

Studying the photochemistry of azobenzene and 4-amino-4'-nitroazobenzene solutions in *iso*propyl alcohol and *iso*-octane, Blaisdell (*loc.cit.*) as discussed above, concluded that the fading reaction is due to reduction of the dye and consists in the addition of hydrogen extracted from the solvent to the azo linkage to form a substituted hydrazine and later substituted anilines.

According to Atherton and Seltzer (*loc.cit*) a possible initial step in the fading reactions is the formation of an excited state of the dye, followed by atmospheric oxidation, presumably with the formation of the azoxy derivative:



$$R - N = N - X \xrightarrow[\text{oxygen}]{\text{atmospheric}} R - \underset{\substack{\downarrow \\ O}}{N} = N - X$$

In this reaction the nitrogen acts as an electron donor. The availability of the "lone-pair" electrons for this reaction will be influenced by the electrophilic properties of the group R, in the sense that a positive "σ" value for the substituent group in R indicates a lower availability compared with that of the unsubstituted molecule, and a consequent retardation of the reaction. Thus a high positive "σ" value would yield a relatively lower destruction efficiency.

It/

It is suggested by Gray (53) that the fading of fabrics in sunlight is due to the ozonising action of the latter in certain atmospheric conditions. Using the Toussaint-Pinte method with a special illuminator and Colorimeter, Brixi (54) found:

(a) Complementary wavelengths are most destructive upon the dyes.

(b) Infra red and ultra violet rays are very destructive in their action upon dyes.

(c) The effect of light is most destructive when the air is saturated with water vapour.

(d) The action of light upon a mixture of dyes is not equal to the sum of the action of light upon the individual dye components.

Although fading of dyed fabrics is induced in most cases by that portion of the incident light which has a wavelength less than 3000 A.U., Heermann (55) found that there are several instances of dyeings which are more affected by longer wavelengths. According to him, the mercury arc should not be used for dye testing as some of the injurious wavelengths are not present in the mercury spectrum.

According to Gebhard (56), photochemical change in dyeing consists in auto-oxidation, resulting in the formation of/

of a peroxide in which at first the oxygen is present in a labile form. In the presence of water, positive OH^+ and negative perhydroxyl OOH^- ions are involved, and very unstable peroxide hydrates of the dyes are formed.

Harrison (57) suggests that, on oxidation of a dyed fabric, the following possible reactions may take place:

(1) The light may convert oxygen into ozone, and this or the oxygen itself may oxidise the dyestuff.

(2) The fibre may reduce the dyestuff.

(3) Both the above reactions may occur at the same time.

(4) The air or ozone may oxidise the fibre and produce substances more capable of reducing the dyestuff.

(5) The air or ozone may oxidise the dyestuff and produce a substance more easily reduced by the fibre or its oxidation products.

(6) The fibre may reduce the dyestuff or otherwise react with it to produce substances more easily oxidised by the air.

(7) The light may cause one portion of the colour molecule to react with another.

The general conclusion to be drawn from the work reviewed is that fading is in some way connected with oxidation.

Blaisdell obtained reduction products by fading azo compounds, but his conditions were entirely different from those encountered in normal fading - the irradiation was made on solutions in organic solvents.

Fastness to light, its measurement and improvement:

The important variables which influence fastness are: the composition of the dye, the intensity of dyeing, the quantity of radiation, the wavelength of radiation, the quality of the substrate, temperature and humidity.

Since the testing of dyes as regards their fastness to actual sunlight is not only slow but involves several variable factors, many intense artificial light sources are being used to hasten the fading reaction and to get fairly reproducible results. There are some drawbacks in their use, e.g. the use of intense artificial light is only permissible when the amount of change is proportional to the product of the intensity of the light with the time of exposure, and in the immediate neighbourhood of a quartz lamp, there may be enough ozone formed to bleach colours which would otherwise be stable.

Seibert and Sylvester (58) studied the effect of fibre pH on the light fastness of dyed cotton. In the pH range between 3 and 5, the light fastness of cotton coloured with many direct, developed and sulphur dyes was inferior to the light/

light fastness exhibited when the cloth had a pH value of 7 or higher. Cloth coloured with azoic and vat dyes exhibited minor differences under these conditions. In the range between 7 and 9.5, cotton coloured with direct, developed, azoic and sulphur dyes exhibited minor differences in light fastness, but vat-dyed cotton was much inferior in light fastness compared with identical vat-dyed cloth in a neutral or acid condition. Variations in pH between 4 and 10 were not responsible for differences in the chlorine fastness of vat-dyed cotton. The retention of as little as 2.5 oz. of mildly alkaline soap by 100 lb. of vat-dyed cotton was sufficient to materially reduce the light fastness.

Jost and Flutsch (59) proposed the "half value time of fading" as a quantitative expression of the fastness of a dye to light. This time is defined as that required to produce half the maximum displacement in a logarithmic isochromatic triangle. Measurements were made with the Pulfrich step photometer.

Morton (60), suggests that fastness to light should be determined in sunlight after a period of exposure sufficient to produce the smallest commercially significant change in shade. This depth of fade may be taken as equivalent to a 10% decrease in the apparent strength of the light fastness standards. The fastness so determined may vary with the climatic conditions at/

at the fading station, and may differ considerably in an appreciable proportion of cases, from the assessments made in one or the other of the commercially available fading lamps. Vickerstaff and Tough (61) calculated mathematically the difference of colour between faded and unfaded patterns in terms of the number of just perceptible steps, and suggested that the light fastness of a dyeing may be measured in terms of the exposure in lux-hours which is required to produce a change of ten just perceptible steps in the colour of the pattern.

According to Vorozhov (62) the fastness of colour is greatly improved by methylation of hydroxyazo dyes by dimethyl sulphate. Watson, Sircar and Dutta (63) studied the light fastness of a series of derivatives of benzeneazophenol and benzeneazoaniline. Their results show that sulphonic groups have a good effect on the fastness to light or at any rate no bad effect; hydroxyl or amino groups on either side have a bad effect; bromine has scarcely any effect; a nitro group has no ill effect on the phenol or aniline side, but on the benzene side it has a decidedly bad effect. The most marked feature is the injurious effect of the carboxyl group on the benzene side. This is not in agreement with the results obtained by the present author.

Griffith/

Griffith (64) studying the influence of position isomerism in azo dyes on their fastness to light, found that the combined effect of fading and darkening by exposure to Fadeometer light is least with the *o*-sulphanilic acid dyes. The *meta*- substituted groups have decidedly the greatest effect on the fastness to light. In general, the dyes having a hydroxyl group in the 2-position are superior to those in which the hydroxyl group is in the 1-position. The exceptions to this generalisation are a 1-naphthol-4-sulphonic acid dye which is comparatively fast to light, and a 2-naphthol-3;6-disulphonic acid dye which is fugitive. The combined effects of light and washing indicate that the o-sulphanilic acid dyes are the least affected. *p*-Sulphanilic acid dyes are more affected than *o*-sulphanilic acid dyes but less affected than *m*-sulphanilic acid dyes. The presence of two sulphonic acid groups in the naphthol nucleus does not decrease the fastness of the dye.

According to Blumberger (65) hydroxyl, amino and monosubstituted amino groups in general are the weakest points in azo dyes. Fastness is improved when these are protected by acetylation, benzoylation~~s~~ or treatment with phosgene. The hydroxyl group may be protected by neighbouring carboxyl groups (salicylic and cresotinic acid dyes). Adjacent sulphonic groups protect auxochrome and chromophore groups as/

as well. In numerous similar ~~like~~ dyes, sulphonic, carboxyl and nitro groups in the primary component confer a marked protection on an adjacent azo group. A mere extension of the molecular chain increases the fastness in polyazo dyes. Methylation of the hydroxyl group, peculiarly, decreased the fastness to light. In the present work on the other hand, it is found that the O-methyl ether of Orange I is faster **than** Orange I on various substrates, e.g. paper, tile and anodised aluminium, although there is little difference in fastness to light of the two compounds on wool. Substantive dyes show different fastness on cotton and on wool, indicating that the weak places of the dye are just those which produce the union with the substrate.

The experiments of Gebhard (66) confirm the hypothesis that if a dye-peroxide retains the characteristic of a dye, it should be possible to hinder the reaction between dyes and oxygen by introducing into the system, in place of oxygen, such substances as have the power of attaching themselves to the groups to which oxygen is added when the dye is exposed to light. This can be done either by a suitable coupling component or by the formation of addition compounds, particularly with metallic salts or ammonium complexes. Copper salts of most oxyacids are effective, as are zinc chloride, and the sulphates of cerium, iron and aluminium.

The/

The theory of auto-oxidation of dyes put forth by Gebhard (56) suggested to him a number of methods for improving the fastness to light of dyeings, (67). The mechanical exclusion of oxygen by evacuation of glass containers is limited to the preservation of valuable dyeings in museums. Water-proofing increases the fastness of certain cotton dyeings. The addition of substances to inhibit oxidation by a chemical process requires that these substances shall react more readily and quickly with oxygen than the dye itself, that they shall not act as oxygen carriers, that they shall unite with both kinds of oxygen, atomic and molecular, and that the products formed shall have no harmful effect upon the dyeing. These products must automatically release their oxygen in molecular form, much in the same way as catalase protects blood pigment against the action of hydrogen peroxide. Since the peroxide oxygen is at first loosely held, there is a possibility of splitting it off again. Practically, this is best accomplished by frequent soaping, as is examplified in the favourable effect of continually soaping vat dyeings. If the peroxide has been formed and oxygen cannot be split off, fastness can be increased by stabilising the peroxide with hydrogen peroxide stabilisers like urea and thiourea.

Gebhard/

Gebhard (68) described three methods differing in principle by which the fading of dyes can be prevented.

(1) Displacement of the equilibrium $O + O + H^+ + OH^- \leftrightharpoons H.O.OO.H \leftrightharpoons OH^+ + OOH^-$ in disfavour of OOH^-. Equilibrium established in darkness will be altered at once by the influence of light. The equilibrium is influenced by all substances in the system. When it is ascertained what kind of influence takes place under the action of light, the equilibrium can be established by a suitable concentration of the substance, and when this is not possible, new substances may be introduced into the system. With wool and fibres not sensitive to H^+ and OH^+ ions, favourable results can be obtained if to begin with the equilibrium is altered in disfavour of the OOH^- ions. This condition is produced by increasing the H-ion concentration in aqueous solutions of acid dyes. With cotton, however, conditions are different, as it reacts easily with H^+ and OH^+ ions. Only if the reaction between H^+ and OH^+ can be prevented by a suitable treatment will there be a prospect of producing dyes fast to light.

(2) Preventing or rendering difficult the reaction between the dye and the perhydroxyl ions. It is possible that substances exist which would prevent reaction between the dye and perhydroxyl ions, and between fibre and OH^+. The facility of reaction between the dye and OOH^- may be decreased by converting the dye into/

into the least reactive state, i.e. making it difficultly soluble. This is the most common method, as illustrated by after-treatment with copper sulphate. The reaction can also be prevented by directing the perhydroxyl ions into other channels. Small quantities of certain substances, e.g. cerium sulphate or calcium citrate, are sufficient to eliminate continually the detrimental perhydroxyl oxygen atom.

(3) Transformation of the dye peroxides into more stable compounds. If their formation cannot be prevented or, if for other reasons, none of the previous methods can be employed, use can be made of the important fact that the dye peroxides still possess the dye character. Such dyes may be used as from their constitution or on account of their combination with certain substances possess the property of splitting off the elements of water from the labile dye, the "peroxyhydrates," thus changing into more stable dye peroxides. When a dye peroxide possesses dye character, the fibre - under certain circumstances - may serve as a radical which replaces the peroxide oxygen in the dye and makes it more stable.

Schmidt and Gabler (69) studied the influence of sizing materials on the fastness to light of cotton dyeings. While some sizes decreased the light fastness, others improved it. Additions/

Additions of aluminium sulphate, disodium hydrogen phosphate, sodium phosphite and aluminium thiosulphate proved best. "Apparitin" decreased the fastness of all dyeings tried, even with additions of aluminium sulphate and disodium hydrogen phosphate. Alkaline sizes, in general, have a harmful effect. Dextrin is a beneficial ingredient, and must be added if soaps, soluble oils or fats are used.

Action of oxidising agents on diazo compounds:

Bamberger and Baudisch (70) found that alkaline hydrogen peroxide converts sodium benzene diazotate, Ph - N = N - ONa, into sodium diazobenzoate, Ph - N = N-OONa, and sodium nitrosophenylhydroxylamine, O N PH = NONa. On account of its instability and small quantity, the latter substance could not be isolated.

Seyewetz and Mounier (71) found that on exposure of diazo compounds to light, nitrogen is evolved with simultaneous formation of phenols, the decomposition proceeding in the same way as the decomposition by boiling. Schmidt and Maier (72) decomposed some diazo compounds by exposing their solutions to sunlight and measuring the nitrogen evolved. Ostroshinskaja (73) proposed a method which consisted in boiling the diazo solution with alkaline arsenite solution and measuring the nitrogen evolved.

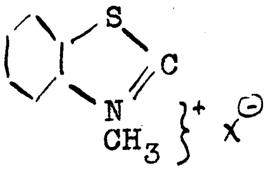
Spencer/

Spencer and Taylor (74) found that the decomposition could be easily effected by means of the light from an ordinary carbon arc lamp. Based on this observation, a semi-micro-apparatus and technique were evolved which formed a very rapid and accurate method of wide general applicability for the determination of diazo compounds.

<u>Oxidation of quinones</u>:

Robinson (75) showed that alkaline permanganate oxidises β-naphthaquinone to phthalonic acid, with no indication of an intermediate diketo acid.

James, Snell and Weissberger, (76) during a study of auto-oxidation of hydroquinone and of the mono-, di- and trimethylhydroquinones, found that hydroquinone, toluhydroquinone, xylohydroquinone and ψ-cumohydroquinone were oxidised in alkaline solution by molecular oxygen with the formation of hydrogen peroxide and the corresponding quinones. This was followed by a reaction between the quinones and hydrogen peroxide. The high rate of the reaction between benzoquinone and hydrogen peroxide made it necessary to use an acceptor, 2-methylbenzothiazolemetho-p-toluene sulphonate,



The condensation product of the quinone with the acceptor can/

can be identified spectroscopically and through it the quinone.

Oxidation of phenylhydrazine:

Miller and Furman (77) found that when phenylhydrazine is oxidised by iodate or by iodine in the presence of hydrogen, a diazonium salt is formed, which hydrolyses slowly with the formation of phenol and evolution of nitrogen. According to Charrier (78) on boiling with nitric acid (sp. gr. 1.48) in ether and chloroform mixture, benzene diazonium nitrate is obtained. Fischer (79) obtained some diazobenzeneimide and benzene diazonium sulphate on covering excess yellow mercuric oxide with aqueous phenylhydrazine sulphate solution. On passing chlorine into a solution of phenylhydrazine in absolute alcohol under cooling with solid carbon dioxide or in acetic acid with addition of ice (about -15°) to saturation, Chattaway (80) obtained benzene diazonium chloride. Oechsner de Coninck (81) observed the formation of a small quantity of phenol by the action of a fairly concentrated aqueous solution of chromic acid or dichromate on phenylhydrazine in the warm. Altschul (82) found that by using 4-6 mols. of sodium nitrite in the presence of excess hydrochloric acid, essentially benzene diazonium chloride is obtained. Oechsner de Coninck (83) obtained phenol on oxidation with arsenic acid.

Chattaway/

Chattaway (84) obtained benzene diazonium perbromide, $C_6H_5N_2Br_3$, by the action of bromine in acetic acid on phenylhydrazine. Bromine added to a mixture of 20 parts phenylhydrazine and 200 parts hydrochloric acid (sp. gr. 1.19) at 0°C. gives 4-bromophenylhydrazine and 4-bromobenzene diazonium salt (Michaelis (85); Vaubel (86)).

The above references show that phenylhydrazine is known to be oxidised to the benzenediazonium salt or subsequently to phenol with various oxidising agents.

Summarising this survey, we may say that the following points appear reasonably well established:

(1) Azo dyes undergo oxidation when faded in light, in presence of air and moisture. Not only have oxidation products been isolated, but it has been shown that fading is considerably retarded, or even stopped, by absence of oxygen.

(2) The initial step in fading is unknown, but the final products include phenols, quinones, phthalic acid etc.

Conflicting results and views are evident when we consider either the suggested mechanisms of fading or the influence of substituents upon light-fastness of dyes, and no very reliable conclusions can be drawn from the literature on these points. The reason is, of course, the complexity of the reactions, the number of variables involved, the lack of rigidly determined methods of measuring fastness, and so on.

It appears, however, that other workers, like the present author/

author, have observed the beneficial effect upon light fastness of alkylation of the hydroxy group in hydroxyazo dyes, and have also noticed the similar beneficial effect of acetylation and benzoylation.

Oxidation of azo dyes in solution has been found by previous workers as well as the present author to give products similar to those obtained in fading.

(ii) Current Views on Oxidation.

In 1858, Kekulé put forward his theory of valency. This was based on the observed compositions of chemical compounds, but without taking into account the structures of the atoms, with the result that in certain fields many difficulties were encountered which could not properly be explained. The electronic theory of valency is based on three fundamental principles stated in 1916 by Kessell and by Lewis. The theory was put forward in a systematic form by Langmuir in 1919 and had been generally accepted by 1927, when Sidgwick published his classical book "The Electronic Theory of Valency."

In terms of the electronic theory, oxidation involves a loss of electrons and reduction a gaining of them. Thus, for example, when ferrous iron is oxidised to ferric, it loses electrons.

$$Fe^{+++} + e \underset{Ox.}{\overset{Red}{\rightleftarrows}} Fe^{++}$$

A major step in the elucidation of the mechanism of various chemical reactions became possible with the discovery of free radicals. These are complexes of abnormal valency which possess additive/

additive properties, but do not carry an electric charge and are not free ions. Unpaired or odd electrons are present in active free atoms, such as Na or I, and can be detected magnetically. Free organic radicals also contain an odd number of electrons, and they too are peramagnetic. The great chemical reactivity of free radicals is assumed to be associated with the available combining energy of the odd electron, and their reactions, whenever possible, result in the completion of electron pairs.

Free radicals can be obtained by a number of methods, including:

(1) Thermal decomposition of organic compounds, e.g.

$$CH_3 - N = N - CH_3 \xrightarrow{400^\circ C.} N_2 + 2\ CH_3$$

(2) Photochemical decomposition, e.g.

$$\underset{\text{(vapour)}}{CH_3 - CO - CH_3} \xrightarrow[\text{light}]{\text{UV}} CH_3 - CH_3 + CO$$

(through an initial decomposition into methyl radicals).

(3) Irradiation of solutions with X-rays or α-particles.

In the main, in this case, the changes are due to an initial decomposition of the solvent, and can be explained by the supposition that the radiation causes electrons to be ejected singly from solvent molecules. Thus: $H_2O + \text{Energy} \rightarrow (H_2O)^+ + e.$ Thereafter, the resulting ionised molecule dissociates to give a neutral radical and a stable positive ion $(H_2O)^+ \rightarrow H^+ + (.OH)$, whilst the ejected electron, when slowed down sufficiently by multiple collisions, reacts with another solvent molecule to give a neutral radical and a negative ion, $e + H_2O \rightarrow H. + (:OH)^-$. The

free /

free radicals H. and .OH from water do not all recombine in pairs. Some persist for sufficiently long to react, in characteristic fashion, with solute molecules, causing oxidation or reduction.

When once a free radical is formed, the surrounding sheath of solvent molecules will tend to prevent its re-combination with a second radical, and will favour the occurrence of a displacement reaction between the radical and a solvent molecule. Radicals can thus be expected to dehydrogenate hydrocarbons, alcohols, ketones and similar molecules, and to remove halogen atoms from substances such as carbon tetrachloride.

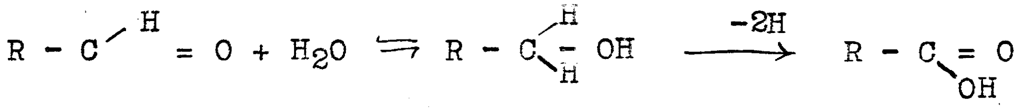
It is obvious that chain reactions initiated by free radicals in solution can very soon become reactions essentially characteristic of the solvent, rather than of particular dissolved substances in low concentrations, e.g. free halogen atoms in water will promptly yield .OH, and will therefore act as hydroxylating rather than as halogenating agents.

Polanyi (110) puts forward an electron-switch theory to explain the mechanism of chemical reactions. Since in a chemical reaction some bonds are always broken and new bonds formed, there results a rearrangement of atoms to new partnerships. According to this theory, a reaction such as A X + B = A + X B involves moving X from its close association with A and linking it to B instead. The AX bond is strained to such a point that the switch-over to the XB bond takes place without any further supply of energy. The configuration of the particles at which the electron-switch occurs is called the transition state of the reaction.

The /

The work done in attaining the transition stage is taken to represent the activation energy. Such a scheme seems to suggest some connection between binding strength and chemical reactivity. Thus, for example, in an oxidation reaction, R-H + .Ox = R. + H Ox, where R is an alkyl group, the ease of oxidation of the R-H bond is an inverse function of the work required to strain it. The bond energy is determined by observing the rate of pyrolysis under conditions in which the rate-determining step is the rupture of the bond under examination.

According to the dehydrogenation theory of oxidation put forward by Wieland (111) the majority of oxidation reactions are either dehydrogenation, e.g. $R - CH_2 - OH \xrightarrow{-2H} R - CHO$, or may be represented as dehydrogenation following the addition of water, which is often an essential component of the reaction mixture, e.g.



$$R - \overset{H}{C} = O + H_2O \rightleftharpoons R - \underset{H}{\overset{H}{C}} - OH \xrightarrow{-2H} R - \underset{OH}{C} = O$$

According to Waters (112), much experimental evidence can be brought forward to show that the removal of hydrogen in the atomic (i.e. uncharged) state and the addition of hydroxyl as a neutral .OH radical constitute the initial steps in many oxidation processes, and thereby substantiate the general hypothesis that oxidation is a process of non-ionic or "homolytic" type. Free radical reactions with dibenzoyl peroxide, diacetyl peroxide, and lead tetra-acetate as oxidising agents, support the dehydrogenation theory so strongly that other oxidising agents which are capable of attacking hydrocarbons, aldehydes or alcohols may very probably act in a similar manner. One piece of evidence in favour of this view is the fact that many oxidations/

oxidations are chain reactions, and therefore are most likely to be reactions of neutral radicals.

The hydrogen peroxide theory of electrolytic oxidation developed by Glasstone and Hickling (113) suggests that the hydroxyl radicals produced at the anode combine to form hydrogen peroxide. In the absence of a depolariser capable of being oxidised, the peroxide decomposes into oxygen and water; but in its presence it brings about oxidation in its own characteristic manner, which may also be accompanied by oxidation due to nascent oxygen from the decomposition of hydrogen peroxide. The peroxide formed at the anode may act in at least five ways as follows:

(1) Oxidation by accepting electrons from depolariser and conversion into OH^- ions, e.g.

$$H_2O_2 + 2\ S_2O_3{++} = S_4O_6^{--} + 2\ OH^-$$

(2) Apparent reduction of highly oxidised compounds such as MnO_4^-. $2\ MnO_4^- + 5\ H_2O_2 + 6H^+ = 6\ Mn^{++} + 8H_2O + 5O_2$

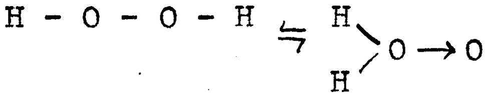
(3) Reaction of the peroxide with non-ionized organic compounds may result in the introduction of hydroxyl groups into their molecules, e.g. conversion of benzene into phenol.

(4) Hydrogen peroxide or the active oxygen arising from its decomposition may bring about oxidation of a general nature.

(5) If no suitable depolariser is present, oxygen is evolved.

The two different modes of behaviour of hydrogen peroxide may be accounted for in a largely speculative way if its tautomeric forms are considered. Thus, Raikov (114) suggested that hydrogen peroxide/

peroxide is a tautomeric system comprising a dihydroxyl and a peroxide form,



$$H-O-O-H \rightleftharpoons \begin{matrix}H\\H\end{matrix}\!\!>O \rightarrow O$$

and Grieb and Harteck (115) claimed to have isolated the latter by the action of atomic hydrogen on oxygen at low temperatures. If Raikov's view is correct, it is possible that the unique reactions of hydrogen peroxide are due to the hydroxyl form, and general oxidation, indistinguishable from that of active oxygen, to the peroxide form. Thus for example:

$$2\ SO_3^{--} + (OH)_2 \longrightarrow S_2O_6^{--} + 2\ OH^-$$

and

$$SO_3^{--} + O.OH_2 \longrightarrow SO_4^{--} + H_2O$$

Haisinsky (116) disagrees with the dehydrogenation theory of Glasstone and Hickling on the ground that although hydrogen peroxide has been detected at the cathode, attempts to detect it at the anode have so far been unsuccessful. His experiments also show that hydrogen peroxide has a retarding effect on the anodic formation of per- compounds with O - O bonds or of higher oxides, from which he concluded that it was improbable that hydrogen peroxide appeared at the anode.

According to Weiss (117), molecules with conjugated double bounds possess loosely-bound π-electrons and can often easily ungergo oxidation and reduction by single electron-transfer processes, yielding positive or negative ions.

The/

The "equi-valence change principle" of Shaffer (118) states that an oxidation-reduction reaction occurs if, on collision of the active molecules of the reducing and the oxidising substances, a decrease of free energy results and provided the number of electrons the reducing agent may lose (or share) is the same as the number the oxidising agent may accept (or share).

Kirk and Browne (119) group oxidising agents into two classes: (1) Monodelectronators, and (2) Didelectronators - a term first suggested by Phelan of Cornell University).

The former include those oxidising agents that are able to accept one electron only per active unit (atom, ion or molecule), for example, such substances as ferric, manganic, ceric or cupric ions. The latter comprises those oxidising agents that are able to accept more than one electron per active unit, for example, peroxide, chlorate and persulphate ions. Tri-dilectronators and poly-delectronators are also included in this class. Oxidation is regarded by Kirk and Browne as essentially a process of delectronation, and reduction that of electronation.

On the basis of the above classification, Remick (120) explains why some oxidation-reduction reactions are fast and others slow by the posulation of "potential humps." Thus, the rapid oxidation of stannous salts by the mono-delectronators, ceric/

ceric salts, may take place in one-electron steps with the intermediate trivalent tin corresponding to a potential jump, thus reacting rapidly with stannous salts because they can easily surmount this hump, whereas weak monodelectronators can surmount it only slowly, because the Maxwell-Boltzmann distribution of energy would endow only a relatively few ions at any given moment with a sufficiently high potential. A didelectronator would not have to surmount the hump. Weiss's suggestion (121) that it is the electrostatic repulsion which determines whether a given ionic oxidation-reduction reaction will be fast or slow is not considered by Remick to be in accordance with the experimental facts.

(iii) Photochemical reactions.

Photochemical reactions are those which occur when substances are exposed to light. Reactions such as hydrolysis, oxidation, reduction, polymerisation and isomerisation can be initiated or accelerated by exposure to suitable light. There are two broad types of photochemical reactions:-

(a) Those which resemble ordinary thermal or "dark" reactions reaching the ordinary equilibrium and suffering a decrease in free energy of the reacting system, e.g. decomposition of H Br.

(b) Those which involve an increase in free energy. They reach a "stationary state" which becomes unstable as soon as the/

the light is removed, e.g. ozonisation of oxygen, decomposition of ammonia, polymerisation of anthracene, photosynthesis of carbohydrates in plants.

There are two important laws of photochemical reactions, viz. the Grotthus and Draper's law, and the Stark-Einstein law of photochemical reactions. The former states that photochemical change is brought about only by radiations which are absorbed by the reacting system, whereas the latter states that for each molecule taking part in a reaction, one quantum of the activating radiation is absorbed. All light that is absorbed is not necessarily effective in bringing about the chemical change. Some of it may be converted into heat and some re-emitted as light of the same or another frequency, thus bringing about fluorescence. Short wavelengths may cause electronic transition, and if extra energy is not removed by collision, as it may be if the substance is in solution or in the solid state, then after a lapse of about 10^{-7} or 10^{-8} second the electron returns to a lower level and emits radiation. According to Stoke's law, which is nearly always obeyed, the light emitted is of longer wavelength than the light absorbed. Thus, the electron must fall to an intermediate level and not to the original one. In fluorescence, the effect persists only as long as the light is there, but when the effect persists for some time after the existing radiation is cut off, the effect is/

is termed phosphorescence. This is most frequently observed in the solid state where some delay in transition from excited to lower energy levels might be anticipated.

Photochemical reactions may alternatively be classified into three types, viz. those (a) where the quantum efficiency is a small integer, (b) where it is very large, and (c) where it is very small. Quantum efficiency, η, is defined as the number of molecules decomposed by each quantum of light absorbed, and for all practical purposes may be expressed in the form:

$$\eta = \frac{\text{Molecules decomposed per sec.}}{\text{Quanta absorbed per sec.}} = \frac{\text{Rate of chemical reaction}}{\text{Quanta absorbed per sec.}}$$

In the case of reactions in the gas phase involving an increase or decrease of volume, the rate may be obtained by measuring changes in pressure with a suitable gauge. Sometimes even when there is no volume change, it may be possible to determine the rate after condensing one or more of the components; for example, in the hydrogen-chlorine reaction, the chlorine and hydrogen chloride can be condensed by liquid air or other refrigerant, and the change in pressure of the residual hydrogen determined. Various other physical methods have been employed; for example, measurement of electric conductivity, or of the change in the absorption of light due to the formation, or removal, of a coloured substance. In other cases it has been necessary/

necessary to resort to chemical analysis.

Knowing the frequency and the intensity of the absorbed radiation, the number of quanta absorbed per second can be calculated from the equation:

$$\text{Number of quanta absorbed per second} = \frac{\text{Intensity of absorbed radiation}}{h\ V}$$

where h is the Planck constant and V the frequency of the absorbing radiation.

The amount of radiation absorbed is determined by measuring the intensity before and after passing through the reacting system. This may be done by having two cells side by side, one empty, the other the reacting system. The actual intensity of the radiation may be determined most accurately by a thermo-pile or a bolometer, both of which are based upon the fact that the absorbed radiation is converted into heat. Photoelectric cells are sometimes used, but these have the disadvantage of different sensitivites for different wave lengths. Actinometers are sometimes used for measuring the intensity of radiation. These depend upon chemical reaction taking place in the presence of light and in these instruments, it is assumed that the total extent of the chemical reaction varies with the wave length of the absorbed radiation.

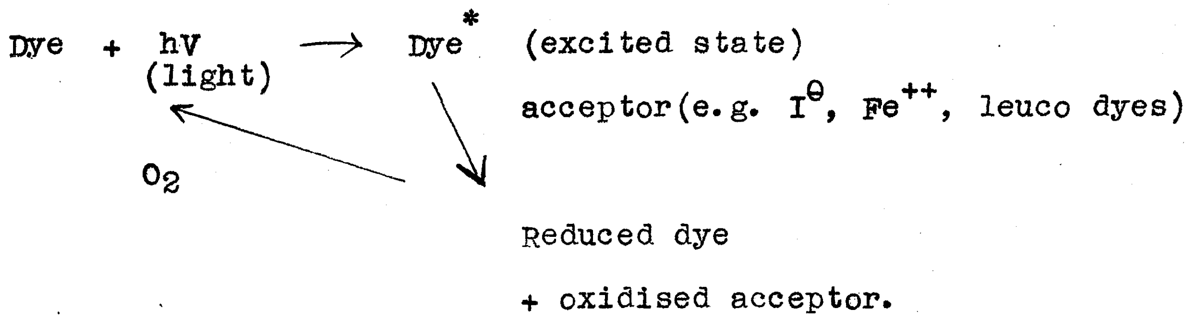
70%/

70% of reactions are of the first type. Very high quantum efficiency is due to chain reactions, whereas very low efficiency may be accounted for by re-combination of the products of the first stage of decomposition, and also by de-activation of the light-absorbing molecule by collision before it has time to react. This interpretation is supported by the fact that very low efficiencies are more common in solution, where the number of collisions is much greater than in the gas phase.

Photochemical reactions are affected to a much smaller extent than thermal reactions by temperature changes.

There are also certain types of photochemical reaction which occur only when they are sensitised by suitable catalysts. The reactions between sulphur dioxide and oxygen: and hydrogen and oxygen; and the decomposition of phosgene and of ozone, occur in light only in presence of chlorine gas. The decomposition of oxalic acid by ultra- violet light is sensitised by uranyl salts. Certain dyes also act as sensitisers causing, indirectly, photochemical degradation of the substrate, such as cellulose. No appreciable oxidation of iodide ions by oxygen in aqueous solution takes place at room temperature until eosin is added, when the process becomes rapid. The mechanism may/

may be explained by the scheme given below:



In the absence of oxygen, the reduced dye and the oxidised acceptor can sometimes be isolated.

According to Rabinowitch (122), one type of photo-oxidation in aqueous solution involves oxidising cations, in which the primary process is an electron transfer from the water to the cation. Thus, for example:

$$Ce^{4+} + \frac{1}{2} H_2O \rightarrow Ce^{3+} + H^+ + \frac{1}{4} O_2$$

Farkas and Farkas (123) suggested that the individual steps in this reaction are:-

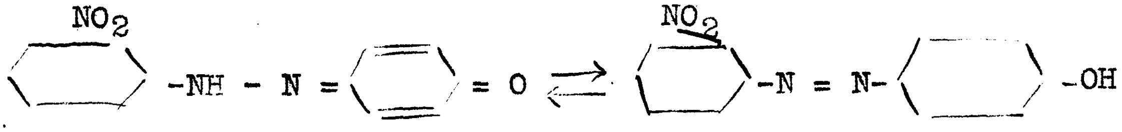
(i) $Ce^{4+} \quad H_2O \quad \xrightleftharpoons{h\nu} \quad Ce^{3+} \quad H_2O^+$

(ii) $H_2O^+ + OH^- \longrightarrow H_2O + OH \rightarrow O_2$

(IV)/

(IV) TAUTOMERISM OF AZO COMPOUNDS.

The tautomerism of hydrazo dyes has been studied by several workers. (Baker, (87)). Thus Borsche condensed *o*-nitrophenylhydrazine with *p*-benzoquinone and obtained the identical compound formed by coupling an *o*-nitrobenzene-diazonium salt with phenol. There must clearly be a tautomeric change between a hydrazone and an azo form



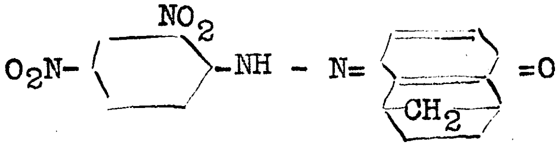
This is confirmed by the fact that when the *p*-quinone-monoxime is used the tautomerisation is prevented, and the product is a hydrazine derivative.

Smith and Mitchell (88) by observing the number of mercuriacetate groups taken up by various *o*- and *p*-hydroxyazo compounds, decided that all these substances exist in the hydroxyazo form.

On the other hand, experimental evidence suggests that the products obtained by coupling aromatic diazonium compounds with aliphatic ketones have the hydrazone configuration. It is stated by Baker that the general rule may be propounded that a hydroazo compound will exist in the azo or hydrazone form according as its oxygenated precursor is an enol or a ketone respectively.

More recently, however, Lauer and Miller (89) have treated/

treated 2:4-dinitro-4-hydroxyazobenzene and its O-methyl, O-acetyl, and O-benzoyl derivatives with cyclopentadiene. They found that the original hydroxy body, but not the other derivatives, formed a condensation product:-



This suggests that the hydroxyazo compound exists in the hydrazone form, whereas as would be expected, its O-methyl, etc. derivatives can exist only as azo forms.

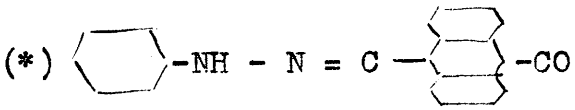
A study of the absorption spectra of the hydroxyazo dyes and their acyl derivatives by Ramart-Lucas, Grumez and Martynoff (90) revealed that the absorption spectra of the acylated derivatives were very similar to those of the azo derivatives in which the acyloxy group was replaced by hydrogen or an alkyl group, but very different from those of the isomeric N-acyl derivatives (the quinone hydrazones). Thus, compounds obtained when o- and p-hydroxyazo compounds were acylated were shown to have the type structure $C_6H_5N = NC_6H_4 - OCOR$ (I) and not $O = C_6H_4 = N - NH - C_6H_5$ (II). It appears that during the course of an acylation, the equilibrium shifts rapidly to the left or that compounds of type (II) isomerize instantaneously to form compounds of type (I). A similar observation was made by Burawoy and Markowitsch (91) and by Kuhn and Bär (92) during their study of/

of the absorption spectra of the acyl o-hydroxyazo compounds. These were shown to have an azo structure in contrast to the quinonoid nature of the parent compounds. According to Puxeddu and Gennari (93) m- and p-hydroxyazo compounds and their acyl derivatives are always azo; o-hydroxyazo compounds are hydrazones, both when free and acylated, but tend to pass to the azo state. From a study of the N-substituted phenylhydrazones and their quinones, Fierz-David, Blangey and Kaul (94) surmised that the o-hydroxyazo compounds probably do not have a quinone hydrazone structure, as the condensation reactions did not give pure quinone-hydrazones. The actual product may represent an intermediate phase between azo and quinonoid structures.

Borsche, Müller and Bodenstein (95) found that p-hydroxyazobenzene derivatives react with primary hydrazines to give p-quinone derivatives, thus giving a chemical proof that they can tautomerise to quinones. They also observed that the ethers of oxyazo compounds do not condense with primary hydrazines in presence of hydrochloric acid to give quinone dihydrazones. Their observation shows that by etherification of an hydroxy group, tautomerism of an azo compound to the hydrazone state could be prevented.

Shingu (96) studied the tautomerism of p-hydroxyazo compounds in the anthracene series as the keto form in this series is more stable than it is in the phenol series. Thus, when/

when benzeneazoanthranol is treated with bromine in acetic acid medium, a quantitative yield of anthraquinone and *p*-bromobenzene diazonium bromide is obtained. Action of dimethyl sulphate or methyl iodide resulted in the formation of N-methyl compound. This and the study of absorption spectra suggested a quinone-hydrazone form for benzeneaxoanthranol, viz.,



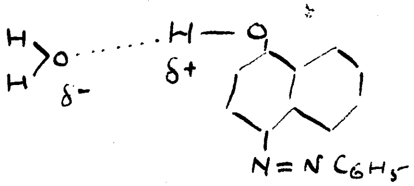
and an azo structure for its acetate or benzoate. The hydrazone structure is retained even when a methoxy group is introduced at the position marked (*) above. In benzeneazo-α-naphthol, the two forms have much the same stability, the proportion being altered by substituents in the benzene ring, or by the nature of the solvent. Thus in ethyl alcohol, *p*-nitro, *o*-carboxylic, *p*-carboxylic, *o*-nitro, *m*-nitro, *m*-chloro, *m*-carboxylic, *o*-methoxy, *m*-methoxy, *p*-chloro, *p*-bromo, *o*-ethoxy and *m*-methyl groups (in decreasing order of magnitude) favour the hydrazone form, and *p*-methoxy, *o*-methoxy, 2:4:6-tribromo, *p*-methyl and *o*-chloro groups (also in decreasing order) favour the azo form, in general accordance with the electron theory of substitution reactions.

Dipole moment measurements made by Bergmann and Weizmann (97) showed that *o*-hydroxyazo compounds are probably quinonoid and that the *p*-hydroxyazo compounds have an azo structure/

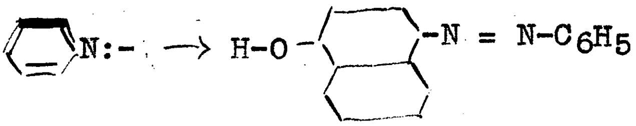
structure, with a tautomeric mixture existing in certain solvents.

Although it is well established that a tautomeric equilibrium can exist, the evidence regarding the nature of the preponderant structure in normal hydroxyazo dyes is conflicting. It is highly probable that the state of the system will depend upon the surrounding medium. Thus, Hodgson and Marsden (98) have discussed the mobility of this tautomeric system. They state that in aqueous solution the azo form is usually regarded as being predominant. In pyridine, benzeneazo-α-naphthol is mainly in the azo form, whereas in nitrobenzene it is mainly a hydrazone and in benzene it is equally divided. They explain these changes as follows:

The azo tautomeride is usually regarded as predominant in aqueous solution, probably due to considerable stabilisation by polarised water molecules

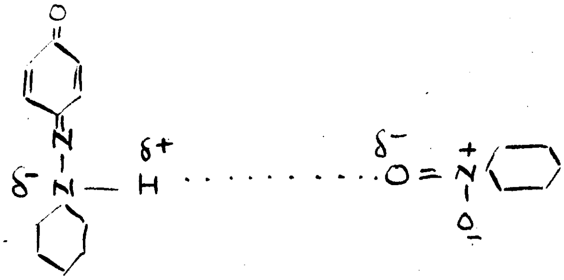


and similarly, will be still more stabilised by anionoid pyridine, which will attach itself to the phenolic hydrogen atom by its lone pair of electrons



and/

and thus by hydrogen bonding preserve the azo structure entirely. On the other hand, the dipolar nitrobenzene will more readily attach itself to the hydrogen atom of the hydrazone form with incipient salt formation by analogy with the salt formation of nitrobenzene with concentrated sulphuric acid (Masson (99)),



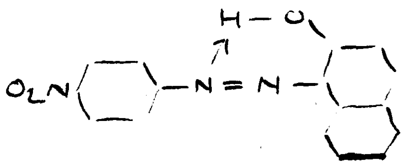
whereas the almost inert (feebly anionoid) benzene will tend to promote some salt formation (by analogy with its double salt formation with picric acid) with the hydrazone tautomeride and thereby bring about an equalisation of the azo-hydrazone concentrations.

Chelation:

It is possible that o-hydroxyazo compounds may exist in a chelated form. Infra red absorption measurements (6200-7500 cm.$^{-1}$) by Hendricks et al (100) reveal that many molecules having hydrogen bonds between ortho atoms have no measurable absorption in this region, whereas characteristic absorption occurs with other hydroxy compounds. It is important, if the bonding between nitrogen and hydroxy groups is to take place, for the nitrogen and oxygen atoms to be spaced/

spaced about 2.6A apart. The ring formed should have a minimum number of single bonds about which there can be free rotation and the entire system should be one relatively free of strain produced by valence angle deformation. These conditions are fulfilled, in the case of <u>ortho</u> compounds by formation of a six-membered ring, including hydrogen. These authors found one possible example of a seven-membered ring, but none of a five-membered ring. Other important factors in deciding whether hydrogen bond formation shall occurr are the electron affinities of the compounds concerned, especially those associated with a conjugated system of double bonds.

The reason for the insolubility in alkali of simple unsulphonated azo dyes from β-naphthol was for a long time not clearly understood. The development of ideas on hydrogen bonding and the work of Morgan and others, who showed that the azo group can form additional bonds with metal atoms in lakes of dyes, have now enabled a simple explanation to be put forward. The hydrogen of the hydroxy group is bonded with an azo nitrogen. Thus the azo form of Para Red (C. L. 44) may be shown thus:



Mason (101) confirmed that a chelate structure exists, by isolating a boroacetate derivative of this dye.

EXPERIMENTAL.

General Remarks.

The work was initially undertaken to discover a method of analysing azo dyes by oxidation so that the disadvantages of the titanous chloride reduction method of analysis might be overcome. Preliminary observations showed that the azo dyes are decolourised immediately on adding a solution of ceric sulphate in the cold. When ceric sulphate and other oxidising agents, however, were tried for quantitative analysis of azo dyes, it was found that the analysis was not reliable owing to the complexity of the reactions.

Titrations with ceric sulphate solution using various indicators, such as Xylene Cyanol FF, N-phenylanthranilic acid and starch iodide paper, were tried, but the end points were far from satisfactory. An indirect method, using excess of ceric sulphate solution and back-titrating the excess against standard sodium thiosulphate solution after liberating iodine with potassium iodide was tried, but it was found that the amount of oxidising agent used up continued to increase with time and no maximum appeared to be reached in a reasonable period. Thus, in the case of Orange II and Azo Geranine 2 GS, it was found that oxygen absorption continued for about eight hours in the cold with various reagents, and a final uptake of about

5-20 atoms of oxygen was observed, as shown in Tables 1 to 8.

A. Quantitative Experiments.

(i) Action of various oxidising agents on Orange II and Azo Geranine 2 GS.

Two dyes, viz. Orange II (62% purity) and Azo Geranine 2 GS (25% purity) were used. To 10 c.c. of a 0.2% solution of the dye were added 10 c.c. of 5 N H_2SO_4 and 10 c.c. of approximately 0.1 N solution of the oxidising agent. The solutions were mixed together and allowed to stand at room temperature. At the end of the stated time, 5 c.c. of 25% K I solution and 50 c.c. of water were added and the iodine liberated titrated against 0.05 N $Na_2S_2O_3$ solution.

In the case of the action of acid $KMnO_4$ on Orange II, 20 c.c. of the oxidising agent was used instead of 10 c.c. and in the case of the oxidising action of neutral permanganate, the addition of sulphuric acid was omitted in the beginning, but at the end of the stated time, 5 c.c. of 25% K I was added first, followed by 10 c.c. of 5 N H_2SO_4 and 50 c.c. of water.

The results are given in Tables 1 and 2. The log of atoms of oxygen used per mol. of dye is plotted against the log of time in minutes as shown in Figs. 1 and 2.

It should be understood that this is not a measure of the rate of oxidation of the dye, as the dye is immediately oxidised on addition of the oxidising agents.

TABLE/

TABLE I.

ACTION OF VARIOUS OXIDISING AGENTS ON ORANGE II.

Time min.	Atoms of oxygen used per mol. of dye.			
	Ceric sulphate.	Potassium dichromate	Neutral potassium permanganate	Acid potassium permanganate
1	1.70	2.70	4.17	10.03
5	1.87	3.07	4.73	11.30
15	2.35	2.99	5.89	12.84
30	2.65	3.18	6.83	14.40
45	2.95	3.18	7.57	14.96
60	3.21	3.60	8.25	15.25
120	3.92	3.63	8.33	15.87
240	4.45	4.45	8.79	17.15
360	4.52	5.22	8.93	18.20
480	4.87	5.29	9.10	18.42
1080	4.87	5.51	9.38	18.50

TABLE 2.

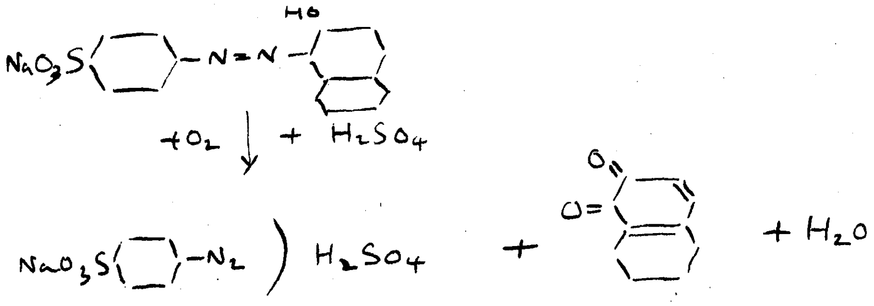
ACTION OF VARIOUS OXIDISING AGENTS ON AZO GERANINE 2GS.

Time, min.	Atoms of oxygen used per mol. of dye.			
	Ceric sulphate	Potassium dichromate	Neutral potassium permanganate	Acid potassium permanganate.
1	2.03	1.79	6.68	9.18
5	2.33	2.94	7.42	12.60
15	2.69	3.92	8.64	14.20
30	3.06	3.18	9.13	15.61
45	3.26	3.50	9.38	15.98
60	3.67	3.38	9.06	16.88
120	6.48	3.96	11.98	15.16
240	6.61	4.77	13.20	15.65
360	9.17	5.14	14.85	18.58
480	9.17	5.75	15.90	21.27
1080	11.20	7.88	17.09	22.00

(ii) Potentiometric titration:

It was thought that by titrating a solution of an azo dye with an oxidising agent potentiometrically, the excess of the oxidising agent could be avoided, thus reducing the chances of complex reactions taking place.

Commercial Orange II (25 c.c. of 0.2% solution) (62% purity) and 25 c.c. of 5 N sulphuric acid were titrated potentiometrically with ceric sulphate solution in the cold. There was a sharp rise in the E.M.F. at a point corresponding to the absorption of 0.91 mol. of oxygen per mol. of dye. This is close to the theoretical value of 1 mol. of oxygen required by the reaction:



Azo Geranine 2 Gs was titrated similarly, but the E.M.F. readings were erratic. This method of analysis has not been pursued further.

The results for potentiometric analysis of Orange II and Azo Geranine 2 Gs are given in Tables 3-5. (Fig. 3).

TABLE/

TABLE 3.

POTENTIOMETRIC TITRATION OF ORANGE II. WITH CERIC SULPHATE.

25 c.c. of 0.2% dye solutions + 25 c.c. water.

C.C. of 0.0314 N Ceric Sulphate.	E.M.F. (mV x 100)	C.C. of 0.0314 N ceric sulphate	E.M.F. (mV x 100)
0	2.54	0	2.74
1	2.77	2	2.78
2	2.85	4	2.90
3	2.90	6	3.10
4	2.92	8	3.15
5	2.96	9	3.15
6	3.16	9.2	3.15
7	3.31	9.~~1~~4	3.18
8	3.22	9.6	>4.2
9	3.18	9.8	>5.2
9.5	3.22		
9.8	>4.4		

$$\% \text{ purity} = \frac{9.6 \times 0.0314 \times 20 \times 100 \times 8 \times 350}{1000 \times 32} = 52.75$$

TABLE 4.

POTENTIOMETRIC TITRATION OF ORANGE II WITH CERIC SULPHATE IN PRESENCE OF EXCESS SULPHURIC ACID.

25 c.c. of 0.2% dye solution~~s~~ + 25 c.c. of 5 N H_2SO_4.

C.C. of 0.0314 N Ceric Sulphate.	E.M.F. (mV x 100)	C.C. of 0.0314 N Ceric Solution	E.M.F. (mV x 100).	C.C. of 0.0314 N Ceric Sulphate.	E.M.F. (mV x 100)
0	2.82	0	2.85	0	3.55
2	3.15	2	3.22	3	3.64
4	3.28	4	3.30	6	3.64
6	3.30	6	3.38	9	3.64
8	3.38	8	3.44	10	3.78
9	3.32	9	3.40	10.1	4.74
9.3	3.36	9.3	3.40	10.3	5.7
9.5	3.28	9.5	3.40		
9.7	3.28	9.7	3.36		
9.9	3.30	9.9	3.56		
10.2	3.74	10.1	3.36		
10.3	3.80	10.2	4.26		
10.5	5.0	10.4	5.38		

$$\% \text{ purity} = \frac{10.27 \times 0.0314 \times 20 \times 100 \times 8 \times 350}{1000 \times 32} = 56.3$$

TABLE 5.

POTENTIOMETRIC TITRATION OF AZO GERANINE 2 GS WITH CERIC SULPHATE.

25 c.c. of 0.2% dye solution + 25 c.c. of 5 N H_2SO_4.

C.C. of 0.0314 N Ceric Sülphate	E.M.F. (mV x 100)
0	2
0.5	2.1
1	1.6
1.5	1.4
2	1.36
2.1	1.42
2.2	1.3
2.3	0.2
2.4	1.1
2.5	2.2
2.7	4.6

(iii) Nitrogen Estimation.

By boiling an azo dye in an acid oxidising solution the diazo compound, which is one of the first products of the reaction, should decompose with liberation of free nitrogen. Owing to the difficulty of isolating any measurable quantity of a solid derivative of the diazo compound, it was thought that an estimation of the nitrogen evolved from the boiling solution would be a better indication of the extent of formation of diazo compound in the original break-up of the dye molecule.

Accordingly, a modified Dumas apparatus was constructed (Fig. 4). In this, a supply of air-free carbon dioxide, obtained from the solid and regulated by two bubblers in series, the first containing mercury and the second water, is passed through the dye and oxidising agent in solution in a 250 c.c. round-bottomed flask under reflux. The gas stream passes up the condenser and is collected in an azotometer over 40% aqueous potassium hydroxide. In the flask is a solution containing a weighed quantity of dye in 100 c.c. of water, to which is added 10 c.c. of 5 N. sulphuric acid and 10 c.c. of 10% potassium dichromate solution. The solutions are previously boiled to remove dissolved air and then cooled. Carbon dioxide is passed through the apparatus first until all air is expelled. (10-15 mins). The azotometer is then closed to the atmosphere, the mixture in the flask boiled, and a stream of gas passed until no more nitrogen is collected. The nitrogen is allowed to cool, and the volume corrected to N.T.P. The results obtained with several dyes are given in Table 6.

TABLE 6.

Dye	Colour Index No.	Purity by Titaneous Chloride Estimation(%)	Nitrogen Theoretical (as azo group)	% obtained
1. Orange II	151	61.4	4.91	4.91
2. Crystal Ponceau (heptahydrate)	89	99.9	4.45	4.51
3. Scarlet R.	79	38.9	2.27	2.20
4. Aniline → G-acid	-	100.0	6.19	6.22
5. R-acid ← Benzidine → R-acid	-	41.4	2.57	2.47
6. Azo Geranine 2 GS	31	29.1	1.60	1.86
7. Chlorazol Sky Blue FFS	518	18.1	1.02	0.60
8. Benzopurpurine 10 BS	495	36.3	2.69	0.52
9. Congo Red WS	370	58.9	4.74	1.50
10. Aniline → naphthionic acid	-	63.1	5.06	1.70

It will be observed that the first five dyes give a substantially quantitative yield of nitrogen. In these all the nitrogen is present in the azo group(s). This is an interesting indication therefore that there must be a quantitative formation of diazo compound in the initial stages of oxidation. Dyes 6-10, all of which give low yields of nitrogen, have nitrogen also in an amino or a substituted amino group in the second component. In No. 8, 9 and 10, the amino group is ortho to the azo group. It is possible, therefore, that these dyes decompose partly in a different manner from No. 1-5. It will be recalled that Zincke (quoted by Haller and Ziersch (2)) and Charrier and Crippa (24a) obtained N-arylphenols and naphthotriazoles by oxidising o-aminoazo compounds.

B. THERMAL OXIDATION IN SOLUTION.

Since the only previous major investigation on azo dye oxidation was concerned with the use of hypochlorite, which in some cases gave chlorinated products, it was decided first to investigate the action of other common oxidising agents, to determine whether the course of the reaction is similar. Ceric sulphate and acid dichromate were chosen. Qualitative tests were made to identify the decomposition products in the reaction mixtures, and these were found to be similar to those reported by previous workers. In some cases unpurified commercial dye samples were used, in others, laboratory preparations. The dye content was in all cases checked by titaneous chloride analysis.

(i) Identification of Oxidation Products.

(a) Diazo Compounds:

Commercial Orange II (61% purity) was used. Excess ceric sulphate was added in the cold to a 2% aqueous solution of dye acidified with sulphuric acid. The mixture was filtered from the precipitate which formed. The filtrate gave a red colouration with alkaline β-naphthol solution. A little of the liquid from this test was evaporated to dryness on a water-bath, the residue extracted with pyridine, the extract diluted with/

with water, and the identity of the colouring matter checked by visual spectroscopic examination against a known sample of the dye, sulphanilic acid → β-naphthol. Thus, the formation of the original diazo compound in the oxidation process was confirmed. Similar results were obtained by using pure samples of sodium p-hydroxyazobenzenesulphonate and pure p-aminoazobenzene, oxidation being carried out in the cold with 1 g. dye, 5 g. potassium dichromate, and 10 g. concentrated sulphuric acid in 100 c.c. water.

(b) Phenol:

The diazo compound should give a phenol on boiling the acid mixture. A satisfactory sample of phenol-p-sulphonic acid could not be obtained in this way from Orange II. A pure sample of the dye aniline → G-acid (2-naphthol-6;8-disulphonic acid) was then prepared and it gave a satisfactory result, as follows. A mixture of 5 g. dye, 5 g. potassium dichromate, and 10 g. concentrated sulphuric acid in 200 c.c. water was boiled and steam-distilled, 200 c.c. of distillate being recovered. Extraction of the distillate with ether produced a yield of 0.5 g. phenol (about 60% of theory), which was identified by colour tests and by preparation of the tribromo derivative, m.p. (from alcohol) and mixed m.p. 91°C. The corresponding dye from R-acid also gave phenol in the same manner.

(c) Nitrogen:/

(c) Nitrogen:

The evolution of nitrogen on boiling the solution after oxidation was made the basis of a quantitative analytical method, ~~w~~as described above.

(d) Quinones:

Very small yields of quinones, as such, were obtained in oxidation experiments. Ether extracts of cold oxidation mixtures from Orange II were shown to contain 1:2-naphthaquinone by means of the green colouration produced with concentrated sulphuric acid. By steam distillation of a dichromate reaction mixture containing 4 g. of p-aminoazobenzene a small quantity of p-benzequinone was obtained. This was identified by forming the yellow addition product with semicarbazide hydrochloride (m.p. 243°C.)

Two other quinone-acceptors were also employed. It is shown below that dyes from 2:4-dinitroaniline are very resistant to oxidation. As a result of this observation, 2:4-dinitrophenylhydrazine was successfully tried as a quinone-acceptor. It condenses with the naphthaquinone as formed, to produce a dinitroazo dye which itself resists oxidation.

Orange II (5 g.) was dissolved in 2 litres of cold water, and 120 c.c. of 0.25 N. ceric sulphate solution was added. The solution was immediately decolorised. On further addition of 2 g. 2:4-dinitrophenylhydrazine (previously dissolved by pasting with 4 c.c. of concentrated sulphuric acid and 30 c.c. methanol/

methanol, with cooling and addition of 10 c.c. water), a precipitate of an orange-red dye (2.3 g.) was immediately formed. This was recrystallised from nitrobenzene. The colour reactions (green with concentrated sulphuric acid, deep blue with alcoholic caustic soda solution) were identical with those of the known compound; m.p. and mixed m.p. 276-278°C.

The reference compound was made by adding similarly 2 g. of 2:4-dinitrophenylhydrazine to a fine dispersion of 1 g. 1:2-naphthaquinone in 100 cc. water. This gave an immediate precipitate of 2.2 g. crude dye. Recrystallised from nitrobenzene it formed fine dark red needles, m.p. 276-278°C.

Similar treatment of the oxidation liquors from the corresponding dyes from α-naphthol (Orange I) and Naphtol AS produced red azo dyes, but these were difficult to crystallise and had very high melting points.

The insoluble azo dyes obtained in the case of Orange I gave a deep purple coloration with concentrated sulphuric acid and a deep blue with alcoholic caustic soda solution:

N_2 (found)............15.2%

N_2 (theoretical) 16.6%

The corresponding dye from oxidation of the dye,

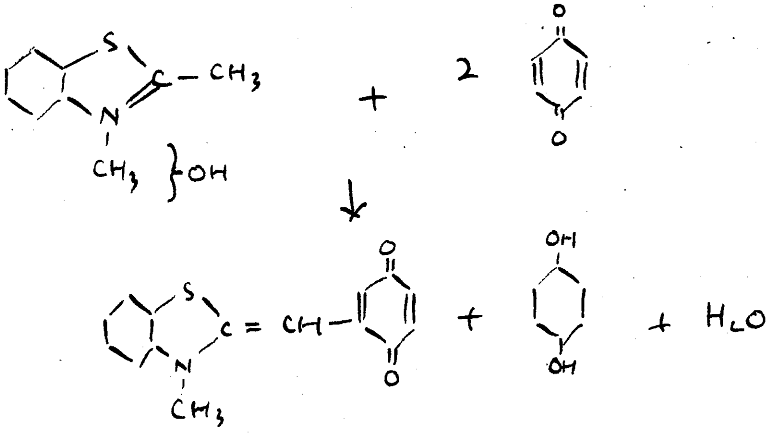
sulphanilic/

sulphanilic acid Naphtol AS, gave a purple colouration with concentrated sulphuric acid and a wine red with alcoholic caustic soda solution.

N_2 (found) 14.6%

N_2 (theoretical) 15.3%

The second quinone-acceptor used was 2-methyl-benzthiazole metho-p-toluenesulphonate, which has been employed by James, Snell and Weissberger (76) for this purpose in investigating the autoxidation of quinol. This immediately reacts in alkaline solution with a quinone to give a deeply coloured condensation product.



The reference compound was prepared by dispersing 0.5 g. 1:2-naphthaquinone in 250 c.c. of a boric acid-potassium chloride-sodium hydroxide buffer solution (pH 8.2) and add~~ed~~ing 1.5 g. of the acceptor dissolved in 5 c.c. water. A dark green colouration/

colouration was produced, which quickly became a dark blue precipitate (0.6 g.).

To a solution of Orange II (1 g. of commercial dye) in 200 c.c. water was added 15 c.c. of 0.25 N. ceric sulphate solution, and the liquid was then made slightly alkaline by addition of caustic soda. Then 50 c.c. of the buffer solution and 1 g. of the acceptor in 10 c.c. water were added. The brown solution became greenish brown at once, and a precipitate consisting of the coloured product together with some ceric hydroxide was filtered off and refluxed with 25 c.c. ethanol. This gave a green solution, which was spectroscopically identical with one prepared from the reference sample in a similar manner in presence of ceric hydroxide.

(e) Phthalic acid: A solution of Orange II (5 g. of commercial dye), 25 g. concentrated sulphuric acid, and 10 g. potassium dichromate in 400 c.c. water was boiled down to about half volume, made alkaline to precipitate chromium, filtered, acidified with hydrochloric acid, and extracted with ether. Evaporation of the combined extracts gave a 30% yield of phthalic acid (white plates, m.p. 194°C., from water; mixed m.p. 193°C.). On heating, it sublimed, giving phthalic anhydride, m.p. 135°C. Its identity was confirmed by formation of fluorescein and phenolphthalein. Yield, about/

about 30%.

Paper Chromatography:

Some preliminary experiments have been done to identify oxidation products by chromatography on paper. Filter-paper strips (40 cm. by 15 cm.) were hung in a large enclosed glass vessel, the top end of the paper being dipped in butyl alcohol saturated with water. A drop of a solution of Orange II which had been oxidised with acidified ceric sulphate in the cold was applied to the upper end of the paper and allowed to develop for 6 hours. The front advanced about 13 cm.

A positive colour reaction for a diazo body was given by a portion of the upper part of the strip with alkaline β-naphthol solution and a lower part of the strip gave positive tests for a quinone, both with the benzthiazole quinone-acceptor and with 2:4-dinitrophenylhydrazine.

It is hoped to pursue this technique further with extracts of light-faded fabrics.

Attempts to Oxidise Azobenzene:

A pure sample of azobenzene (0.1 g.), finely ground with a sulphated fatty alcohol dispersing agent, was refluxed for 30 min. with 120 c.c. of water, containing 1 g. potassium dichromate and 2.5 g. concentrated sulphuric acid. The whole of/

of the sample was recovered unchanged after the experiment, by filtration, washing with water, and drying.

Action of dilute nitric acid on azo dyes:

The ease of oxidation of soluble azo dyes with dilute nitric acid was studied as part of the present work and it was necessary to determine if oxidation proceeds in a similar manner here to the oxidation with other oxidising agents. For this purpose, 60 c.c. nitric acid (sp.gr. 1.42) and 100 c.c. water were added to a solution of Orange II (2 g.) in 800 c.c. water. After allowing to stand overnight, the brown crystals that were formed were filtered, and washed with water. Recrystallised from ethanol, they had m.p. 93-94°C., and gave a positive test for nitrogen. The compound did not condense with 2:4-dinitrophenylhydrazine. As a dinitro-derivative of β-naphthol seems to be formed on heating, as shown later on, it is probable that the present substance is a mono-nitro-derivative of β-naphthol. The nearest melting point (103°C) is that of 1-nitro-2-naphthol. It may be that this is a mixture of more than one nitro compound.

Another sample of dye was similarly treated, but the solution was boiled, after adding dilute nitric acid, until oxidised. On cooling, yellow crystals were obtained. Recrystallised from aqueous methanol, these had m.p. 192-193°C., and gave a positive test for nitrogen. Found, C, 51.1%; H, 2.4%; N, 12%; O (by diff.), 34.5%. The empirical formula, $C_{10}H_6N_2O_5$, obtained/

obtained from analysis, suggests that the unknown substance is either 1:6-dinitro-2-naphthol (m.p. 195°C.)or 1:8-dinitro-2-naphthol (m.p. 198°C.). As, however, known samples of these compounds could not be obtained mixed melting points could not be taken. These experiments suggest that nitration of the naphthol component of the dye occurs even in the cold with dilute nitric acid, and that the oxidation of the dye probably proceeds in a different manner from that with other oxidising agents. It may be recalled that Meldola and Morgan (10) obtained dinitro-derivatives of the naphthol components by the action of nitric acid (sp.gr. 1.42) on phenylazonaphthols and their ethyl ethers.

To discover how the oxidation of the primary component of the dye proceeds, 0.5 g. of the dye, aniline → G-acid, was dissolved in 80 c.c. water, and 40 c.c. of 1 N. dilute nitric acid added. After allowing the solution to stand at room temperature until it turned yellow, an alkaline solution of β-naphthol was added. On standing overnight, a small quantity of dye had settled out. This was filtered and washed with water. Crystallised from aqueous methanol, it had a melting point and a mixed melting point, with a known sample of phenylazo-β-naphthol of 128°C. However, on steam-distillation and ether-extraction, phenol was not detected, but a very small quantity of yellow crystals giving a positive test for nitrogen was obtained. The compound is probably o-nitrophenol, which is volatile in steam. On/

On ether-extraction of the residue from steam-distillation, yellow crystals, m.p. 95°C., were obtained. This appears to be the non-steam-volatile *m*-nitrophenol. This shows that the nitration of the diazo compound does not take place in the cold, but when boiled, the phenol formed is nitrated.

Action of alkaline hydrogen peroxide on azo dyes:

Qualitative evidence was obtained that the later course of the reaction is the same as with the acid reagents. The liquors after the oxidation gave definite though rather weak colour reactions for diazo compounds and naphthaquinone and by acidification and extraction with ether a small quantity of phthalic acid was obtained.

(ii) Action of oxidising agents on phenylhydrazine.

In the present research, as a working hypothesis, it is postulated (102) that one of the initial products of oxidation of the dye, aniline → R-acid, is phenylhydrazine, which readily undergoes oxidation to the diazonium compound. The following two tests were applied to detect the presence of phenylhydrazine:-

(1) 0.05 N. ceric sulphate solution was added drop by drop to 5 c.c. of 0.1% solution of the dye, until just oxidised. On adding alkaline β-naphthol, coupling still took place, indicating the formation of a diazo salt.

(2) An aqueous dispersion of β-naphthaquinone (2 c.c.) was added to the dye solution before adding ceric sulphate, with the hope/

hope that if phenylhydrazine is formed, it might condense with β-naphthaquinone to form an insoluble due, but no dye formation was observed, the solution still coupled, however, with alkaline β-naphthol.

The inference from the above two tests is that phenylhydrazine either is not formed, or if formed, is immediately oxidised to the diazo compound by atmospheric oxidation, or that the condensation between phenylhydrazine and β-naphthaquinone does take place, but since the dye is in very small quantity, it remains in clear dispersion and hence is easily oxidised again. The ease of oxidation of insoluble dyes, discussed later, may be of importance in this connection.

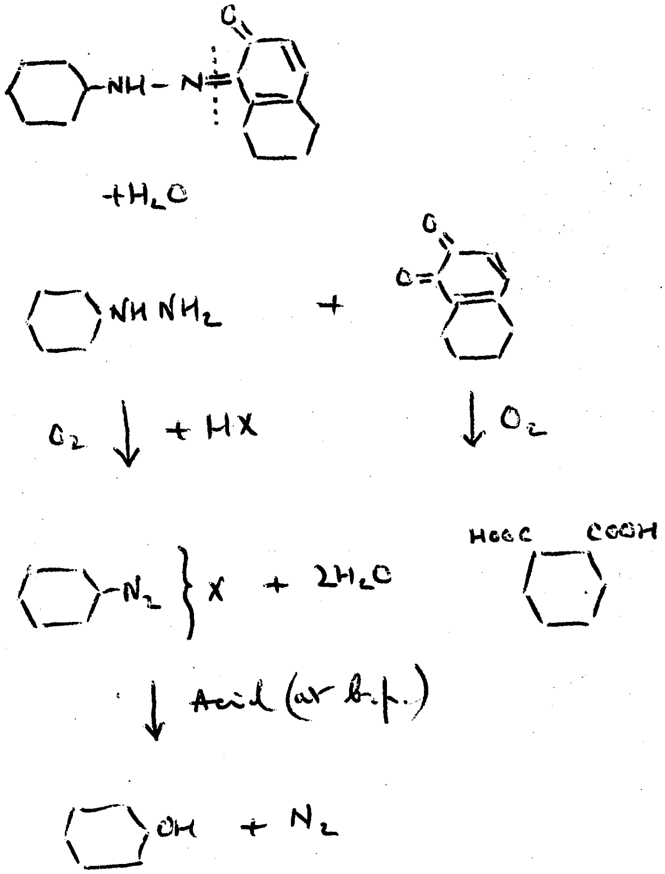
As described in the Survey of Previous Work (above), phenylhydrazine is known to oxidise to a diazonium compound with various oxidising agents. This was confirmed by the author, using atmospheric air and acid dichromate as the oxidising agents. A dilute aqueous solution of phenylhydrazine on shaking in air was found to couple with alkaline β-naphthol solution. This cannot be due to condensation of phenylhydrazine itself with any naphthaquinone which might be present as an impurity in the naphthol solution, for this latter condensation takes place only in acid media. In another experiment, 20 c.c. of 10% potassium dichromate and 20 c.c. of 5 N. sulphuric acid were added/

added to a dispersion of 2 g. phenylhydrazine hydrochloride in 100 c.c. water, and allowed to stand at room temperature for nine days. On steam-distillation and ether-extraction, 0.25 g. of a substance having a phenolic odour was obtained. It condensed with phthalic acid forming phenolphthalein. The tri-bromo derivative, however, had a low melting point (84-85°C.) even after four crystallisations from aqueous methanol, and was therefore not a pure sample. The melting point of 2:4:6-tribromophenol is 93°C.

DISCUSSION.

(i) POSTULATED OXIDATION MECHANISM OF AZO COMPOUNDS.

As a working hypothesis in the present investigation, it is postulated that the mechanism of the oxidation reaction in acid solutions is one of hydrolysis of the hydrazone form of the dye, followed by oxidation of the products (102). Further boiling of the acid solution should cause the diazonium salt to decompose, producing a phenol and nitrogen. The sequence of reactions may be illustrated thus for the dye aniline β-naphthol.



It was further assumed that light fading is due to a similar series of reactions. Hence those dyes which exist preponderantly in the azo form should be faster to light, *ceteria paribus*, than those in which the hydrazone form is the more stable.

The study of a series of dyes from nitroanilines should help to confirm or disprove the general hypothesis. Consideration of the two possible forms of the dye aniline → β-naphthol shows that the change from hydrazone to azo form should be favoured by increased positive charge on the nitrogen atom nearest the phenyl nucleus, which will assist mobility of the attached hydrogen. This would be expected to occur if a strongly electron-accepting group, e.g. a nitro group, were attached *ortho* to the nitrogen mentioned. A *para*-nitro group should be slightly less effective, and a *meta* one considerably less so; and two nitro groups present together, in the *ortho* and *para* positions, should have a very powerful effect. It would therefore be expected that dyes from a given second component coupled with aniline and its nitro-derivatives respectively, would show increased resistance both to ~~chemic~~thermal oxidation and possibly also to light fading, in the following descending order :- 2:4-dinitroaniline ,> *o*-nitroaniline > *p*-nitroaniline > *m*-nitroaniline > aniline. O-Alkyl ethers of hydroxyazo dyes should also have greater resistance to ~~chemic~~thermal oxidation and light fading than their parent hydroxy compounds.

This/

This hypothesis would account for the difficulty observed by Seyewetz and Chaix (27), and confirmed in the present work, of oxidising azobenzene, because this must exist almost entirely in the azo form.

EXPERIMENTAL. (cont).

C. Dry Oxidation:

It follows from the hypothesis outlined above that in absence of water, the oxidation of azo compounds should not follow the same course as in aqueous media.

Haller and Ziersch (2) obtained diazo compounds and quinones in oxidations of azo dyes with ozonised oxygen in aqueous solutions. It was thought, therefore, that the action of the same oxidising agent in absence of water would be worth investigating.

Dry ozonised oxygen was bubbled through a solution of dry phenylazo-β-naphthol (0.7 g.) in 50 c.c. dry acetone. The solution changed from orange to yellow. It would not couple with alkaline β-naphthol nor with a solution of R-salt. When the solvent was removed under vacuum, an oily residue remained. This gave a positive test with starch-iodide and was strongly acidic, but no 1:2-naphthaquinone was detected.

It appears, therefore, that dry oxidation must follow a different course from wet oxidation, but no further investigation has been made on this aspect of the subject.

D/

D. EASE OF OXIDATION OF SOLUBLE AZO DYES.

General Remarks:

The ease of oxidation of several soluble azo dyes, obtained by coupling aniline and its simple substituted derivatives with R-acid (β-naphthol-3:6-disulphonic acid) and Oxy-L-Acid (α-naphthol-6-Sulphonic acid) respectively, was quantitatively studied using various oxidising agents, e.g. ozone, neutral and alkaline hydrogen peroxide, potassium persulphate and dilute nitric acid. This was to correlate the results with the "σ" value of Hammett (103) and with light fading experiments. Details of the methods employed are given below.

(1) Oxidation with ozone:

Various experiments on oxidation of azo dyes with ozonised oxygen were carried out using the Eel Photoelectric colorimeter (Evans Electroselenium Ltd) for colour strength measurement. This instrument was found to be very convenient for the purpose as it is readily portable. However, although apparently all the factors, such as concentration, volume and temperature of dye solution, and the rate of bubbling of ozone, were kept constant, reproducible results could not be obtained.

(2) Oxidation with neutral hydrogen peroxide.

A mixture of 5 c.c. of dye solution (0.01%), 5 c.c. of hydrogen peroxide (300 g./litre), and 40 c.c. of water was placed in a Pyrex test-tube and kept in a thermostat at 25°C. The/

The rate of change of colour was measured at intervals by withdrawing small samples for examination in the Spekker photoelectric absorptiometer. The solution was poured back after examination. In the case of the dyes, Sulphanilic acid → phenol, naphthionic acid →phenol, and their methyl ethers, 5 c.c. of 0.05% solution of the dye was used, as the Spekker readings using 5 c.c. of 0.01% solution were too low. The results are given below in Table 7 and plotted in Figs. 5-38.

(3) Oxidation with alkaline hydrogen peroxide:

Some experiments were carried out using sodium hydroxide and hydrogen peroxide as the oxidising agent, but in later experiments, this alkali was replaced by 0.05 M. borax-buffer solution (pH 9.2).

(a) (i) Dyes without nitro groups:

A mixture of 20 c.c. of dye solution (0.01%), 25 c.c. of 1 N. sodium hydroxide solution, 25 c.c. of hydrogen peroxide (310 g./litre) and 30 c.c. of water was placed in a flask fitted with a Bunsen valve and kept in a thermostat at 25°C. The rate of change of colour was measured as before. The results are plotted in Fig. 39. A marked resistance to oxidation of the O-methyl ether of Orange I, as compared with that of Orange I, is quite evident.

(ii)/

(ii) Dyes containing nitro groups: (Experiments by Mr. R. S. McKee).

The experiments were repeated using 25 c.c. of 0.02% dye solution, 20 c.c. of 1 N. sodium hydroxide solution, 25 c.c. of hydrogen peroxide (310 g./litre) and 30 c.c. of water at 23°C. The dyes selected were laboratory preparations of aniline and its nitro-derivatives coupled with R-acid in alkaline solution. The results are plotted in Fig. 40.

(b) In this series of experiments, sodium hydroxide was replaced by 0.05 M. borax solution, with a pH value of 9.2. A mixture of 5 c.c. of dye solution (0.01%), 25 c.c. of buffer solution, 5 c.c. of hydrogen peroxide (300 g./litre), and 15 c.c. of water was placed in a Pyrex test-tube and kept in a thermostat at 25°C. At intervals, 5 c.c. samples of the solution were withdrawn, made slightly acid by 5 c.c. of 0.05N hydrochloric acid, and examined for colour strength as before. The addition of acid helps to arrest the evolution of oxygen bubbles and thus facilitates measurements. The results are given in Table 8, and plotted in Figs. 41-48.

(4) Oxidation with potassium persulphate:

A mixture of 5 c.c. of dye solution (0.01%), 25 c.c. of 0.1 M. potassium persulphate, and 20 c.c. of water was placed in a Pyrex test-tube and kept in a thermostat at 25°C. The rate of change of colour was measured at intervals by withdrawing small samples for examination in the Spekker photoelectric absorptiometer

In/

In the case of the dyes, sulphanilic acid → phenol, naphthionic acid → phenol, and their methyl ethers, 5 c.c. of 0.05% solution of the dye was used instead of 5 c.c. of 0.0~~5~~1% solution. The results are given in Table 9, and plotted in Figs. 49-84.

(5) <u>Oxidation with dilute nitric acid</u>:

A 1N. solution of nitric acid was also used for oxidation. The sample of concentrated nitric acid used for these experiments was yellowish in colour, and when it was replaced by a fresh sample, colourless in appearance, it was found that the latter had much less oxidising power. The stronger action seems to be due to the decomposition products of nitric acid, which decomposes as follows. (This decomposition is favoured by high temperature and light).

$$4\ HNO_3 \rightarrow 2\ NO_2 + 2\ H_2O + O_2$$

By bubbling oxygen through the yellow sample of acid, the nitrogen dioxide can be removed by oxidation. To determine if the difference in the two reaction rates is due to such decomposition products, oxygen was bubbled through the yellow acid until it became nearly colourless, and the two samples were used for qualitative rate tests in the oxidation of Orange II. The treated acid was much weaker in action than the untreated one. A mixture of 5 c.c. of dye solution (0.01%), 10 c.c. of 5 N. nitric acid, and 35 c.c. of water was placed in/

in a Pyrex test-tube and kept in a thermostat at 25°C. The rate of change of colour was measured at intervals as before. The results, using a colourless sample of acid, oxygen being bubbled through to ensure oxidation of decomposition products, are given in Table 10, and plotted in Fig. 85-90. The results of experiments with yellow acid are given in Table 11, and plotted in Figs. 91-94. To distinguish between the two, the yellow acid is represented as $HNO_3(d)$.

TABLE 7.

(i) OXIDATION OF WATER-SOLUBLE AZO DYES WITH NEUTRAL HYDROGEN PEROXIDE.

Dye	Unoxidised dye, %, after				
	3 hr.	6 hr.	9 hr.	12 hr.	24 hr.
Orange I		94.5	92.3	90.6	81.6
O-Methyl ether of above	nil	nil	nil	nil	nil
Orange II	93.0	82.0	80.2	71.6	56.0
Aniline → R-acid	90.3	81.6	76.9	69.0	55.9
o-Nitroaniline → R-acid	83.9	67.0	60.1	48.8	22.4
m " "	91.7	73.7	72.0	63.0	41.3
p " "	89.5	73.9	67.4	58.7	36.8
o-Chloroaniline "	88.1	72.4	61.3	51.6	24.9
m- " "	90.3	75.6	75.6	65.0	51.8
p " "	85.4	71.1	65.4	56.6	35.2
2:4-Dichloroaniline "	87.4	67.6	60.7	49.0	18.7
m-Toluidine "	-	89.0	83.2	79.8	65.2
p " "	90.6	81.6	77.6	70.5	51.3
o-Anisidine "	96.9	85.4	82.6	74.7	50.3
p- " "	100.0	92.4	92.4	90.2	81.5
Metanilic acid "	97.5	94.7	93.5	-	89.4 (20 hr)

Sulphanilic/

Dye		Unoxidised dye, %, after				
		3 hr.	6 hr.	9 hr.	12 hr.	24 hr.
Sulphanilic acid →	R-acid	96.6	94.2	92.0	-	80.0 (20 hr).
Anthranilic acid	"	98.1	91.7	91.0	84.6	75.6
p-Aminobenzoic acid	"	92.6	77.9	74.9	63.6	43.0
Aniline ⟶	Oxy-L-acid	-	86.6	80.6	76.9	57.5
o-Nitroaniline	"	-	87.1	80.7	76.~~6~~7	46.6
m- "	"	97.0	93.3	91.0	88.0	80.7
p- "	"	-	93.8	89.5	87.1	75.0
o-Chloroaniline	"	93.8	89.7	85.2	82.8	69.7
m-Chloroaniline	"	91.3	84.6	79.8	76.9	64.4
p-Chloroaniline	"	-	88.9	79.6	74.5	52.3
2:4-Dichloroaniline	"	-	92.9	85.8	82.9	72.5
m-Toluidine	"	95.8	94.2	92.9	92.9	87.9
p- "	"	95.1	92.6	90.4	89.5	84.0
o-Anisidine	"	97.1	95.9	96.5	95.3	89.4
p- "	"	98.3	97.9	96.8	96.8	92.9
Metanilic acid	"	95.7	92.3	91.1	90.0	83.0
Sulphanilic acid	"	97.7	95.5	94.3	93.2	88.7
Anthranilic acid	"	100.0	97.1	97.1	96.1	93.2
p-Aminobenzoic acid	"	96.8	93.4	91.5	90.4	84.4

TABLE 8.

(ii) OXIDATION OF WATER-SOLUBLE AZO DYES WITH ALKALINE HYDROGEN PEROXIDE.

Dye			Unoxidised dye, %, after				
			2 hr.	4 hr.	6 hr.	8 hr.	24 hr.
Aniline	→	R-acid	70.0	60.8	49.6	48.1	5.0
o-Nitroaniline		"	65.2	43.9	30.4	23.9	4.4
m-	"	"	69.0	59.1	51.7	49.3	11.3
p-	"	"	56.4	42.2	29.1	23.6	4.4
o-Chloroaniline		"	57.1	36.5	21.9	14.2	-
m-	"	"	70.9	61.4	53.6	47.7	6.8
p-	"	"	70.8	60.0	51.6	46.0	8.0
2:4-Dichloroaniline		"	60.5	40.4	26.9	18.8	4.5
m-Toluidine		"	69.6	57.2	51.4	43.2	6.2
p-Toluidine		"	63.2	51.6	45.7	38.8	7.0
o-Anisidine		"	42.3	25.1	16.7	12.1	-
p-Anisidine		"	61.7	45.5	37.8	31.1	6.2
Metanilic acid		"	82.0	76.3	-	61.9	17.0 (20hr.)
Sulphanilic acid		"	69.6	64.4	-	47.8	13.0 (20 hr).
Anthranalic acid		"	96.8	89.8	-	81.4	49.3
p-Aminobenzoic acid		"	64.3	53.1	-	37.4	7.5

TABLE 9.

(iii) OXIDATION OF WATER-SOLUBLE AZO DYES WITH POTASSIUM PERSULPHATE.

R-acid dyes:

Time, hr.	Unoxidised dye, %.					
	Aniline	o-NO_2-Aniline	m-NO_2-Aniline	p-NO_2-Aniline	m-Toluidine	p-Toluidine
1	86.5	87.2	87.1	87.1	88.0	84.6
2	73.3	75.6	72.4	74.9	73.6	66.4
3	60.3	60.8	59.4	62.5	62.0	51.2
4	50.0	48.1	47.1	52.3	52.4	36.9
5	40.4	37.5	37.1	42.6	43.5	25.3
6	35.3	30.0	29.1	34.8	37.5	15.7
7	28.9	23.6	17.7	28.0	28.4	5.2
8	22.1	16.7	11.3	20.5	23.1	3.3
9	18.1	13.3	7.5	15.2	18.3	-
10	15.7	9.3	-	11.0	14.4	-

Contd.

Time, hr.	Unoxidised dye, %.					
	O-CL-Aniline	m-CL-Aniline	p-CL-Aniline	2:4-CL$_2$-Aniline.	o-Anisidine	p-Anisidine
1	85.2	86.4	85.7	83.2	86.5	79.0
2	70.7	75.6	76.5	70.6	76.5	59.1
3	60.9	65.4	63.3	59.9	65.4	40.9
4	46.4	56.3	55.6	47.5	56.2	26.7
5	34.8	47.2	44.9	36.8	45.4	15.9
6	27.0	37.5	34.9	26.1	38.5	11.4
7	-	-	-	-	31.3	9.1
8	11.6	18.8	15.3	9.9	21.7	9.1
9	-	-	-	-	16.6	6.8
10	-	10.2	6.1	6.6	11.7	6.8

Contd.

Time, hr.	Unoxidised dye, %			
	Metanilic acid	Sulphanilic acid	Anthranilic acid	p-Aminobenzoic acid
1	79.4	79.2	91.2	86.5
2	60.4	61.8	79.0	70.6
3	41.1	43.3	66.5	57.3
4	26.2	28.7	53.6	44.2
5	13.8	15.7	44.8	33.7
6	9.1	9.0	35.3	24.6
7	7.1	6.7	21.7	12.7
8	7.1	6.7	13.6	7.6
9	-	-	8.1	5.0

Oxy-L-acid dyes:

Time, hr.	Unoxidised dye, %					
	Aniline	o-NO_2-Aniline	m-NO_2-Aniline	p-NO_2-Aniline	m-Toluidine	p-Toluidine
1	80.2	91.6	79.6	80.4	76.7	65.9
2	58.1	78.7	53.0	60.7	54.0	40.5
3.25	34.3	65.1	30.2	40.2	29.6	-
3.5	-	-	-	-	-	18.1
4	20.1	54.9	21.5	27.7	16.1	-
5	13.4	46.8	14.1	18.8	9.8	-
5.5	-	-	-	-	-	8.0
6	3.5	36.3	6.5	10.7	2.6	-
9	-	25.0	-	-	-	-
11	-	16.3	-	-	-	-

Contd.

Time, hr.	Unoxidised dye, %					
	o-CL-Aniline	M-CL-Aniline	p-CL-Aniline	2:4-CL_2-Aniline	o-Anisidine	p-Anisidine
0.25	-	-	-	76.8	-	86.0
0.50	-	-	-	67.4	-	73.5
1	91.5	77.0	62.5	50.4	71.9	49.2
2	81.0	55.6	36.7	35.7	49.5	21.9
3.25	65.3	26.2	13.5	26.8	-	-
3.5	-	-	-	-	29.6	15.1
4	54.8	11.8	6.3	21.0	-	-
5	44.4	4.4	3.3	17.9	-	-
5.5	-	-	-	-	11.2	9.4
6	31.6	-	-	11.6	-	-
9	16.1	-	-	-	-	-
11	12.9	-	-	~~0~~	-	-

Contd.

Time, hr.	Unoxidised dye, %			
	Metanilic acid	Sulphanilic acid	Anthranilic acid	p-Aminobenzoic acid
1	81.3	83.0	86.9	86.5
2	61.9	64.9	77.0	74.4
3.5	41.9	46.4	69.8	62.6
5.5	11.0	17.9	55.9	44.0
7	-	8.3	48.4	34.8
10	-	-	38.1	21.3

Time	Unoxidised dye, %		
	Orange II.	Orange I	O-Methyl ether of Orange I.
5 min.	-	88.1	-
10 "	-	76.4	-
15 "	-	67.5	97.9
20 "	-	59.9	-
25 "	-	52.4	-
30 "	-	46.4	96.3
45 "	-	32.5	-
1 hr.	91.5	24.8	96.3
1.5 "	-	17.5	-
2 "	84.9	-	90.4
3 "	-	10.3	83.0
4 "	75.0	-	-
5 "	66.1	-	69.1
6 "	54.9	-	-
7 "	44.8	-	62.8
9 "	38.4	-	-
10 "	-	-	44.7
11 "	24.5	-	-
12 "	15.1	-	29.8
24 "	-	-	12.8

TABLE 10.

(iv) OXIDATION OF WATER SOLUBLE AZO DYES WITH DILUTE NITRIC ACID.

Dye		Unoxidised dye, %, after.				
		2 hr.	4 hr.	7 hr.	20 hr.	24 hr.
Aniline →	R-acid	91.6	76.6	55.3	27.4	23.5
o-Nitroaniline	"	100.0	100.0	99.0	96.6	96.6
m- "	"	98.4 (3 hr)	95.3 (6 hr)	93.0 (9 hr)	-	85.4
p- "	"	96.8	96.7	96.7	93.3	93.3
o-Chloroaniline	"	98.3	98.3	97.2	94.1	91.5
m- "	"	97.4	96.7	95.6	87.9	83.8
p- "	"	96.1 (3 hr)	92.2 (6 hr)	86.3 (9 hr)	81.4 (12 hr)	60.8
2:4-Dichloroaniline	"	97.7	97.7	97.3	93.5	92.4
m-Toluidine	"	95.0	90.0	81.0	47.4	41.6
p-Toluidine	"	65.0	36.3	20.8	4.4	-
o-Anisidine	"	83.8	74.5	63.5	47.2	42.1
p-Anisidine	"	9.2	5.3	-	-	-
Metanilic acid	"	96.2	95.5	94.4	88.0	88.0
Sulphanilic acid	"	98.4 (3 hr)	96.9 (6 hr)	94.2 (9 hr)	92.1 (12 hr)	87.5
Anthranilic acid	"	100.0 (3 hr)	98.8 (6 hr)	97.8 (9 hr)	-	95.6
p-Aminobenzoic acid	"	93.8 (3 hr)	88.7 (6 hr)	82.5 (9 hr)	79.4 (12 hr).	56.7

TABLE 11.

OXIDATION OF WATER-SOLUBLE AZO DYES WITH DILUTE NITRIC ACID (d).

Time, hr.	Unoxidised dye, %				
	Aniline→ R-acid	o-NO_2-aniline→R-acid	m-NO_2-aniline→R-acid	p-NO_2-aniline→R-acid	Orange II
0.25	87.9	-	-	-	88.8
0.50	73.3	-	-	-	75.7
0.75	63.4	-	-	-	64.2
1.00	59.0	-	-	-	53.5
1.25	-	-	-	-	44.5
1.50	48.8	-	-	-	34.9
1.75	-	-	-	-	28.0
2.00	42.0	-	-	-	21.3
2.25	-	-	-	-	16.1
2.50	38.8	-	-	-	11.5
2.75	-	-	-	-	8.7
3.00	34.0	97.8	89.9	94.0	-
4	28.6	-	-	-	-
5	27.2	-	-	-	-
6	22.3	98.5	81.9	91.3	-
9	-	98.5	72.2	89.0	-
13	-	-	58.2	83.8	-
18	-	-	47.8	78.5	-
24	-	97.8	40.2	74.7	-

Time	Unoxidised dye, %				
	o-CL-aniline→R-acid	*m*-CL-aniline→R-acid	*p*-CL-aniline→R-acid	2:4-CL-aniline→R-acid	*p*-Toluidine→R-acid
2.5 min.	-	-	-	-	88.5
5	-	-	-	-	78.9
7.5	-	-	-	-	69.7
10	-	-	-	-	60.8
15	-	-	-	-	50.5
30	-	-	91.5	-	35.0
1 hr.	-	-	82.5	-	24.8
1.5 "	-	-	-	-	20.2
2 "	-	-	68.0	-	15.4
3 "	96.6	-	56.0	-	8.9
4 "	-	72.7	47.2	89.7	-
5 "	-	-	40.2	-	-
6 "	92.6	63.1	32.5	86.8	-
8 "	-	54.1	-	84.2	-
14 "	-	-	14.0	-	-
18 "	-	-	7.0	-	-
20 "	61.4	-	-	-	-
24 "	48.9	23.8	4.2	50.0	-

E. OXIDATION OF DYES ON WOOL WITH CERIC SULPHATE.

The oxidation of soluble azo dyes was next studied on dyed wool. For this purpose 1% dyeings were produced on woollen cloth with various dyes. Samples of dyed wool (approx. 0.2 g.) were wetted out with Calsolene Oil HS (I.C.I.) - a proprietory wetting agent, washed with water, and kept at 25°C. in a 1:100 bath containing 0.05N ceric sulphate solution for various periods of time. They were then taken out, washed, dried and extracted with pyridine in a Soxhlet extraction apparatus. The extracts were made up to 100 c.c. and their colour density determined on the Spekker photoelectric absorptiometer. The results are given in Table 12 and plotted in Figs. 95-107.

TABLE 12.

OXIDATION OF DYES (1%) * ON WOOL WITH CERIC SULPHATE.

Dye	* % on wool found	Unoxidised dye, %					
		3 hr.	6 hr.	9 hr.	12 hr.	18 hr.	24 hr.
Orange II	0.62	59.6	34.8	20.1	12.3	10.0	5.5
Orange I	1.13	67.2	45.4	41.0	31.9	22.7	21.8
O-Methyl ether of above	1.11	73.6	51.5	37.6	30.8	18.8	14.3
Aniline ⟶ R-acid	0.94	61.5	38.9	29.5	17.4	12.6	7.8
o-Nitroaniline "	0.90	71.6	56.0	50.0	33.1	16.1	12.6
m- " "	0.74	77.2	62.9	54.0	36.0	23.3	15.4
p- " "	0.91	60.9	45.5	37.9	25.9	16.4	11.0
o-Chloroaniline "	0.97	71.1	51.0	40.9	28.2	16.2	12.1
m- " "	0.81	77.2	50.0	40.9	26.0	14.9	11.1
p-Chloroaniline "	0.73	79.0	59.3	42.3	35.0	21.3	13.7
2:4-Dichloroaniline ⟶ R-acid	0.84	92.4	78.7	65.9	49.5	39.7	28.1
p-Toluidine "	0.88	78.5	63.5	58.1	40.0	29.3	18.7
p-Anisidine "	0.99	66.0	44.5	33.3	21.5	13.6	8.3

F. EASE OF OXIDATION OF VARIOUS WATER-INSOLUBLE DYES.

The rate of nitrogen evolution was examined as a measure of ease of acid oxidation of azo dyes. The soluble dyes are much too rapidly acted upon in acid solution for this method to be used, but insoluble dyes can be employed.

A sample (0.1 g.) of the pure dye was ground up finely with a little water, and boiled in the modified Dumas apparatus with 120 c.c. of water containing 1 g. potassium dichromate and 2.5 concentrated sulphuric acid. The nitrogen evolved was measured after the boiling commenced. The results are given in Table 13, and illutrated in part by Fig. 108 and 109.

TABLE 13.

EASE OF OXIDATION OF WATER-INSOLUBLE DYES.

Dye	c.c. of N_2 evolved						Yield of (Azo group) Nitrogen after 30 min. (%)
	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	
Aniline → β Naphthol	0.30	4.10	7.50	9.10	9.70	9.80	98
o-Nitroaniline "	0.20	0.50	1.00	1.60	2.30	2.60	31
m-Nitroaniline "	0.10	0.45	0.80	1.05	1.20	1.40	16
p-Nitroaniline "	0.40	0.70	1.00	1.20	1.30	1.50	18
2:4-Dinitroaniline "	0.20	0.30	0.30	0.35	0.50	0.55	7
2:4-Dichloro- "	0.20	0.20	0.30	0.40	0.50	0.60	8
p-hydroxyazobenzene	0.20	3.00	4.20	5.20	5.60	5.90	44
p-Methoxyazobenzene	0.20	0.40	0.60	0.70	0.85	0.90	7
Azobenzene	-	-	-	-	-	-	Nil *

* Nitrogen not measured, but original sample recovered unchanged in weight after the experiment.

It is interesting to note that these dyes fall roughly into the order required by the hypothesis outlined above, though a complicating factor may be the particle size of the dyes. It was thought that if these insoluble dyes were brought into solution in some way, so that the solution would remain stable on adding aqueous solutions of oxidising agents, then perhaps the ease of oxidation could be studied in a similar manner to the ease of oxidation of soluble azo dyes.

Consequently, ethylene glycol mono-methyl ether, and Lissapol NX (I.C.I. Ltd.) - a proprietary dispersing agent, were found to be very successful in producing a clear dispersion on adding water to the solution of the dye in a water-miscible organic solvent. Phenylazo β-naphthol was found to be oxidised instantaneously on adding ceric sulphate. However, preliminary observations on the oxidation with hydrogen peroxide and potassium persulphate showed that there was no change in the strength of the colour after 24 hours, and so this line of work was not pursued further.

G. FADING EXPERIMENTS.

General Remarks.

In order to correlate the oxidation of dyes in solution with light fading, a series of exposure tests were carried out. These were made with dyes prepared from aniline and its simple derivatives coupled with β-naphthol, α-naphthol, three typical Brenthols, R-acid and Oxy-L-acid, respectively. Several other dyes, e.g. Orange II, Orange I and its O-methyl ether, were also tested for their light fastness. These dyes were exposed in graded depths on substrates of wool, cellulose (cotton and filter paper), unglazed tile and anodised aluminium. The last two materials were chosen to represent inert substrates. The various methods of application of the dyes are given below.

(1) Acid dyes on wool:

Wool (1 g.) was dyed as usual from a 1:100 bath containing the requisite quantity of the dye, 1.5 c.c. of 5% sodium sulphate solution and 2.7 c.c. of sulphuric acid (1%).

(2) Brenthol - Fast Base combinations on cotton:

Mercerised cotton sateen was wetted out with water and worked in the Brenthol solution for 15 minutes, the material-liquor ratio being 1:20. It was hand-squeezed and then developed with a 1% solution of the diazotised base for 30 minutes. The dyeings were then treated at the boil with an anionic detergent, Lissapol C (approx. 5/1000), and soda-ash (approx/

(approx. 5/1000) for fifteen minutes.

(3) Soluble and insoluble azo dyes on filter paper.

Strips of filter paper (10 cm. x 1.5 cm.) were dipped in the solutions of the dyes in water or the organic solvents specified in the Tables below. In the case of soluble dyes, the strips were taken out immediately and air-dried, but in the case of insoluble dyes, they were pressed between clean filter paper and carefully dried over a flame.

(4) Soluble and insoluble azo dyes on unglazed tile:

The surface of the tile was cleaned by emery-paper, and the solution of the dye was applied to it by a small paint brush. The tile was then allowed to dry in the air.

(5) Acid dyes on anodised aluminium:

Strips of anodised aluminium (5 cm. x 1 cm.) obtained by the Sulphuric Acid method, were dyed at 25°C. in 15 c.c. of 0.02% solutions of the dyes for 24 hours, after which they were removed, washed with water and dried at 105°C.

Exposure to light.

The fading of Orange I (and its methyl ether) and Orange II; several of the dyes from R-acid* all those from β-naphthol and the Brenthols was carried out by exposure to daylight. The samples were mounted on cardboard by stapling, and after covering half of each sample by another piece of cardboard, they were exposed to daylight behind a well-ventilated glass frame. The Society of Dyers' and Colourists' Standards

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* All those from aniline, nitro- and chloro-anilines.

(B.S. 1006, British Standards Institution) graded in light fastness on a 1 to 8 scale were used side by side for comparison. These standards are so graded that the fading of each standard is half as rapid as that of the one preceding it. The judging of the samples was done when the standard showed a just perceptible change in shade, and the light fastness figures given accordingly. Since more experiments on fading were carried out in the winter months, recourse had to be made to the use of an artificial source of fading. For this purpose, a patent Photo-Copying Frame (J. Halden & Co. Ltd., Manchester), as shown in the photograph, was used quite successfully. The samples mounted as above were hung by thread on the inside of a large cylinder (about 20 in. diameter). The source of light was from a carbon arc, situated in the middle of the cylinder. The number of hours required for fading of a standard increased by approximately twice as much as that required for a standard preceding it. The temperature inside the cylinder was in the region of 40°C. The relative humidity, as determined by the hair hygrometer ("Edney" type) was about 30%. The temperature of a woollen pattern, as roughly measured by placing it round the thermometer bulb during exposure, was 50°C. In spite of these conditions of rather high temperature and low humidity, the fading of the standard series of patterns was in the correct order. Further, all the tests were exposed under the same conditions and so are comparable amongst themselves.

Some/

Some of the insoluble dyes were also examined for their light fastness in oil medium by kindness of Messrs. James Anderson & Co. (Colours) Ltd. The dyes were prepared in a finely dispersed form by dissolving the crystallised dyes in concentrated sulphuric acid and precipitating in water, dried, and spread on paper after rubbing out in lithol varnish. The resistance to fading was determined by exposure to a Fadeometer, using madder as the Standard. The results, in decreasing order of fastness, are given in Table 14. They are in general agreement with the postulated hypothesis.

TABLE 14.

Dye	Light Fastness (madder = 10) (not all exactly assessed).
2:4-Dinitroaniline → β-naphthol	10
2:4-Dinitroaniline → α-naphthol	
p-Nitroaniline → β-Naphthol	8
p-Hydroxyazobenzene.	
p-Methoxyazobenzene.	
o-Nitroaniline → β-Naphthol	6-7
Aniline → β-Naphthol	
m-Nitroaniline → β-Naphthol	
Aniline → α-Naphthol	
2:4-Dichloroaniline → β-Naphthol	

TABLE 15.

(i) LIGHT FASTNESS OF WATER-SOLUBLE AZO DYES ON WOOL.

Dye	Light Fastness		Dye	Light Fastness	
Orange II	(0.25%)	3	p-Nitroaniline→R-acid	(0.25%)	3
"	(1%)	4-5	"	(1%)	4-5
"	(2%)	5	"	(2%)	4-5
Orange I	(0.25%)	2-3	o-Chloroaniline "	(0.25%)	1
"	(1%)	3	"	(1%)	1-2
"	(2%)	3-4	"	(2%)	2
O-Methyl ether of Orange I	(0.25%)	3	m-Chloroaniline "	(0.25%)	4
"	(1%)	3-4	"	(1%)	5
"	(2%)	4	"	(2%)	5-6
Aniline → R-acid	(0.25%)	5	p-Chloroaniline "	(0.25%)	4-5
"	(1%)	6	"	(1%)	6
"	(2%)	>6	"	(2%)	6
o-Nitroaniline "	(0.25%)	2-3	2:4-Dichloroaniline → R-acid	(0.25%)	1
"	(1%)	3	"	(1%)	1-2
"	(2%)	3	"	(2%)	1-2
m-Nitroaniline → R-acid	(0.25%)	3	m-Toluidine → R-acid	(1%)	>6
"	(1%)	4-5	"	(2%)	>6
"	(2%)	4-5	p-Toluidine "	(1%)	>6

Dye		Light Fastness	Dye		Light Fastness
p-Toluidine → R-acid	(2%)	>6	o-Nitroaniline→Oxy-L-acid	(1%)	5
o-Anisidine "	(1%)	4	"	(2%)	>5
"	(2%)	>5	m-Nitroaniline "	(1%)	>5
p-Anisidine "	(1%)	5	"	(2%)	>5
"	(2%)	>5	p-Nitroaniline "	(1%)	4-5
R-acid←Dianisidine→ R-acid	(1%)	2-3	" "	(2%)	>5
"	(2%)	2-3	o-Chloroaniline "	(1%)	4
Metanilic acid→ R-acid	(1%)	>6	" "	(2%)	5
"	(2%)	>6	m-Chloroaniline "	(1%)	4
Sulphanilic acid→ R-acid	(1%)	>6	" "	(2%)	5
"	(2%)	>6	p " "	(1%)	4
Anthranilic acid→ R-acid	(1%)	>5	" "	(2%)	5
"	(2%)	>5	2:4-Dichloroaniline "	(1%)	4
p-Aminobenzoic acid→ R-acid	(1%)	>5	" "	(2%)	4
"	(2%)	>5	m-Toluidine "	(1%)	>5
Aniline→Oxy-L-acid	(1%)	>5	" "	(2%)	>5
"	(2%)	>5	p-Toluidine "	(1%)	>5

Dye	Light Fastness	Dye	Light Fastness
p-Toluidine → Oxy-L-acid	(2%) >5	p-Aminobenzoic acid → Oxy-L-acid	(1%) >5
o-Anisidine "	(1%) >5	"	(2%) >5
" "	(2%) >5	Naphthionic acid → phenol	(1%) >5
p-Anisidine "	(1%) >5	"	(2%) >5
" "	(2%) >5	O-Methyl ether of above dye	(1%) >5
Metanilic acid "	(1%) >5	"	(2%) >5
" "	(2%) >5	Sulphanilic acid → phenol	(1%) 5
Sulphanilic acid "	(1%) 4-5	"	(2%) 5-6
" "	(2%) >5	O-Methyl ether of above dye	(1%) 5
Anthranilic acid "	(1%) >5	"	(2%) 5-6
" "	(2%) >5	Sulphanilic acid → Guaiacol	(1%) 4
		"	(2%) 4

TABLE 16.

(ii) LIGHT FASTNESS OF WATER-SOLUBLE AZO DYES ON PAPER.

Dye	Light Fastness		Dye	Light Fastness	
Orange II	(0.1%)	1	p-Nitroaniline →R-acid	(0.1%)	4-5
"	(0.5%)	2		(0.5%)	4
"	(1%)	2	"	(1%)	4
Orange I	(0.1%)	1	o-Chloroaniline "	(0.1%)	1
"	(0.5%)	1	"	(0.5%)	2
"	(1%)	1	"	(1%)	2
O-Methyl ether of Orange I	(0.1%)	3	m-Chloroaniline "	(0.1%)	4
"	(0.5%)	3	"	(0.5%)	3
"	(1%)	3	"	(1%)	3
Aniline →R-acid	(0.1%)	3	p-Chloroaniline "	(0.1%)	4-5
"	(0.5%)	2-3	"	(0.5%)	4
"	(1%)	2-3	"	(1%)	4
o-Nitroaniline "	(0.1%)	3-4	2:4-Dichloroaniline "	(0.1%)	1
"	(0.5%)	3	"	(0.5%)	1
"	(1%)	3	"	(1%)	1
m-Dinitroaniline	(0.1%)	3-4	m-Toluidine → R-acid	(0.1%)	3-4
"	(0.5%)	3	"	(0.5%)	3-4
"	(1%)	3	"	(1%)	4

Dye	Light Fastness	Dye	Light Fastness
p-Toluidine → R-acid	(0.1%) 2-3	Anthranilic acid → R-acid	(0.1%) 3
"	(0.5%) 2-3	"	(0.5%) 3-4
"	(1%) 3	"	(1%) 3-4
o-Anisidine "	(0.1%) 3-4	*p*-Aminobenzoic acid "	(0.1%) 4-5
" "	(0.5%) 3-4	"	(0.5%) 4-5
" "	(1%) 2	"	(1%) 5
p-Anisidine "	(0.1%) 2	Aniline → Oxy-L-acid	(0.1%) 2
" "	(0.5%) 3-4	"	(0.5%) 2-3
" "	(1%) 3-4	"	(1%) 3
R-acid ← Dianisidine → R-acid	(0.1%) 1	*o*-Nitroaniline "	(0.1%) 2
"	(0.5%) 1	"	(0.5%) 2
"	(1%) 1	"	(1%) 3
Metanilic acid → R-acid	(0.1%) 4	*m*-Nitroaniline "	(0.1%) 1
"	(0.5%) >5	"	(0.5%) 1
"	(1%) >5	"	(1%) 1
Sulphanilic acid "	(0.1%) 5	*p*-Nitroaniline "	(0.1%) 2
"	(0.5%) >5	"	(0.5%) 2
"	(1%) >5	"	(1%) 2

Dye	Light Fastness	Dye	Light Fastness
o-Chloroaniline→Oxy-L-acid	(0.1%) 1	o-Anisidine→Oxy-L-acid	(0.1%) 1
" "	(0.5%) 1	" "	(0.5%) 2
" "	(1%) 2	" "	(1%) 2
m " "	(0.1%) 1	p- " "	(0.1%) 1
" "	(0.5%) 1	" "	(0.5%) 2
" "	(1%) 1	" "	(1%) 2
p-Chloroaniline "	(0.1%) 1	Metanilic acid "	(0.1%) 2
" "	(0.5%) 1	" "	(0.5%) 2-3
" "	(1%) 1	" "	(1%) 2-3
2:4-Dichloroaniline "	(0.1%) 1	Sulphanilic acid "	(0.1%) 2
" "	(0.5%) 1	" "	(0.5%) 3-4
" "	(1%) 1	" "	(1%) 4
m-Toluidine "	(0.1%) 1	Anthranilic acid "	(0.1%) 2
" "	(0.5%) 2	" "	(0.5%) 2
" "	(1%) 2	" "	(1%) 3
p-Toluidine "	(0.1%) 1	p-Aminobenzoic acid→ Oxy-L-acid	(0.1%) 2
" "	(0.5%) 2	" "	(0.5%) 2
" "	(1%) 2	" "	(1%) 2
Napthionic acid→ phenol	(0.1%) 4	Sulphanilic acid→phenol	(0.1%) >5
" "	(0.5%) 4	O-Methyl ether of above	(1%) >5
" "	(1%) 4		

Dye		Light Fastness	Dye		Light Fastness
O-Methyl ether of Naphthionic acid —> phenol	(0.1%)	4	Sulphanilic acid—>Guaiacol	(0.1%)	3-4
"	(0.5%)	4	"	(0.5%)	4
"	(1%)	4	"	(1%)	4

The % represents the concentration of the dye solution used.

TABLE 17.

(iii) LIGHT FASTNESS OF WATER SOLUBLE AZO DYES ON TILE.

Dye	Light Fastness	Dye	Light Fastness
Orange II	(1%) 2	*p*-Chloroaniline → R-acid	(1%) 2
"	(2%) 1-2	"	(2%) 2
Orange I	(1%) 1	2:4-Dichloroaniline "	(1%) 2
"	(2%) 1	"	(2%) 2-3
O-Methyl ether of Orange I	(1%) 4-5	*m*-Toluidine "	(1%) 1
"	(2%) 4-5	"	(2%) 1
Aniline → R-acid	(1%) 1	*p*-Toluidine "	(1%) 1
" "	(2%) 1-2	" "	(2%) 2
o-Nitroaniline "	(1%) 3	*o*-Anisidine "	(1%) 1
" "	(2%) 3	" "	(2%) 1-2
m " "	(1%) 2	*p*-Anisidine "	(1%) 3-4
" "	(2%) 2	" "	(2%) 3-4
p " "	(1%) 4	R-acid ← Dianisidine → R-acid	(1%) 1
" "	(2%) 4	" "	(2%) 1
o-Chloroaniline "	(1%) 1	Metanilic acid "	(1%) 4-5
" "	(2%) 1	" "	(2%) 4-5
m-Chloroaniline "	(1%) 1	Sulphanilic acid "	(1%) 3-4
" "	(2%) 1	" "	(2%) 3-4

Dye	Light Fastness	Dye	Light Fastness
Anthranilic acid→R-acid	(1%) 1-2	2:4-Dichloroaniline → Oxy-L-acid	(1%) 1
" "	(2%) 1-2	" "	(2%) 2-3
p-Aminobenzoic acid "	(1%) 1-2	m-Toluidine "	(1%) 1
" "	(2%) 1-2	" "	(2%) 2-3
Aniline → Oxy-L-acid	(1%) 2	p " "	(1%) 2
" "	(2%) 4	" "	(2%) 3
o-Nitroaniline "	(1%) 2	o-Anisidine "	(1%) 2
" "	(2%) 5	" "	(2%) 3
m- " "	(1%) 2	p-Anisidine "	(1%) 2
" "	(2%) 3-4	" "	(2%) 3
p- " "	(1%) 2	Metanilic acid "	(1%) 4-5
" "	(2%) 2-3	" "	(2%) 4-5
o-Chloroaniline "	(1%) 2	Sulphanilic acid "	(1%) 4
" "	(2%) 3-4	" "	(2%) 4
m " "	(1%) 2	Anthranilic acid "	(1%) 3
" "	(2%) 3	" "	(2%) 3
p " "	(1%) 2	p-Aminobenzoic acid "	(1%) 3
" "	(2%) 2	" "	(2%) 3
Naphthionic acid→phenol	(1%) 1	Sulphanilic acid→phenol	(1%) 1-2
" "	(2%) 1	" "	(2%) 1-2

Dye	Light Fastness	Dye	Light Fastness
O-Methyl ether of Naphthionic acid → Phenol (1%)	1	O-Methyl ether of Sulphanilic acid → Phenol (1%)	1-2
" (2%)	1	" (2%)	1-2
		Sulphanilic acid → Guaiacol (1%)	1
		" (2%)	1

TABLE 18

(iv) LIGHT FASTNESS OF WATER-SOLUBLE AZO DYES ON ANODISED ALUMINIUM.

Dye	Light Fastness	Dye	Light Fastness
Orange II	2	Anthranilic acid → R-acid	3
Orange I	1	p-Aminobenzoic acid "	4
O-Methyl ether of Orange I	4	Aniline → Oxy-L-acid	3
Aniline → R-acid	2	o-Nitroaniline "	3
o-Nitroaniline "	2	m- " "	2
m- " "	2	p- " "	1
p-Nitroaniline "	2	o-Chloroaniline "	1
o-Chloroaniline "	1	m-Chloroaniline "	1
m- " "	2	p- " "	1
p- " "	1	2:4-Dichloroaniline "	1-2
2:4-Dichloroaniline "	1	m-Toluidine "	1
m-Toluidine "	2	p-Toluidine "	3
p-Toluidine "	1	o-Anisidine "	1
o-Anisidine "	2	p-Anisidine "	2
p-Anisidine "	1	Metanilic acid "	1
$(\text{R-acid})_2$ ← Dianisidine "	1	Sulphanilic acid "	1
Metanilic acid → R Acid	3	Anthranilic acid "	2
Sulphanilic acid "	1-2	p-Aminobenzoic acid "	1

TABLE 19.

(v) LIGHT FASTNESS OF BRENTHOL - FAST BASE COMBINATIONS ON MERCERISED COTTON SATEEN.

Brenthol	Base	Light Fastness	Brenthol	Base	Light Fastness
AS(0.05%	Aniline	3	AS(0.05%)	p-Chloroaniline	4
" (0.2%)	"	4	" (0.2%)	"	4
" (0.7%)	"	4	" (0.7%)	"	5
AS(0.05%)	o-Nitroaniline	4-5	AS(0.05%)	2:4-Dichloroaniline	4
" (0.2%)	"	5	" (0.2%)	"	4
" (0.7%)	"	5	" (0.7%)	"	5
AS(0.05%)	m-Nitroaniline	5	AS(0.05%)	p-Toluidine	3-4
" (0.2%)	"	5	" (0.2%)	"	3-4
" (0.7%)	"	5-6	" (0.7%)	"	4
AS(0.05%)	p-Nitroaniline	5	FR(0.05%)	Aniline	4
" (0.2%)	"	5	" (0.2%)	"	4
" (0.7%)	"	5	" (0.7%)	"	4
AS(0.05%)	2:4-Dinitroaniline	5	FR(0.05%)	o-Nitroaniline	4-5
" (0.2%)	"	5	" (0.2%)	"	5
" (0.7%)	"	5-6	" (0.7%)	"	5-6
A S(0.05%)	o-Chloroaniline	4	FR(0.05%)	m-Nitroaniline	4
" (0.2%)	"	4	" (0.2%)	"	4-5
" (0.7%)	"	4-5	" (0.7%)	"	5-6
AS (0.05%)	m-Chloroaniline	4	FR(0.05%)	p-Nitroaniline	4
" (0.2%)	"	4-5	"(0.2%)	"	4-5
" (0.7%)	"	5	"(0.7%)	"	5

Brenthol	Base	Light Fastness	Brenthol	Base	Light Fastness
FR(0.05%)	2:4-Dinitroaniline	4-5	OT(0.05%)	*o*-Nitroaniline	4
" (0.2%)	"	5	" (0.2%)	"	5
" (0.7%)	"	5	" (0.7%)	"	6
FR(0.05%)	*o*-Chloroaniline	4	OT(0.05%)	*m* "	4-5
" (0.2%)	"	4-5	" (0.2%)	"	4-5
" (0.7%	"	5	" (0.7%)	"	5
FR(0.05%)	*m*- "	4	OT(0.05%)	*p*- "	5
" (0.2%)	"	4-5	" (0.2%)	"	5
" (0.7%)	"	5	" (0.7%)	"	5
FR(0.05%)	*p*- "	4	OT(0.05%)	2:4-Dinitroaniline	4-5
" (0.2%)	"	4	" (0.2%)	"	6
" (0.7%)	"	4-5	" (0.7%)	"	6
FR(0.05%)	2:4-Dichloroaniline	4	OT(0.05%)	*o*-Chloroaniline	4
" (0.2%)	"	4	" (0.2%)	"	4
" (0.7%)	"	5-6	" (0.7%)	"	5
FR(0.05%)	*p*-Toluidine	4	OT(0.05%)	*m*- "	4
" (0.2%)	"	4	" (0.2%)	"	5
" (0.7%)	"	5	" (0.7%)	"	5
OT(0.05%)	Aniline	4	OT(0.05%)	*p*-Chloroaniline	4
" (0.2%)	"	4	" (0.2%)	"	5
" (0.7%)	"	4-5	" (0.7%)	"	5

Brenthol	Base	Light Fastness	Brenthol	Base	Light Fastness
OT (0.05%)	2:4-Dichloroaniline	4	OT(0.05%)	p-Toluidine	4
" (0.2%)	"	4	" (0.2%)	"	4
" (0.7%)	"	4-5	" (0.7%)	"	4-5

TABLE 20.

(vi) LIGHT FASTNESS OF WATER-INSOLUBLE AZO DYES ON PAPER.

Dye	Light Fastness	Dye	Light Fastness
Aniline →β-Naphthol	(0.1%) 1	o-Chloroaniline→β-Naphthol	(0.1%) 1
" (Ac)	(0.5%) 2	" (Ac)	(0.5%) 1-2
"	(1%) 2	"	(1%) 2
o-Nitroaniline →β-Naphthol	(0.1%) 3	m- " →β-Naphthol	(0.1%) 1
" (Ac)	(0.5%) 3-4	" (Ac)	(0.1%) 2
"	(1%) 3-4	"	(1%) 3
m-Nitroaniline →β-Naphthol	(0.1%) 2-3	p- " →β-Naphthol	(0.1%) 1
" (Tol)	(0.5%) 2-3	" (Ac)	(0.5%1-2
"	(1%) 3	"	(1%) 1-2
p-Nitroaniline →β-Naphthol	(0.1%) 2-3	2:4-Dichloroaniline →β-Naphthol	(0.1%) 1
" (Pyr)	(0.5%) 3	" (Ac)	(0.5%) 1
"	(1%) 3	"	(1%) 1
2:4-Dinitroaniline→β Naphthol	(0.1%) 5	p-Toluidine →β-Naphthol	(0.1%) 2
" (N.B.)	(0.5%) 5	" (B)	(0.5%) 3
"	(1%) 5	"	(1%) 3
o-Anisidine→β-Naphthol	(0.1%) 1	2:-4-Dinitroaniline→α-Naphthol	(0.1%) 3
" (B)	(0.5%) 1	" (NB)	(0.5%) 3
"	(1%) 1	"	(1%) 4

Dye	Light Fastness	Dye	Light Fastness
p-Anisidine→β-Naphthol	(0.1%) 2	*o*-Chloroaniline→α-Naphthol	(0.1%) 1
" (B)	(0.5%) 3-4	" (B)	(0.5%) 1
"	(1%) 3-4	"	(1%) 1
Aniline → α-Naphthol	(0.1%) 1	*m*-Chloroaniline→α-Naphthol	(0.1%) 1
" (Ac)	(0.5%) 1	" (D)	(0.5%) 1
"	(1%) 1	"	(1%) 1
o-Nitroaniline "	(0.1%) 4	*p*-Chloroaniline "	(0.1%) 1
" (D)	(0.5%) 4	" (B)	(0.5%) 1
"	(1%) 4	"	(1%) 1-2
m-Nitroaniline "	(0.1%) 1	2:4-Dichloroaniline →α-Naphthol	(0.1%) 1
" (D)	(0.5%) 1	" (B)	(0.5%) 2
"	(1%) 1-2	"	(1%) 2
p-Dinitroaniline→ α-Naphthol	(0.1%) 2	*p*-Toluidine →α-Naphthol	(0.1%) 1
" (D)	(0.5%) 3	" (NB)	(0.5%) 2
"	(1%) 3	"	(1%) 2

Dye	Light Fastness	Dye	Light Fastness
o-Anisidine $\rightarrow$ α-Naphthol	(0.1%) 1	p-Anisidine$\rightarrow$$\alpha$-Naphthol	(0.1%) 1
" (B)	(0.5%) 1	" (B)	(0.5%) 1
"	(1%) 1	"	(1%) 1-2

The % represents the concentration of the dye solution used. The symbols in brackets represent the solvents used for dissolving the dyes.

Ac = Glacial acetic acid

B = Benzene

D = Dioxane

NB = Nitrobenzene

Pyr = Pyridine

Tol = Toluene.

TABLE 21

(vii) LIGHT FASTNESS OF WATER-INSOLUBLE AZO DYES ON TILE.

Dye			Light Fastness	Dye			Light Fastness
Aniline	→ β- Naphthol	(1%)	4	2:4-Dichloroaniline	→ β- Naphthol	(1%)	4-5
"		(2%)	4	"		(2%)	5
o-Nitroaniline	"	(1%)	5-6	p-Toluidine	"	(1%)	2-3
"	"	(2%)	5-6	"	"	(2%)	2-3
m-Nitroaniline	"	(1%)	5	o-Anisidine	"	(1%)	2
"	"	(2%)	>5	"	"	(2%)	2-3
p-Nitroaniline	"	(1%)	5	p-Anisidine	"	(1%)	4
"	"	(2%)	>5	"	"	(2%)	>4
2:4-Dinitroaniline	"	(1%)	>5	Aniline	→ α - naphthol	(1%)	>4
"	"	(2%)	>5	"	"	(2%)	>4
o-Chloroaniline	"	(1%)	4	o-Nitroaniline	"	(1%)	4
"	"	(2%)	4-5	"	"	(2%)	4-5
m-Chloroaniline	"	(1%)	4-5	m-~~Chloro~~ Nitro aniline	"	(1%)	2
"	"	(2%)	4-5	"	"	(2%)	3
p-Chloroaniline	"	(1%)	4	p-Nitroaniline	"	(1%)	4
"	"	(2%)	4-5	"	"	(2%)	4
2:4-Di ~~chloro~~ ~~nitro~~ nitro aniline	"	(1%)	4	2:4-Dichloroaniline	"	(1%)	3
"	"	(2%)	4	"	"	(2%)	3

Dye	Light Fastness	Dye	Light Fastness
o-Chloroaniline→α-Naphthol	(1%) 2-3	*p*-Toluidine→α-Naphthol	(1%) 3
" "	(2%) 4	" "	(2%) 3
m-Chloroaniline "	(1%) 2-3	*o*-Anisidine "	(1%) 2-3
" "	(2%) 4	" "	(2%) 3
p-Chloroaniline "	(1%) 3	*p*-Anisidine "	(1%) 3
" "	(2%) 3	" "	(2%) 4

The % represents the concentration of the dye solution. The dyes were dissolved in the same solvents as mentioned in Table 20.

DISCUSSION.

(ii) General:

~~Chemical~~ Thermal Oxidation:

The present work has confirmed the similarity of the products (initially a quinone and a diazonium compound) obtained from azo dyes by oxidising with a variety of aqueous oxidising agents. The action of dilute nitric acid on Orange II, however, seems to be different, because neither β-naphthaquinone, nor phthalic acid, nor their nitro-derivatives could be detected, but a nitro β-naphthol derivative(s) seemed to be formed. The values of the rates of oxidation of Orange I and its O-methyl ether by alkaline hydrogen peroxide (Fig. 39) and by potassium persulphate show that the O-methyl ether of Orange I~~I~~,* which can exist only in the azo form, is much more resistant to ~~chemical~~ thermal oxidation than Orange I, thus supporting the postulated hypothesis that the initial rate-determining step in the oxidation is hydrolysis of the hydrazone form of the dye. Two more ethers of the dye, obtained by coupling diazotised naphthionic acid and sulphanilic acid, respectively, with phenol were prepared. These and their parent dyes, however, were found to be totally resistant to the action of two oxidising agents which were tried.

In order to confirm or disprove the general hypothesis, several dyes containing nitro, chloro, methyl, methoxy, sulphonic and carboxyl groups in various positions in the phenyl ring/

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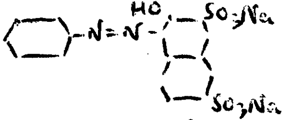
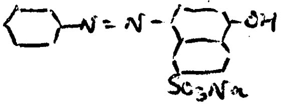
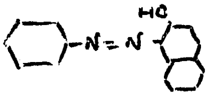
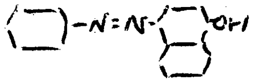
* It should be noted, however, that the sample of the ether employed was somewhat impure, being included in Class 2.

ring in the following parent dyes, were prepared:









The oxidation of a dye is presumed to be a bimolecular reaction, but since of the of the reactants, viz. the oxidising agent, is present in very large excess, the amount used up in the course of the reaction is negligible in comparison with the total, so that the concentration may be regarded as remaining constant throughout, and the reaction tends to be of the first order. The specific reaction rate, k, is given by the following equation:

$$t = \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a - x)$$

where a is the initialconcentration, and (a-x) the concentration at time t. Since the first term on the right hand side is constant, it follows that for a reaction of the first order the plot of t against log (a - x) should be linear; the slope of the line is given by $-2.303/k$, thus enabling the specific reaction rate to be evaluated.

The reaction rates, calculated for oxidation of dyes in aqueeus solution with a variety of oxidising agents, and of dyes (1%) on wool, with ceric sulphate, are given in Table 23, a~~s~~long with the reaction rate figures given by Kienle *et al* (39) for light fading of dyed wool. In the case of potassium persulphate/

persulphate the oxidation, with most of the dyes, seemed to proceed with two successive velocities. The final stage of oxidation was, as a rule, quicker than the initial stage. Kienle's figures were calculated as the average rates over an 80-hour exposure period on the basis of a first-order reaction.

The data given in Table 23 have been divided amongst groups of dyes of arbitrarily chosen categories as given below, because many of the dyes were not entirely pure samples (See Appendix, Table 24), though the impurity is very probably in each case either inorganic salt or firmly bound water.

Class 1 - Purity (on a moisture-free basis) above 95%

Class 2 - Purity (on a moisture-free basis) between 85% and 95%

Class 3 - Purity (on a moisture-free basis) below 85%

It would be expected that relationships between the data in Class 1 will be more reliable than in Classes 2 or 3. However, results of oxidation of a typical dye, viz. p-chloroaniline ⟶ R-acid, with neutral hydrogen peroxide and potassium persulphate, respectively, showed that addition of 20 mg. of sodium chloride to 100 c.c. of dye and oxidising agent mixture (an amount about five times the maximum likely to be present as impurity) has no effect on the reaction rates.

Light Fastness of insoluble dyes.

The three dyes made by coupling β-naphthol with o-nitroaniline, p-nitroaniline and 2:4-dinitroaniline respectively, are manufactured commercially as pigments and rated (104) as

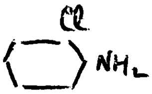
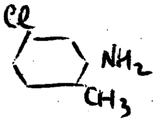
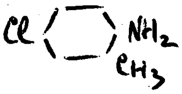
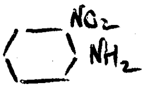
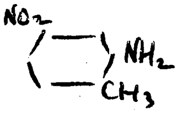
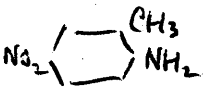
"good/

"good," "fair," and "excellent," respectively, in light fastness. This grading is in exact agreement with the anticipated order.

The commercial light fastness assessments for a number of Brenthol-Fast Base combinations are available (105) and are given in Table 22. In the second column, figures are given for a series of many depths of shade. In this case, figures for only three Brenthols common to all the bases are available. Those representing depths between 0.35 and 1.5 parts of Brenthol per 100 parts of material have been averaged; thus each figure in the column represents a mean of fourteen light fastness figures. The data are unfortunately limited in that they do not include aniline or any derivative of it containing only electron-repelling substituents, but the nitro compounds do show a general agreement with the present hypothesis. The figure for the corresponding aniline dye, as determined in the present work, is added for comparison. Further results, in the present work, have confirmed the trend of these figures.

TABLE 22.

LIGHT FASTNESS OF INSOLUBLE AZO DYES.

Fast Base	Constitution (106)	Mean Light Fastness	
		Sixteen Brentholds	Three Brentholds (AN, BT, FO)
Yellow GC		4.75	3.66
Red KB		4.78	4.57
Red TR		4.34	4.29
Orange GR		5.63	5.36
Scarlet G		4.72	4.75
Red RL		5.56	5.25
	(Aniline)	4.0 (3 Brentholds)	

In the present work, the light fastness of both soluble and insoluble dyes was determined by exposures in graded depths on substrates of wool, cellulose (cotton and filter paper), unglazed tile and anodised aluminium. The last two materials were chosen in the hope that they might be inert substrates. The percentage shades of the dyeings were calculated from the amount of 100% pure dye employed.

The mean light fastness figures on various substrates are given in Table 26 (Appendix). The overall mean results of light fastness tests of all dyes of o-hydroxyazo structure, except R-acid dyes on wool, when exposed in various depths of shade on a variety of substrates, are shown in Table 28 (Appendix).

The figures after the decimal points, shown in the light fastness data in various tables, are not considered very significant, since such data represent the mean values for two or three depths of shade only, intermediate gradings being assigned half-values; thus, Grade 2-3 is reckoned as 2.5, and so on.

TABLE 23.

REACTION RATES OF WATER-SOLUBLE AZO DYES.

(Classified on purity basis).

Dye	Reaction rate (in solution) (10^{-6}sec.$^{-1}$).					Reaction rate (on wool) 10^{-6}sec^{-1}	Reaction rate(on wool) Kienle 10^{-6}sec^{-1}
	Neutral H_2O_2	Alkaline H_2O_2	$K_2S_2O_8$	Dilute HNO_3	Dilute HNO_3(d)	Ceric Sulphate	Light
Class 1.							
Orange II	7.11	-	30.1 82.5	-	614.0 149.0	49.2	-
Orange I	2.13	-	394.0 120.0	-	-	26.0	-
o-Nitro-aniline → R-acid	17.07	49.9	66.6 53.3	nil	nil	24.0	4.70
m "	10.31	24.3	128.0	1.78	3.41	21.3	(2.41)
p "	12.09	51.2	53.3 87.4	0.89	10.70	27.6	(3.02)
o-Chloro-aniline → R-acid	16.73	30.5	50.8 101.3	0.93	7.80	27.5	7.10
p "	12.80	28.8	44.8 96.1	4.48	50.10	23.3	2.55
2:4-Dichloroaniline → R-acid	17.07	56.5	55.4 121.6	0.93	6.90	15.3	-
o-Anisidine → R-acid	6.75	76.8	42.9 119.0	9.06	-	-	2.41
Aniline → Oxy-L-acid	6.04	-	104.0 168.0	-	-	-	-

Dye	Reaction rate (in solution) (10^{-6} sec.$^{-1}$)					Reaction rate (on wool) 10^{-6} sec^{-1}	Reaction rate (on wool) Kienle *et al.* 10^{-6} sec^{-1}
	Neutral H_2O_2	Alkaline H_2O_2	$K_2S_2O_8$	Dilute HNO_3	Dilute HNO_3(d)	Ceric Sulphate	Light
m-Chloro-aniline → Oxy-L-acid	4.97	-	81.9 199.0	-	-	-	-
m-Toluidine → Oxy-L-acid	1.78	-	83.2 159.0	-	-	-	-
p-Toluidine → Oxy-L-acid	2.35	-	126.0	-	-	-	-
o-Anisidine → Oxy-L-acid	1.21	-	102.0	-	-	-	-
Sulphanilic acid → phenol	nil	-	nil	-	-	-	-
O-Methyl ether of above dye	nil	-	nil	-	-	-	-
Class 2.							
O-Methyl ether of Orange I	nil	-	24.0	-	-	26.7	-
Aniline → R-acid	8.53	33.5	51.2	16.80	43.2	40.9	2.09
m-Chloro-aniline → R-acid	9.24	60.8	42.7 86.4	1.87	21.3	29.9	2.70
p-Toluidine → R-acid	7.82	27.1	62.4 104.5	64.20	595.0	19.2	2.15
Metanilic acid → R-acid	3.20	20.0	67.2 140.0	1.87	-	-	2.09

Dye	Reaction rate (in solution) (10^{-6} sec.$^{-1}$)					Reaction rate (on wool) 10^{-6} sec.$^{-1}$	Reaction rate (on wool). Kienle et al. 10^{-6} sec^{-1}
	Neutral H_2O_2	Alkaline H_2O_2	$K_2S_2O_8$	Dilute HNO_3	Dilute HNO_3(d)	Ceric Sulphate	Light
Anthranilic acid → R-acid	3.20	10.4	48.0 132.0	0.53	-	-	1.00
o-Nitroaniline → Oxy-L-acid	5.69	-	45.6	-	-	-	-
m-Nitroaniline → Oxy-L-acid	2.49	-	112.0	-	-	-	-
Metanilic acid → Oxy-L-acid	2.49	-	72.0 156.0	-	-	-	-
Anthranilic acid → Oxy-L-acid	6.40	-	26.9	-	-	-	-
p-Aminobenzoic acid → Oxy-L-acid	1.92	-	43.5	-	-	-	-
Naphthionic acid → phenol	nil	-	nil	-	-	-	-
O-Methyl ether of above dye	nil	-	nil	-	-	-	-
Class 3							
m-Toluidine → R-acid	5.12	31.4	67.8 64.0	10.70	-	-	2.09
p-Anisidine → R-acid	2.13	28.3	93.2	240.0	-	32.9	2.78

Dye	Reaction rate (in solution) $(10^{-6}\ sec.^{-1})$					Reaction rate (on wool) $10^{-6}\ sec.^{-1}$	Reaction rate (on wool) Kienle *et al.* $10^{-6}\ sec.^{-1}$
	Neutral H_2O_2	Alkaline H_2O_2	$K_2S_2O_8$	Dilute HNO_3	Dilute HNO_3(d)	Ceric Sulphate	Light
Sulphanilic acid → R-acid	1.56	22.7	76.1 144.0	1.49	-	-	1.61
p-Amino-benzoic → R-acid	9.95	34.4	64.0 136.0	5.33	-	-	2.41
p-Nitro-aniline → Oxy-L-acid	3.20	-	104.0	-	-	-	-
o-Chloro-aniline → Oxy-L-acid	4.41	-	51.2 71.4	-	-	-	-
p-Chloro-aniline → Oxy-L-acid	7.11	-	198.0	-	-	-	-
2:4-Dichloro-aniline → Oxy-L-acid	3.70	-	95.3	-	-	-	-
p-Anisidine → Oxy-L-acid	0.78	-	216.0 66.7	-	-	-	-
Sulphanilic acid → Oxy-L-acid	1.35	-	62.4 139.0	-	-	-	-

Comparison of Reaction Rates with Hammett's "σ" value.

The "σ" value of Hammett is frequently used in the study of organic reactions involving meta- and para- substituted benzene ring structures. This has already been used by Kienle et al. (39) and by Atherton and Seltzer(41) in a study of light fading of dyes. The "σ" value is defined as the logarithm of the ratio of the ionisation constant of the substituted benzoic acid to that of the unsubstituted, and is given by the equation:

$$\log \frac{k}{k_0} = \rho\sigma$$

where k and k_0 are the rate constants for substituted and unsubstituted reactants, respectively, and ρ is the reaction constant.

For any reaction series where data for a reasonable number of meta- and para- substituted derivatives are available, the value of the reaction constant is obtained by plotting $\log \frac{k}{k_0}$ against σ. The slope of the best straight line through the points, determined preferably by the method of least squares, is the value of ρ. The reaction constant is, by the nature of the linear relationship, a constant for all substituents and depends only on the reaction series.

In the present work, the values of $\log \frac{k}{k_0}$ for the results of oxidation of R-acid dyes with neutral and alkaline hydrogen peroxide, potassium persulphate and nitric acid, respectively, are plotted against the "σ" values as shown in Figs. 110-113. Where there is more than one reaction rate, the initial/

initial rate is used in calculation. The light fastness data for o-hydroxyazo dyes on various substrates are also plotted in a similar manner in Figs. 114-118. Light fastness grades are based on a logarithmic scale, and in the present work they represent the time required for a just perceptible change in the shade to take place. (The standard pattern representing each grade fades twice as fast as the one numerically above it). Since, however, the reaction rate represents the amount of change in a given time, it may be assumed that this rate is proportional to the reciprocal of the antilogarithm of the light fastness "grade" figure.

This assumption seems to be justified, since the points obtained by plotting the reciprocal anti-log values of the light fastness gradings, against the corresponding "σ" values lie closely about straight lines. The slopes of these lines have all the same sign, except that of the curve for dyes on wool. It therefore seemed justifiable to take mean values of all the figures, <u>except</u> those for wool, and thus to plot a similar graph which should show the effect of the substituent groups in a more consistent manner. The approximations necessarily involved in visual assessment of light fading would thus tend to be "ironed out." That this is justified is shown by the closeness with which the points so obtained lie to a straight line (Fig. 119). The/

The fit indeed, is surprisingly good and does suggest that the fading of these dyes is dependent upon some reaction uniform for all the cases involved.

Dyes with a purity less than 85% (Class 3) usually have points off the curves, so that in the curves shown, Class 3 dyes are not included, and Class 1 underlined to differentiate them from Class 2 dyes.

The slope in all the (oxidations and light fading) curves is of the same sign except for those curves relating to oxidation of soluble dyes with neutral hydrogen peroxide and fading of the same dyes on wool. The slopes in these cases agree in sign with those of Kienle <u>et al</u>. (39) (Figs. 120 and 121), on wool and gelatine respectively, which are included here for reference.

The results for alkaline peroxide oxidation (Fig. 111) are clearly much less consistent than those for the neutral reagent (Fig. 110), but, by the method of least squares, the most probable line has been drawn, and this has a slope of the same sign.

The data of Fig. 116, calculated on the same basis as the other light fading curves, are based on the mean light fastness figures, given by the manufacturers, for sixteen commercial Brenthols on cotton; and Fig. 117 is based on the three purified Brenthols used in the present work. The slope is again of/

of the same sign as that of the other *o*-hydroxyazo dyes. In calculating these results, the average light fastness figure for the dyes from aniline itself has been taken from the present work, as it is not given in the publication quoted. In calculating the "σ" values the effect of the methyl group *ortho* to the amino group is assumed unimportant, though there is no positive evidence for this. A good fit of the points to a straight line justifies this assumption.

In the oxidation of R-acid dyes on wool with ceric sulphate, the percentage dyeings are not of the same strength in every case. However, since the curves of the logarithm of unoxidised dye against time are linear, the reaction rates determined should be comparable with one another. The values of $\log \frac{k}{K_o}$ are plotted in Fig. 122 against the "σ" values. Although a good straight line cannot be drawn, the slope of the best line, obtained in accordance with the method of least squares, appears to be opposite in sign to that of the curves for light fading on wool and for the results of thermal oxidation with neutral and alkaline hydrogen peroxide.

p-Hydroxyazo dyes.

Figs. 123 to 125 show respectively (i) the curves based on the oxidation of Oxy-L-acid dyes with neutral hydrogen peroxide and with potassium persulphate; (ii) the light fastness derived values of the same dyes on tile and paper; and (iii) the light fastness derived values of α-naphthol dyes on tile. No curves are shown where light tests do not differentiate, because either the

fastness/

fastness is too low or because it is too high to enable results to be obtained in the time available during the present work. Since some ortho coupling may well occur in the case of α-naphthol and Oxy-L-acid dyes, these were tested for homogeneity by paper chromatography, and dyes for which the chromatograms were doubtful have not been taken into consideration in drawing the "σ" value curves. The curves for α-naphthol dyes have been drawn using the p-toluidine dyes as a standard. The curves showing mean light fastness data for α-naphthol dyes on tile and paper plotted against the "σ" values ~~is~~ are given in Fig. 126.

The chromatographic tests showed that all the Oxy-L-acid dyes from m- and p-substituted anilines, with the exception of those from aniline and m- and p-toluidine, had traces of coloured impurity; presumably these are o-hydroxy or o-p-dihydroxy compounds, because it is known that bases containing nitro, etc. groups, tend when diaztotised to couple ortho as well as para to the hydroxy group of α-naphthol. For Oxy-L-acid dyes, therefore, only three samples are available for light fastness, etc., assessments to be plotted against "σ" values. Though rather inconclusive, they at least are not inconsistent with the expected trend. The same remark applies to the corresponding curves for oxidations with potassium persulphate and hydrogen peroxide (neutral). Here, as in the case of the o-hydroxyazo dyes, the three points do seem to show some slight evidence of slopes with opposite sign in the two cases, that of the persulphate tests agreeing in sign with that of the light fastness tests.

The /

The chromatograms of α-naphthol dyes showed that most of them were free from traces of coloured impurities. Though the experimental results (Figs. 125 and 126) were too erratic to be interpreted with full confidence, the sign of the slope of the curves for light fastness data on tile and paper, is the same as that of the curves for o-hydroxyazo dyes, the method of least squares being employed in both calculations.

Speculations on reaction-mechanisms.

The available information on azo dye oxidation and photolysis is meagre, and speculations upon their reaction-mechanisms cannot therefore be adequately checked by existing experimental data. Nevertheless, a few of the relevant facts which have been disclosed in the recent Society of Dyers and Colourists' Symposium (1949) on "Photochemistry in relation to Textiles," and in other publications, may at this stage be considered, along with the results of the present work, and speculations made upon their implications. The following paragraphs summarise some relevant facts.

(A) Thermal oxidation in solution.

(a) Thermal oxidation of azo dyes yields a quinone and a diazonium compound.

(b) The effect of a substituent~~s~~ in the first component of a water-soluble azo dye upon the oxidation rate with neutral or alkaline hydrogen peroxide is in the reverse sense to ~~their~~ its effect upon the rate with other oxidising agents employed in the present work.

(B)/

(B) Photolysis.

(a) Fading of an azo dye in air on a cellulosic substrate produces a quinone and a diazonium compound.

(b) The influence of a substituent~~s~~ in the first component of the azo dye upon light fastness on substrates other than protein is in the same sense as th~~eir~~is influence on thermal oxidation with agents other than hydrogen peroxide.

(c) The reverse of (b) applies to fading on wool or gelatine.

(d) Photolysis of proteins by ultra-violet radiation leads to the production of hydrogen peroxide (Roberts, 108). Roberts (loc.cit.) detected hydrogen peroxide when a protein (serum albumin) was irradiated. He showed that it is formed from hydroxyl radicals released by reaction of a protein carboxylic acid side chain with a free radical formed by disruption of a -CO-NH-bond. He used light of 2500A wavelength in absence of oxygen. Fading of dyed fabrics, of course, occurs even behind glass, where light of less than 3400A is not present, but fibres, including wool, are degraded under these conditions in air. Breare (109) showed that most dyes, including azo dyes, retard such photochemical degradation of wool. This may be due to their preferential absorption of the light energy, leaving less available for acting on the protein.

(e) Hydrogen peroxide is not formed when azo dyes lacking an otherwise active nucleus, are irradiated by light on a cellulose substrate.

The above remarks may also be considered in relation to the light fastness of Orange I and its O-methyl ether. On several substrates, the light fastness of the latter dye is much higher than that of the former. On wool, this superiority disappears, and both have/

have similar rates of fading. ~~It may also be recalled that these two dyes have rather similar reaction rates with neutral hydrogen peroxide (2.1×10^{-6} sec.$^{-1}$ for Orange I and nil for its ether),~~ ~~whereas with other agents there is a much more marked difference.~~

The following hypothesis is now suggested to cover the evidence so far disclosed:

(a) The active agent in the fading of benzeneazonaphthol dyes on protein substrates is hydrogen peroxide, formed by photolysis of the protein itself.

(b) The active agent in fading azo dyes on cellulose substrates is not hydrogen peroxide. It may perhaps be oxygen.

(c) The attack on the dye (on cellulose) is at the carbon-nitrogen bond nearest the phenolic hydroxy group of the "coupling component." (No evidence is available upon the nature of the attack when the dye is on a protein substrate).

(d) The influence of substituents in the benzene ring of the diazo component, whether this is coupled with α-naphthol, α-naphthylamine, or β-naphthol, suggests that the initial attack on the molecule, in the case of a hydrogen peroxide-initiated photolysis or thermal oxidation, is favoured by an induced positive charge on the nitrogen nearest the hydroxy group, while in the case of photolysis, or thermal oxidation by other agents, it is favoured by an induced negative charge thereon.

The original working hypothesis of the present thesis suggests that the nature of this induced charge determines the position of the azo-hydrazone equilibrium. This may be so; but it/

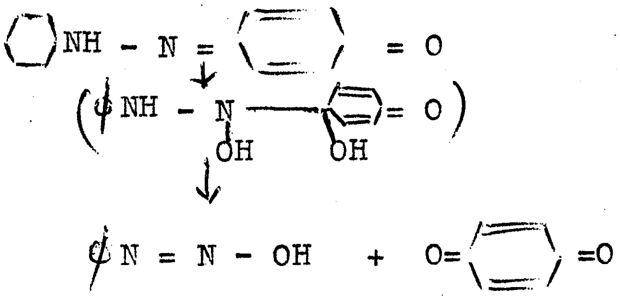
it is well to point out that the position of this equilibrium in the different series of azo dyes is not finally settled, and a certain amount of conflicting evidence on the subject is found in the literature. Some authors have claimed that *p*-hydroxyazo dyes are either entirely of azo form or are tautomeric mixtures, some say that the *o*-hydroxyazo dyes are entirely hydrazones. It is clear that further evidence is required before these points can be settled and no dogmatic statements regarding the actual structures of these dyes should be made at this juncture.

The oxidation mechanism put forward in the present work suggests that the initial attack on the azo dye is a hydrolytic one. It would at first sight appear therefore that the reaction rate determined should be independent of the nature of the oxidising agent used. The fact that this is not the case may be attributed to different pH values of the oxidising agents employed. In this connection, the work of Balfe, Kenyon and collaborators (124) on hydrolysis of carboxylic esters may be quoted. ~~here.~~ These authors have, for example, shown that when optically pure (+) and (-) hydrogen phthalic esters of γ-phenyl-α-methylallyl alcohol are saponified with sodium carbonate solution~~,~~ they unexpectedly give the di-alcohol. The optically active alcohols can be obtained, however, by saponifying the esters with caustic soda solution. The more concentrated the alkaline solution employed, the higher the rotatory powers of the resulting alcohols. A high concentration of/

of hydroxyl ions thus appears to favour the reaction which leads to the carbinol of the same configuration as the reacting hydrogen phthalic ester, as is the case when the hydrogen phthalic esters of saturated alcohol~~ic~~s undergo saponification. At lower concentrations of hydroxyl ions, part of the hydrogen phthalic ester presumably reacts with intermediate formation of a carbonium cation leading to inversion and racemisation, a type of scission which is possible in esters of substituted allyl alcohols.

Although the hydrolysis of carboxylic esters may occur by a mechanism quite different from that of hydrazones, it is not safe to predict without further kinetic studies that the reaction rate in the latter case is independent of the nature of the oxidising agent. The fact that Kenyon <u>et al</u>. (124) observed alkyl-oxygen scission (R'.CO.O ↓ R") of esters by an S_N1 mechanism when using a neutral medium, and acyl-oxygen scission (R'.CO. ↓ OR") by an S_N2 mechanism when using an alkaline medium, at least suggests caution in predicting the kinetics of hydrazone hydrolysis in the presence of different oxidising agents.

Other mechanisms may also be suggested - for example, one somewhat resembling the oxidation of an ethylene double bond:



where the hydroxyl radicals are formed by an energy transfer from exited dyes to water.

Comments on Burawoy's remarks upon Desai and Giles paper. (102):

Burawoy (102) raised objections to certain statements made by Desai and Giles (op.cit). regarding the present work. His main objections may be summarised as follows:-

(1) Burawoy's own work shows no indication of a tautomeric equilibrium in solution of o-hydroxyazo compounds (unsulphonated). They exist only as the quinone structures.

(2) Evidence from spectra shows that the interpretation of the structure of o-hydroxyazo dyes as resonance hybrids of the quinone-hydrazone forms is unjustified. (Burawoy admits that this "more or less supported the authors' views.." (i.e. Desai and Giles'))

(3) Schmidt (11) and also Rowe (13) obtained products by the action of nitric acid on azo compounds, which preclude the formation of a quinone intermediate.

(4) o-Hydroxyazo compounds and their O-methyl ethers have similar absorption spectra in concentrated inorganic acids, suggesting in both cases a positively charged imino-nitrogen atom and not an azo structure.

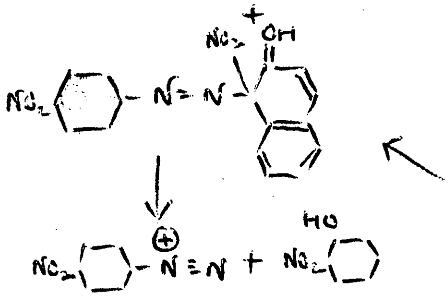
(5) Kuhn and Bär (92) found by spectroscopic investigation that 4-phenylazo-1-naphthol solutions contain an equilibrium mixture of the two tautomeric forms.

(6) Shingu (96) showed that the influence of substituents on such an equilibrium is in the reverse order to that postulated by Desai and Giles.

(7)/

(7) The correlation between structure and ease of oxidation shown by Desai and Giles is ~~a~~only approximate.

(8) Schmidt's suggested mechanism (11) of nitric acid oxidation of azo dyes might better explain Desai and Giles's results. His mechanism is as follows:-



(transition compound, formed after previous nitration).

(9) Burawoy directed a two-fold criticism principally against the paper by Atherton and Seltzer (loc.cit.), but also against the paper by Desai and Giles. (a) It was queried whether the known rules of the effect of substitution on equilibria and the rate of thermal reactions can be applied to photosensitised processes, where the energy uptake by light absorption is high. (b) It was found difficult to see why the order of fading should be reversed by a change of substrate.

Replies to all these objections were made at the time of the above-mentioned Symposium, but in the light of further evidence presented in this thesis, these should be revised and the author now gives the following comments on Burawoy's points in the above sequence.

(1) This is difficult to reconcile with the synthetic chemical evidence of tautomerism of o-hydroxyazo compounds (See Mason/

Mason, 101). Further, the present work refers to azo compounds in aqueous solution or dispersed on a fibrous surface in presence of air and moisture; and these conditions are not strictly comparable with those obtaining in solutions in organic solvents. For example, Blaisdell (loc. cit.) has reported that photolysis of azo compounds in organic solvents causes reduction, whereas - as other workers have shown - photolysis in air causes oxidation. Hodgson and Marsden (98) also emphasise the influence of a solvent on the structure of azo dyes.

These remarks are also advanced in reply to Burawoy's comment (6). Further, Shingu's statements regarding the relative abundance of the tautomers in different species of azo compounds do not appear to be very clearly supported by the actual absorption curves he shows.

(3) The present author has now confirmed that nitric acid oxidation gives products different from those produced by other oxidising agents. Hence, Burawoy's comment (3) is not relevant to the present discussion.

(4) See reply to comment (1). Solution in concentrated inorganic acids may not necessarily be comparable with the conditions applying in the present work.

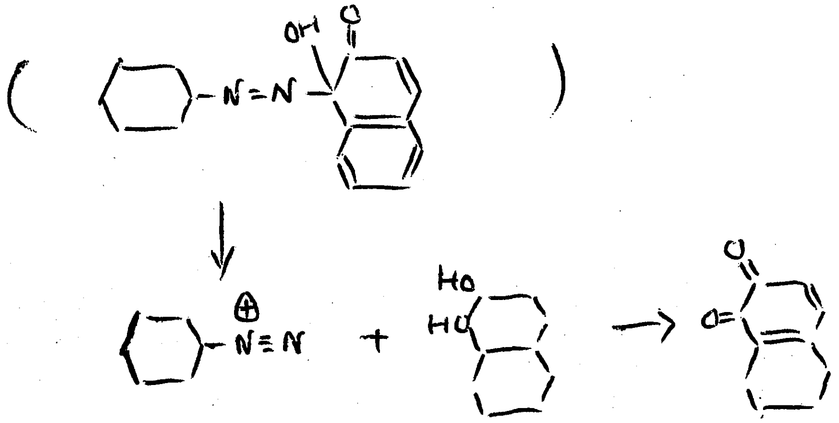
(5) The observation of Kuhn and Bär is in agreement with the present author's suggestions that tautomeric equilibrium is concerned in the reaction of p-hydroxyazo compound.

(6) Shingu's result may be due to the effect of the organic solvents/

solvents used. (See Comment (1) above). If the influence of substitutents in aqueous media follows the same sequence suggested by Shingu, it would mean a modification of the present suggestions. Such a modification would not, of course, invalidate the results of the experiments presented in this thesis. In any case, the author realises that these suggestions are not necessarily final and that other reaction mechanisms might well be found to explain his results.

(7) The more complete results (now presented in this thesis) show a much closer correlation between structure and ease of oxidation than those in the paper by Desai and Giles.

(8) Some mechanism similar to th~~os~~at proposed by Schmidt might possibly serve as a hypothesis to explain oxidation by other reagents (say, hydrogen peroxide), which might proceed by way of a transition compound, thus:



Such a reaction, taking place as it does via the <u>azo</u> form, might account for the reversed order of effect of substituents upon peroxide oxidation compared with their effect upon other oxidising agents.

(9) These points were replied to at the time of the Symposium by Seltzer as follows:-

(a) While the differences in activation energy caused by different substituents may be of a low order ($<$10 Kg. cal.), the order of total activation energy will be larger, and may well be of the same order as that of the visible quantal energies, when the possibility of energy transfer to the substrate is concerned. On the basis of the observed results, the initial process of dye-destruction does appear to be one of electron donation.

(b) There is also evidence (41) that the order of light fastness in a given series of compounds is reversed by a change of solvent; and the present author would further point out that the results now presented show definitely that the order of fastness can also be reversed by a change of substrate.

<u>Note regarding Curves.</u>

The numbered points on the curves showing "σ" values refer to dyes with substituent groups according to the following scheme:

<u>Point on the Curve, No.</u>	<u>Substituent Group.</u>	<u>"σ" value.</u>
1	-	0
2	*m*-NO_2	+0.71
3	*p*-NO_2	+1.27
4	*m*-Cl	+0.37
5	*p*-Cl	+0.23
6	*m*-CH_3	-0.07
7	*p*-CH_3	-0.17
8	*p*-OCH_3	-0.27
9	*p*-COOH	+0.73

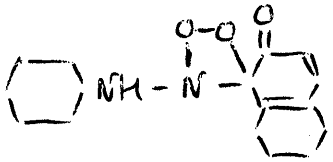
CONCLUSIONS.

There is a general similarity in the products obtained on oxidation of azo dyes with a variety of aqueous oxidising agents. Dry oxidation, however, seems to follow a different course since neither a diazonium compound nor β-naphthaquinone was detected when phenylazo-β-naphthol dissolved in dry acetone was oxidised with dry ozonised oxygen. In light exposure tests, it is found that most of the dyes fade much more quickly on an anodised aluminium substrate than on wool. This suggests that this substrate may be more suitable for the purpose of analysing the products of light fading of azo dyes. A suitable oxidation method for the analysis of azo dyes will probably be difficult to work out, because of the complex nature of the reactions involved.

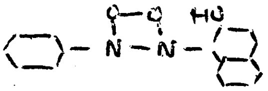
The most important stage in the series of reactions is undoubtedly the initial one. This will almost certainly be an attack on one or other of the unsaturated centres of the molecule, and since these are responsible for its colour, it is presumably in this first stage that the actual fading occurs. Hence, the facility with which the molecule undergoes this initial step should be a measure of the light fastness.

Few suggestions appear to have been made regarding the initial stage of azo fading, which has great theoretical and practical importance. Haller and Ziersch (33) postulated a hypothetical peroxide formation. Since this involves the hydrazone form/

form of dye, e.g.



it would appear to be subject to the same relative influences from substituents as is the hydrolysis mechanism suggested above, and is therefore in conformity with the available evidence. In the case of insoluble dyes, especially when exposed in an oily medium, peroxide formation is indeed a more reasonable possibility than hydrolysis by water. One might perhaps suggest that the peroxides are formed from the azo form of the dye:



but it is difficult to see how such a compound could break down to give naphthaquinone and a diazo body. The fibre itself appears also to play a part; thus Haller and Ziersch (33) found that fading was more rapid on cotton fibre than in solution; Kienle, Stearns and Van der Meulen (39) however found the reverse in the case of wool. The effect of wool has been discussed above (see page 152). It is clear that much more information must be obtained before speculation is pursued further.

One consideration that emerges is of practical importance however. It is unlikely that a simple chemical test will be found for the rapid sorting of all types of dyes in their order of light fastness, though as a suggestion for future examination, the use of neutral hydrogen peroxide could be tried to evaluate light fastness of azo dyes for wool, and dilute nitric acid for those used on non-protein substrates.

Based/

Based on the sign of the slope of the curves showing "σ" values plotted against reaction rates of water-soluble dyes, the mechanism of oxidation by hydrogen peroxide appears to be different from that by nitric acid. The slope of the curve for potassium persulphate is uncertain in the case of both ortho- and para-hydroxyazo dyes.

Detailed consideration of the whole series of oxidation experiments and light fastness tests, as described above under ~~the foregoing~~ "Discussion," does however enable us to state certain conclusions with reasonable confidence.

In the first place, fading experiments with o-hydroxyazo dyes (of both soluble and insoluble types), on all substrates other than wool, are in agreement with prediction from the hypothesis that the hydrazone structure is the one attacked. So also are the results of Atherton and Seltzer (loc.cit.) (Fig. 127) on p-aminoazo dyes. Our own results on p-hydroxyazo compounds, while tending to agreement, are unfortunately inconclusive. We do not state dogmatically that the suggested mode of attack is the correct one, and other alternative mechanisms are conceivable; but, whatever may be the actual mechanism~~s~~, it must be subject to the same influence by substituents as that postulated above.

In the second place, our own results with soluble o-hydroxyazo dyes on wool are in agreement with those of Kienle et.al. (loc.cit.), using wool and gelative as substrates. They show an influence of substituents on fading opposite to their

influence/

influence on dyeings on other substrates. The effect has the same sense as that observed in thermal oxidation in neutral or alkaline aqueous hydrogen peroxide solution. This, coupled with the known facts (a) that irradiation of protein by light can produce hydrogen peroxide and (b) that peroxide cannot be detected when azo dyes on a cellulose substrate are faded, enables us to put forward the hypothesis that fading on wool is in some way caused by hydrogen peroxide, whereas on other substrates disruption of the dye molecule occurs by some other process - perhaps by attack of atmospheric oxygen.

Fading results observed for non-substantive azo dyes on a paper substrate, which are strictly only "paddings" and not true dyeings, should nevertheless be truly comparable with those observed for dyeings with substantive dyes on cotton, because the difference in substantivity is now generally believed (e.g. Marshall and Peters, J.S.D.C., 1947, <u>58</u>, 446) to be due only to the difference in the number of hydrogen bonds involved. These would not generally be expected to interfere with the fading mechanism.

The curve obtained when the grand mean light fastness data are plotted against the "σ" values (Fig. 119) is of special interest. The conformity of the points to this straight-line relationship shows that light fastness tests are quite reliable when a sufficient number are taken and averaged; and the device of using the reciprocal of the antilogarithms of the light fastness grade number in place of a reaction rate seems to be justified/

justified. (See page 146). Finally, it signifies that fading is a simple reaction involving attack at one of the unsaturated centres of the dye molecule.

It is clear that the reaction mechanisms are not yet fully elucidated, and that further investigation is required before a comprehensive interpretation of the present results can be given; but it is considered that the conclusions outlined in this thesis to some extent clarify the chemical aspects of azo dye fading, a subject which has previously been almost entirely obscure. The author therefore puts them forward as a small but definite contribution to knowledge in this complex field.

SUGGESTIONS FOR FUTURE WORK.

The data in this thesis should be statistically analysed to determine their relative significance and to discover if any further generalisations regarding the reaction mechanisms thereby arise.

The oxidation tests with certain agents (especially alkaline peroxide) should be repeated in an endeavour to discover the disturbing factor(s) and thus to obtain more consistent results. A series of tests at different pH values might be carried out with hydrogen peroxide.

Further attempts should be made to elucidate details of the reaction mechanism(s), e.g., to find if phenylhydrazine derivatives are actually formed. Aceto- or benzophenone might be tried as acceptor for a hydrazine.

Attempts should be made to isolate breakdown products from faded patterns of wool, aluminium, etc.

****

APPENDIX.

(i) Preparation of Dyes.

Most of the dyes were prepared in the normal way by coupling the diazo solution with the coupling component in alkaline solution. The soluble dyes were purified by crystallisation from water, and the insoluble ones from suitable organic solvents. The preparation of the remaining dyes is given below.

(1) 2:4-dinitroaniline→β-Naphthol:

2:4-Dinitroaniline (4.6 g.) was dissolved in glacial acetic acid (100 c.c.) containing concentrated sulphuric acid (3 c.c.) and cooled in ice, and an ice-cold solution of 5 g. sodium nitrite in 25 c.c. concentrated sulphuric acid was added. The diazo solution thus formed was added slowly to an ice-cold solution of 4 g. β-naphthol dissolved in 25 c.c. glacial acetic acid. The dye which separated was recrystallised from nitrobenzene. It formed reddish-brown crystals, mp. 284-286°C (yield 0.7 g.) giving a violet colour with concentrated sulphuric acid, and a deep blue with alcoholic sodium hydroxide solution.

(2) 2:4-Dinitroaniline→α-Naphthel:

Sodium nitrite (2.2. g.) was added to concentrated sulphuric acid (7.5 c.c.) and dissolved by heating to 75°C. The clear liquid thus obtained was cooled in ice and 2:4-Dinitroaniline (5 g.) added with stirring. After two hours/

hours, the pasty mess was diluted to 700 c.c. with ice-cold water. The diazo solution thus formed was added slowly to an ice-cold solution of 4 g. α-naphthol dissolved in 80 c.c. of sodium hydroxide solution (14% $^{w}/v$). The solution was acidified after coupling, filtered, and washed with water. After drying, it was washed with cold alcohol, and then recrystallised from nitrobenzene. It formed orange crystals, m.p. 266-268°C. (Yield 2 g.)

(3) *o*-Nitroaniline → α-Naphthol.

o-Nitroaniline (1.7 g.) was heated with concentrated hydrochloric acid (5 c.c.), cooled, and diluted with ice-cold water (30 c.c.). Sodium nitrite (1 g.) dissolved in water (5 c.c.) was added, and after 15 min., when the diazotisation was complete, the mineral acid was neutralised by addition of sodium acetate. The diazo solution thus formed was added slowly to an ice-cold solution of α-naphthol (1.7 g.) dissolved in alcohol (30 c.c.) and water (10 c.c.) and containing sodium acetate (5 g.) Crystallised from *m*-xylene, it formed brown crystals, m.p. 242°C. (yield 0.7 g.)

(4) *o*-Anisidine → α-Naphthol:

o-Anisidine (2 g.) was dissolved in concentrated hydrochloric acid (7.5 c.c.) and diluted with ice-cold water (30 c.c.). Sodium nitrite (1.5 g.) dissolved in water (5 c.c.) was added, neutralised, and after 15 min., the mineral acid was neutralised by/

by addition of sodium acetate. The diazo solution thus formed was added slowly to an ice-cold solution of α-naphthol (2-4 g.) dissolved in alcohol (30 c.c.) and water (10 c.c.) and containing sodium acetate (5 g.). Recrystallised from aqueous methanol, it formed reddish-brown crystals, m.p. 160-162°C. (Yield 1 g.)

(5) <u>p-Anisidine → α-naphthol</u>:

Preparation similar to above. Crystallised from methanol, it formed dark brown crystals, m.p. 168-169°C. (Yield 0.5 g.)

(6) <u>p-Methoxyazobenzene</u>:

<u>p</u>-Hydroxyazobenzene (5 g.) was dissolved in a solution of 3 g. potassium hydroxide in 40 c.c. methanol containing 3 c.c. methyl iodide and refluxed on a water-bath for two hours. The solution was then evaporated to about 20 c.c., and the methoxy compound which separated was filtered off and crystallised from ethanol; m.p. 52-53°C. (yield 1 g.).

(7) <u>O-Methyl ether of Orange I</u>.

(It was not found possible to prepare the O-methyl ether of Orange II either by direct methylation of Orange II or by coupling diazotised sulphanilic acid with 2-methoxy-naphthalene). The O-methyl ether of Orange I was, however, prepared as follows (Pfister (107)).

Orange I (6 g.), purified by the sodium acetate salting-out/

out method and dissolved in 25 c.c. water, was treated with 1.5 g. sodium hydroxide and 3.8 c.c. dimethyl sulphate, in the cold, over one hour. The methylated product separated from solution, together with some unchanged Orange I, but the latter was re-dissolved by addition of a cold solution of 3 g. sodium hydroxide in 40 c.c. water at the end of the reaction period. The insoluble dye was then filtered off, washed well with water, and recrystallised from hot water. It formed light yellowish-brown crystals (Yield 0.7 g.), insoluble in 2% sodium hydroxide solution (cold); the aqueous solution is unaffected in colour by addition of alkali. Purity, sample dried over P_2O_5, by nitrogen estimation, 92.2%. Methoxy content (for 92.2% purity); theoretical 7.85%, found, 8.19%.

(8) <u>O-Methyl ether of sulphanilic acid → Phenol</u>.

A sample of the purified dye, sulphanilic acid→phenol, (3 g.), dissolved in 50 c.c. water, was treated with 1 g. sodium hydroxide and 3 c.c. dimethyl sulphate, on the boiling water-bath for one hour. The methylated product separated from solution, together with some unchanged original dye, but the latter was re-dissolved by addition of a cold solution of 2 g. sodium hydroxide in 50 c.c. water at the end of the reaction period. The insoluble dye was then filtered off, washed well with water, and recrystallised from hot water.

It/

It formed light yellow crystals (Yield 1.2 g.), insoluble in 2% sodium hydroxide solution (cold); soluble with difficulty in water (yellow colour), but on adding alkali, a precipitate is formed. Analysis: N = 8.61%, theoretical 8.92%, OCH_3 10.3%, theoretical 9.87% (sample dried over P_2O_5).

(9) <u>O-Methyl ether of naphthionic acid ⟶ phenol.</u>

The purified dye (5 g.) dissolved in 50 c.c. water, was treated with 1.5 g. sodium hydroxide and 4 c.c. dimethyl sulphate on the boiling water-bath for three hours. The methylated product separated from solution, together with some unchanged original dye, but the latter was redissolved by addition of a cold solution of 2 g. sodium hydroxide in 40 c.c. water at the end of the reaction period. The insoluble dye was then filtered off, and washed well with dilute sodium hydroxide solution instead of water, since the dye was found to be more soluble in water. Crystallised from water, it formed orange crystals (yield 1.6 g.), insoluble in 2% sodium hydroxide solution (cold); the aqueous yellow solution forms minute crystals on addition of alkali. Analysis: N, found, 7.51%; theoretical 7.69%; OCH_3, found 9.1%; theoretical, 8.52% (sample dried over P_2O_5).

(ii) PURITY OF DYES.

The insoluble dyes from α- and β-naphthol were purified by/

by crystallisation from an organic solvent, and their melting points checked against the published figures.

The soluble dyes from R-acid and Oxy-L-acid were purified either by salting out with sodium chloride, followed by recrystallisation from water or, in a few cases, by salting out with sodium acetate, followed by refluxing twice with fresh ethanol. R-acid dyes were twice recrystallised from water, Oxy-L-acid dyes only once, on account of the difficulty of separation and low yields. The purity was then checked by titanous chloride analysis and by moisture content determination (drying to constant weight at 140°C). The low figures shown by a few of the dyes must be attributed, in view of the purification methods used, either to sodium chloride or firmly bound water. A few ash determinations were made, the results being shown in Table 24. These are not considered reliable because (a) any sodium chloride present may volatilise during the ashing process and, (b) the calculated ash contents assume that the ash consists of sodium sulphate alone, whereas sodium carbonate may also be formed.

In all cases, the solutions used for the oxidation tests were made up on the basis of the titanous chloride analysis figures.

The /

The Brenthol dyeings used for light exposures were prepared on the fibre from purified samples of Brenthols and bases.

Table 24 gives a summary of the purity determinations of the soluble dyes and Table 25, details of the melting-points of the insoluble dyes. It will be observed that a few of the α-naphthol dyes either have indefinite melting-points or the melting-points do not agree with published information. Unfortunately this series of dyes was prepared late in the course of the work and it has not been possible to have elementary analyses made.

It may be pointed out that the purity figures quoted for the soluble R-acid dyes used by Kienle _et al_ (39) (p. 17 above), are in several cases low (one figure is given as 28.2%) though most of them lie between 95% and 100%.

TABLE 24/

TABLE 24.

PURITY DATA ON SOLUBLE DYES.

Dye	Purity by $TiCL_3$ method %	Moisture % (140^0C)	Ash		Purity of dye calc. on moisture-free bases %
			Found	Calc. as Na_2SO_4	
Orange II	94.5	7.5	16.7	19.2	102
Orange I	83.9	14.9	14.8	17.0	98.6
O-Methyl ether of Orange I	86.1	7.4	-	-	94.0
*Aniline ⟶ R-acid	79.0	15.1	24.7	24.8	93.1
o-Nitroaniline "	86.8	10.3	-	-	97.0
m " "	86.6	11.9	-	-	99.0
p " "	85.6	11.3	-	-	96.6
o-Chloroaniline "	88.2	11.6	24.6	25.8	99.6
m- " "	80.9	12.5	30.1	23.6	99.9 ++
p- " "	91.2	12.1	24.5	26.6	104.0
2:4-Dichloroaniline ⟶ R-acid	89.0	13.6	-	-	102.5
m-Toluidine "	71.4	10.4	-	-	80.0
p-Toluidine "	85.4	7.9	24.5	26.0	92.7
o-Anisidine "	87.3	10.6	-	-	98.0
p " "	63.2	11.4	-	-	71.5
*R-acid ⟵ Dianisidine ⟶ R-acid	29.4	5.8	42.2	-	73.5 ++
Metanilic acid "	76.1	11.6	-	-	86.0

Sulphanilic/

Dye	Purity by $TiCl_3$ method %	Moisture % (140°C.)	Ash %		Purity of dye calc. on moisture-free basis%
			Found	Calc. as Na_2SO_4	
Sulphanilic acid → R-acid	69.8	13.0	-	-	80.5
Anthranilic acid → R-acid	79.1	8.2	-	-	86.0
p-Aminobenzoic acid → R-acid	39.8	12.6	28.4	12.0	56.1^{++}
Aniline → Oxy-L-acid	99.4	2.4	-	-	101.5
o-Nitroaniline "	77.1	9.0	-	-	84.8
m- " "	79.5	11.5	-	-	89.8
p- " "	21.4	2.0	-	-	21.8
o-Chloroaniline "	57.0	3.6	-	-	59.0
m-Chloroaniline "	96.6	3.4	-	-	100.0
p " "	59.9	5.0	-	-	63.0
2:4-Dichloroaniline → Oxy-L-acid	60.9	2.2	-	-	62.3
m-Toluidine "	96.8	3.6	-	-	100.2
p-Toluidine "	98.8	1.0	-	-	100.0
o-Anisidine "	97.2	4.0	-	-	101.0
p " "	47.4	1.5	-	-	48.3
Metanilic acid "	79.6	6.6	-	-	85.2
Sulphanilic " "	44.0	1.6	-	-	44.8
Anthranilic " "	74.9	18.2	-	-	91.5
p-Aminobenzoic acid "	80.3	7.8	-	-	87.0

Sulphanilic/

Dye	Purity by $TiCl_3$ method %	Moisture % (140°C.)	Ash %		Purity of dye calc. on moisture - free basis %
			Found	Calc. as Na_2SO_4	
Sulphanilic acid → Guaiacol	75.6	8.0	-	-	82.2
Sulphanilic acid → phenol	91.0	9.2	-	-	100.0
O-Methyl ether of Sulphanilic acid → Phenol	100.0	nil	-	-	100.0
Naphthionic acid → Phenol	74.6	14.2	-	-	86.8
O-Methyl ether of Naphthionic acid → Phenol	80.9	7.5	-	-	87.8

* Purified by sodium acetate method.

\+ Assuming ash is sodium carbonate.

++ Moisture free and extra ash-free basis.

TABLE 25.

Melting-point ~~on~~ data for insoluble dyes.

Dye		Crystallised from	M.P. (°C)	M.P. from literature (°C)
Aniline →	β- Naphthol	ethanol	127-128	
o-Nitroaniline	"	glacial acetic acid	207-208	
m- "	"	toluene	193	
p- "	"	glacial acetic acid	250-251	
2:4-Dinitroaniline	"	nitrobenzene	284-286	302 BN
o-Chloroaniline	"	glacial acetic acid	161	
m- "	"	"	158	
p- "	"	"	160	
2:4-Dichloroaniline	"	ethanol	187-188	
p-Toluidine	"	methanol	132	
o-Anisidine	"	benzene	170-172	178 Bl
p-Anisidine	"	methanol	135-136	
Aniline →	α- naphthol	Carbon tetrachloride	195-202 d	206 Bl.
o-Nitroaniline	"	*m*-Xylene	242	244-245 Bl 250-251 S
m "	"	methanol	208-210	288 Bl 242 d. S
p- "	"	nitrobenzene, diluted with methanol	decomp. above 300	277-279 Bl 282-284 S
2:4-Dinitroaniline	"	nitrobenzene	266-268	288 Bl

o-Chloroaniline/

Dye	Crystallised from	M.P. (^{o}C).	M.P. from literature(^{o}C).
o-Chloroaniline → α-Naphthol	benzene	147-148	184-186 S
m- " "	methanol	166-167	220-222 d. S.
p- " "	glacial acetic acid	185-187	230 d. S.
2:4-Dichloroaniline "	benzene	208	
p-Toluidine "	nitrobenzene diluted with carbon tetra chloride	decomp. above 300	208 Bl
o-Anisidine "	aqueous methanol	160-162	173 d. Bl.
p- " "	methanol	168-169	
p-Hydroxyazobenzene	aqueous ethanol	150	
p-Methoxyazobenzene X	ethanol	52-53	

The published M.P. is given only where it differs from the figures above.

(Bl = Beilstein; BN = Brunner, Analysé der Azofarbstoffe; S = Shingu, Chem. Abs., 1939, 33, 3369).

TABLE 26.

(iii) MEAN LIGHT FASTNESS FIGURES FOR SOLUBLE AZO DYES ON VARIOUS SUBSTRATES.

Dye	Wool	Anodised Aluminium	Filter paper	Unglazed tile
*Class 1.				
Orange II	4.2	2.0	1.7	1.8
Orange I	3.0	1.0	1.0	1.0
o-Nitroaniline → R-acid	2.8	2.0	3.2	3.0
m- " "	4.0	2.0	3.2	2.0
p- " "	4.0	2.0	4.2	4.0
o-Chloroaniline "	1.5	1.0	1.7	1.0
p- " "	5.5	1.0	4.2	2.0
2:4-Dichloroaniline "	1.3	1.0	1.0	2.3
o-Anisidine "	5.0	2.0	3.0	1.3
Aniline → Oxy-L-acid	>5	3.0	2.4	3.0
m-Chloroaniline "	4.5	1.0	1.0	2.5
m-Toluidine "	>5	1.0	1.7	1.8
p-Toluidine "	5	3.0	1.7	2.5
o-Anisidine "	5	1.0	1.7	2.5
Sulphanilic acid → Phenol	5.3	-	5	1.5
O-Methyl ether of above	5.3	-	5	1.5
*Class 2.				
O-Methyl ether of Orange I	3.5	4.0	3.0	4.5
Aniline → R-acid	5.7	2.0	2.7	1.3

Dye	Wool	Anodised Aluminium	Filter paper	Unglazed tile
m-Chloroaniline → R-acid	4.8	2.0	3.3	1.0
p-Toluidine "	>6	1.0	2.7	1.5
Metanilic acid "	>6	3.0	>5	4.5
Anthranilic acid "	>5	3.0	3.3	1.5
o-Nitroaniline → Oxy-L-acid	5.5	3.0	2.3	3.5
m- " "	>5	2.0	1.0	2.8
Metanilic acid "	>5	1.0	2.3	4.5
Anthranilic acid "	>5	2.0	2.3	3.0
p-Aminobenzoic acid "	>5	1.0	2.0	3.0
Naphthionic acid → Phenol	>5	1.0	4.0	1.0
O-Methyl ether of above "	>5.5	1.3	4.0	1.3
* Class 3.				
m-Toluidine → R-acid	>6	2.0	3.7	1.0
p-Anisidine "	5.5	1.0	3.0	3.5
Sulphanilic acid "	>6	1.5	>5	3.5
p-Aminobenzoic acid "	>5	4.0	4.7	1.5
p-Nitroaniline → Oxy-L-acid	5	1.0	2.0	2.3
o-Chloroaniline "	4.5	1.0	1.3	2.8
p-Chloroaniline "	4.5	1.0	1.0	2.0
2:4-Dichloroaniline "	4.0	1.5	1.0	1.8
p-Anisidine "	>5	2.0	1.7	2.5
Sulphanilic acid "	5.0	1.0	3.2	4.0

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* Classed by $TiCl_3$. Some α-naphthol dyes contain isomers – see pp.137,149.

TABLE 27.

(iv) MEAN LIGHT FASTNESS FIGURES FOR INSOLUBLE AZO DYES ON VARIOUS SUBSTRATES.

Dye	Filter paper	Unglazed tile	Dye	Filter paper	Unglazed tile
Aniline→β-Naphthol	1.7	4.0	Aniline→α-Naphthol	1.0	4.5
o-Nitro-aniline "	3.3	5.5	o-Nitro-aniline "	4.0	4.3
m-Nitro aniline "	2.7	5.3	m-Nitro-aniline "	1.2	2.5
p-Nitro-aniline "	2.8	5.3	p-Nitro-aniline "	2.7	4.0
2:4-Dinitro-aniline "	5.0	5.5	2:4-Dinitro-aniline "	3.3	4.0
o-Chloro-aniline "	1.5	4.3	o-Chloro-aniline "	1.0	3.3
m-Chloro-aniline "	2.0	4.5	m-Chloro-aniline "	1.0	3.3
p-Chloro-aniline "	1.3	4.3	p-Chloro-aniline "	1.2	3.0
2:4-Dichloro-aniline "	1.0	4.8	2:4-Dichloro-aniline "	1.7	3.0
p-Toluidine "	2.7	2.5	p-Toluidine "	1.7	3.0
o-Anisidine "	1.0	2.8	o-Anisidine "	1.0	2.8
p-Anisidine "	2.8	4.2	p-Anisidine "	1.2	3.5

TABLE 28.

(v) OVERALL MEAN LIGHT FASTNESS FIGURES* FOR O-HYDROXYAZO DYES (EXCLUDING FIGURES FOR R-ACID DYES ON WOOL).

Substituent group in base, (aniline)	Overall mean light fastness figure.
-	3.05
o-$\mathrm{NO_2}$	4.15
m-$\mathrm{NO_2}$	3.85
p-$\mathrm{NO_2}$	4.23
2 + 4-$\mathrm{(NO_2)_2}$	5.18
o-Cl	3.00
m-Cl	3.68
p-Cl	3.48
2:4-$\mathrm{Cl_2}$	3.00
p-$\mathrm{CH_3}$	3.08
o-$\mathrm{OCH_3}$	1.91
m-$\mathrm{SO_3H}$	4.33
o-COOH	2.67

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* Class 3 water-soluble dyes not included above.

TABLE 29.

(vi) REPORTED OXIDATION PRODUCTS OF AZO COMPOUNDS.

Authors	Azo Compounds.	Method of decomposition.	Products obtained.
Petriew	Azobenzene	CrO_3 in bomb at 150-200°C.	Azobenzene.
Angeli	"	30% H_2O_2 and glacial acetic acid	"
Fichter	"	Electrochemical oxidation	p-p'-Dihydroxyazobenzene, diphenyl disazophenol, phenol and acetic acid. The formation of azoxybenzene was taken to be the first stage of oxidation although it could not be identified in the reaction mixture.
Lauth	Azo dyes	PbO_2 & H_2SO_4	Diazonium salt and quinone.
Haller & Ziersch	Benzeneazo-β-naphthol	Glacial acetic acid and H_2O_2	Phthalic acid, phthalonic acid and a phenolic high molecular compound.
"	"	O_3 through a glacial acetic acid solution of dye.	Similar substances to above.
Linton, Holder & Bigelow	p-Nitro-p'-hydroxyazobenzene, p-hydroxyazobenzene and p-amino-azobenzene	30% H_2O_2	Prolonged treatment disrupts both benzene rings in the case of first two compounds, CO_2, H_2O, and N_2 or oxides of N being formed, Oxidation of third compound is not complete after 6 days.

Authors.	Azo compounds.	Method of decomposition.	Products obtained.
Seyewetz & Chaix	Azobenzene, Azotoluene	NaOCl in acid medium	No change.
(See also text of thesis for other dyes used)	Azo dyes	"	Original diazonium compound and an oxidation or chlorination product of the amine or phenol residue.
"	Orange I	"	Diazosulphanilic acid chloride, and 2-chloro-α-naphthaquinone.
"	Orange II	"	Diazosulphanilic acid chloride, dihydro β-naphthaquinone dichloride, the latter being converted into dihydroxy-β-naphthaquinone.
"	Aminoazobenzene	"	Diazobenzene chloride and chloranil
"	Polyazo derivatives of diazotised aminoazo compounds	"	Diazo compounds and oxidation products of the residues of amines or phenols used in preparation, similar to monoazo compounds.
"	Polyazo compounds from diamines	"	Tetrazo derivative~~s~~ of the original diamine and oxidation products analogous to those in the case of monoazo compounds.
"	Tartrazine (C. I. No. 640)	"	CO_2, diazo compound and a quinone.
Wallach & Kiepenheur	*p*-Hydroxyazobenzene	HNO_3 (Sp. gr. 1.2)	*m*-Dinitrophenol.

Authors.	Azo Compounds.	Method of decomposition.	Products Obtained.
Bohn and Heumann	p-Hydroxyazobenzene	Cold fuming or warm warm conc. HNO_3	m-Dinitrophenol.
Meldola & Morgan	Benzeneazonaphthols and their ethyl ethers	HNO_3(sp. gr. 1.42)	Dinitro derivatives of the naphthol components.
Schmidt	Azo dyes	Cold red fuming HNO_3	Nitrate of the diazo compound and a nitro derivative of the coupling component.
Rowe and Levin.	Azo derivatives of β- naphthol	Cold fuming HNO_3	Fission may or may not be accompanied by nitration of the diazo residue according to the constitution of the latter.
Rowe & Dangerfield	Azo dyes	Various strengths of H_2SO_4	Re-formation of the primary component base without reduction of NO_2 group, if present.
	Orange I	"	First component base, ammonia and α-naphthaquinone.
	Orange II	"	First component base, ammonia and β-hydroxy-α-naphthaquinone.
Haller & Ziersch	Azo β-naphthol dyes	Photochemical	Dye peroxide, β-naphthaquinone, phthalic acid, phthalonic acid and phenolic decomposition products.

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ABBREVIATIONS USED FOR REFERENCES.

J. S. D. C.	Journal of the Society of Dyers and Colourists.
Melliand Textilber.	Melliand Textilberichte.
Z. angew. Chem.	Zeitschrift für Angewandte Chemie.
J. Textile Inst.	Journal of the Textile Institute.
Ber.	Berichte der Deutschen Chemischen Gesselschaft.
J. C. S.	Journal of the Chemical Society.
Annalen.	Annalen der Chemie.
J. pr. Chem.	Journal für Praktische Chemie.
J. Ind. Chem. Soc.	Journal of the Indian Chemical Society.
Biochem. Z.	Biochemische Zeitschrift.
Canadian J. Res.	Canadian Journal of Research.
Bull. Soc. Chim.	Bulletin de la Société Chimique de France.
Helv. Chim. Acta.	Helvetica Chimica Acta.
Chem. Ztg.	Chemiker-Zeitung.
J. Phys. Chem.	Journal of Physical Chemistry.
Atti R. Accad. Lincei.	Atti della Reale Accademia dei Lincei. (Rendiconti).
Z. f. Elektrochem.	Zeitschrift für Elektrochemie.
Chim. et. Ind.	Chimie et Industrie.
Z. physik. Chem.	Zeitschrift für physikalische Chemie.
Ann. Phys.	Annalen der Physik (Wien and Planck).
Chem. and. Ind.	Chemistry and Industry.
Chem. Obzor.	Chemicky Obzor Praha.
Farber-Ztg.	Färber-Zeitung.
Amer. Dyestuff Rep.	American Dyestuff Reporter.

J. S. C. I.	Journal of the Society of Chemical Industry.
J. Russ. Phys. Chem. Soc.	Journal der Russischen Physikalisch chemischen Gesselschaft.
Chem. Weekblad	Chemische Weekblad.
Phot. Kerr.	Photochemische Korrespondenz.
Anilinokras., Prom.	Anilinokrasočnaja Promyšlennost (russ).
J. Am. Chem. Soc.	Journal of the American Chemical Society.
Gazz. chim. ital.	Gazzetta Chimica Italiana.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Chem. Rev.	Chemical Reviews.
Z. anorg. Chem.	Zeitschrift für anorganische Chemie.

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PATENT PHOTOCOPYING FRAME
USED IN FADING EXPERIMENTS.

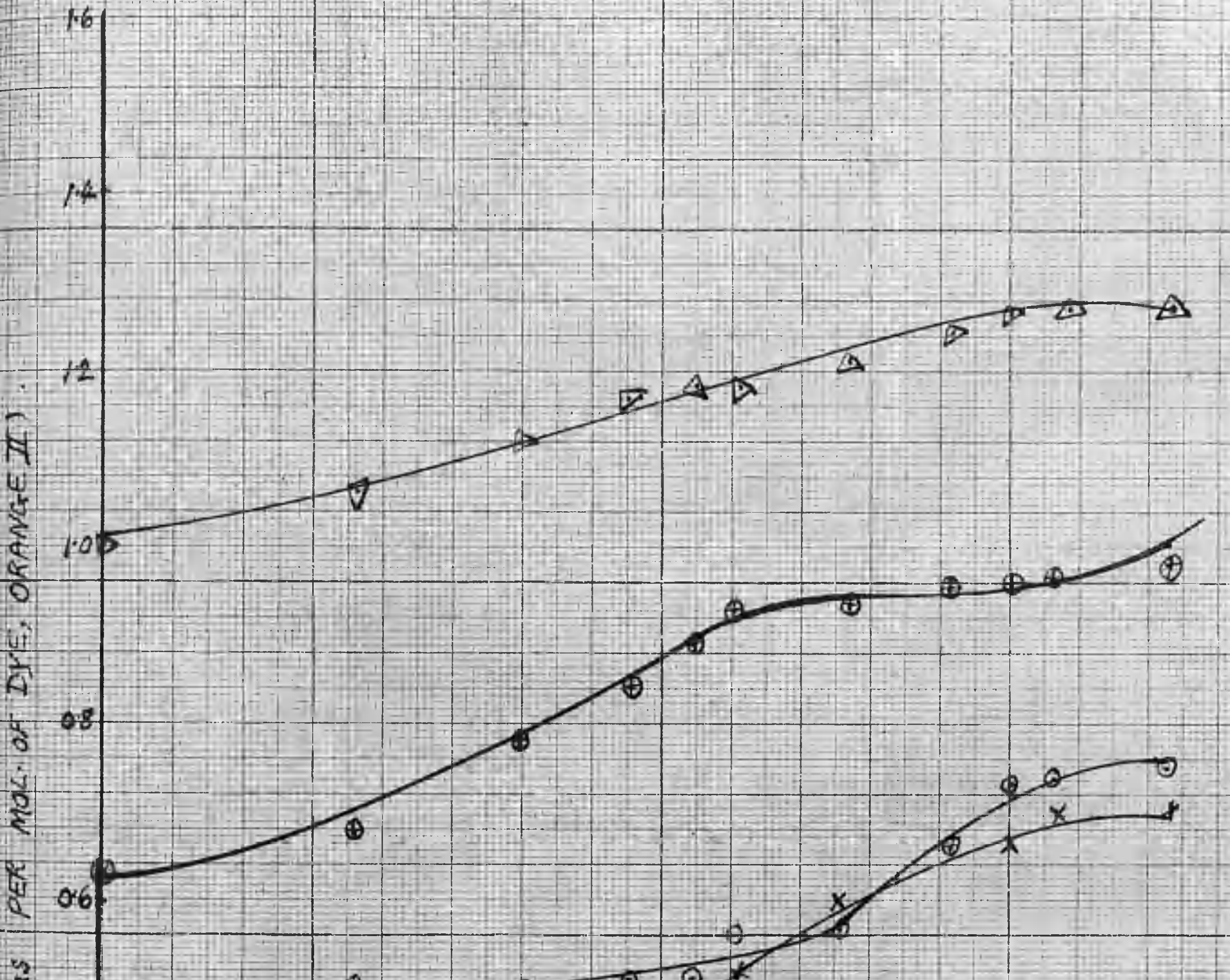


FIG. 1 – OXIDATION OF ORANGE II WITH VARIOUS OXIDISING AGENTS.

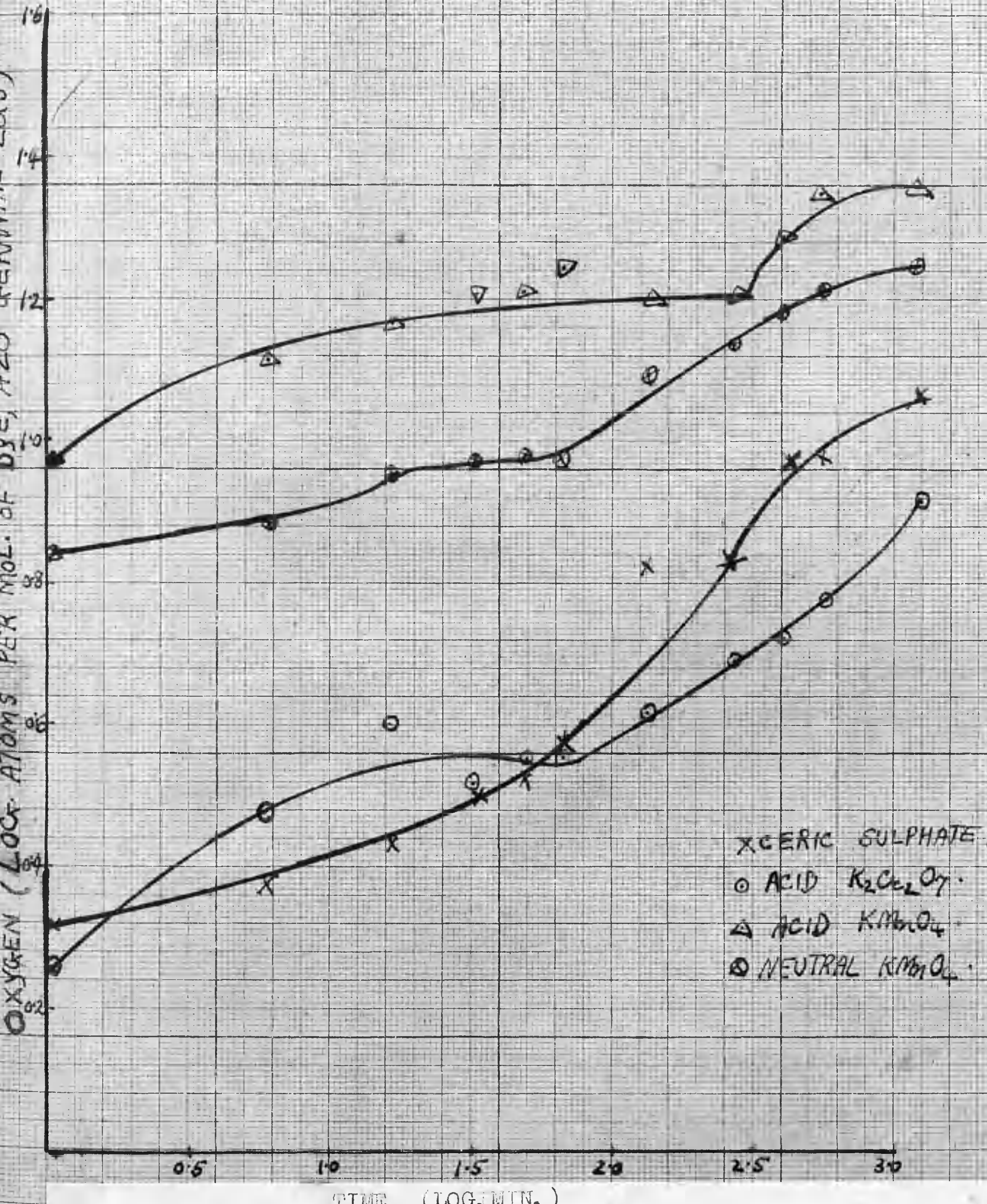
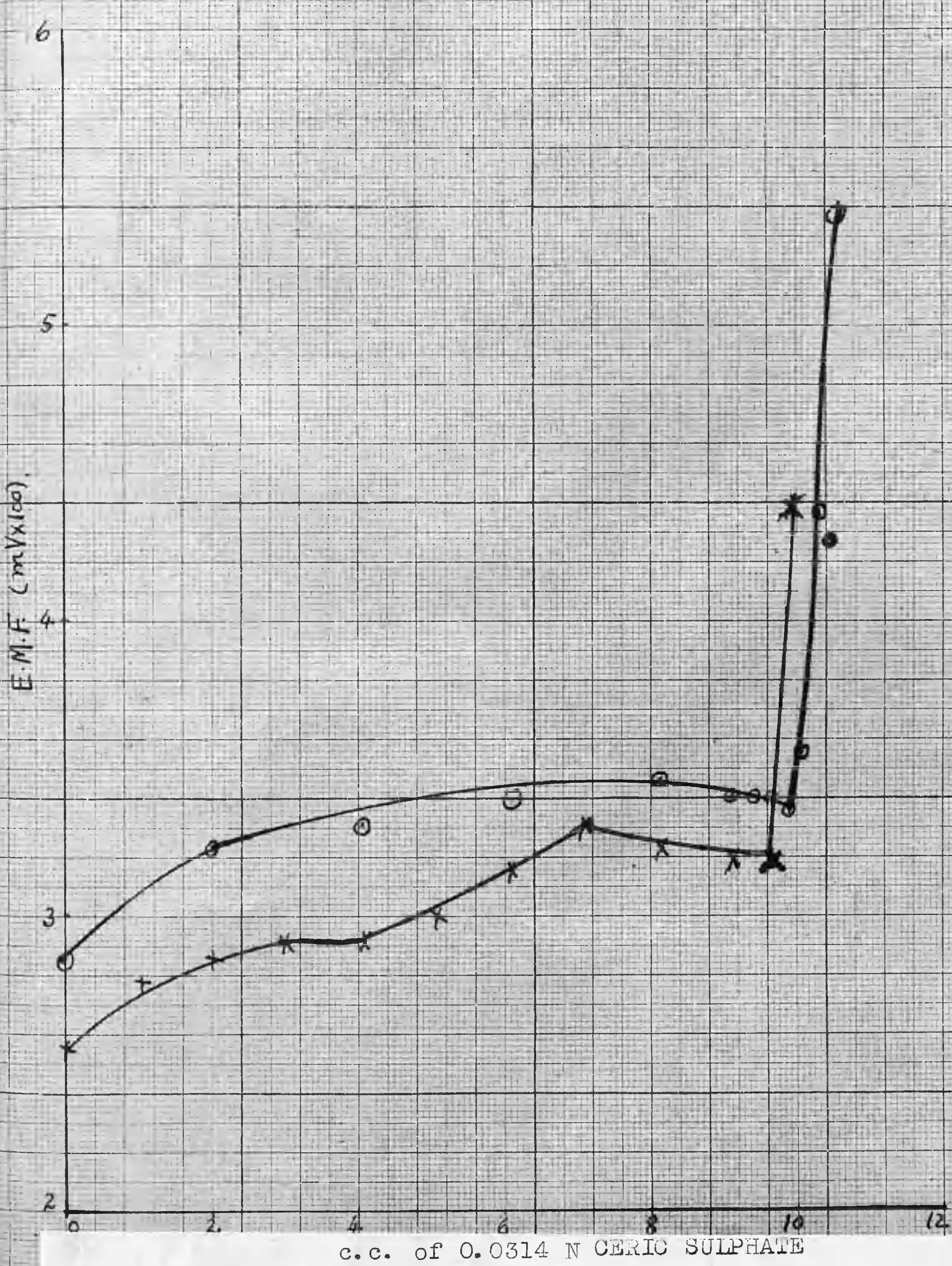


FIG. 2 - OXIDATION OF AZO GERAN~~D~~INE 2 GS WITH VARIOUS OXIDISING AGENTS.



c.c. of 0.0314 N CERIC SULPHATE

FIG. 3. - POTENTIOMETRIC TITRATION OF ORANGE II WITH CERIC SULPHATE IN PRESENCE OF EXCESS H_2SO_4(O) AND IN ABSENCE OF EXCESS H_2SO_4(X)

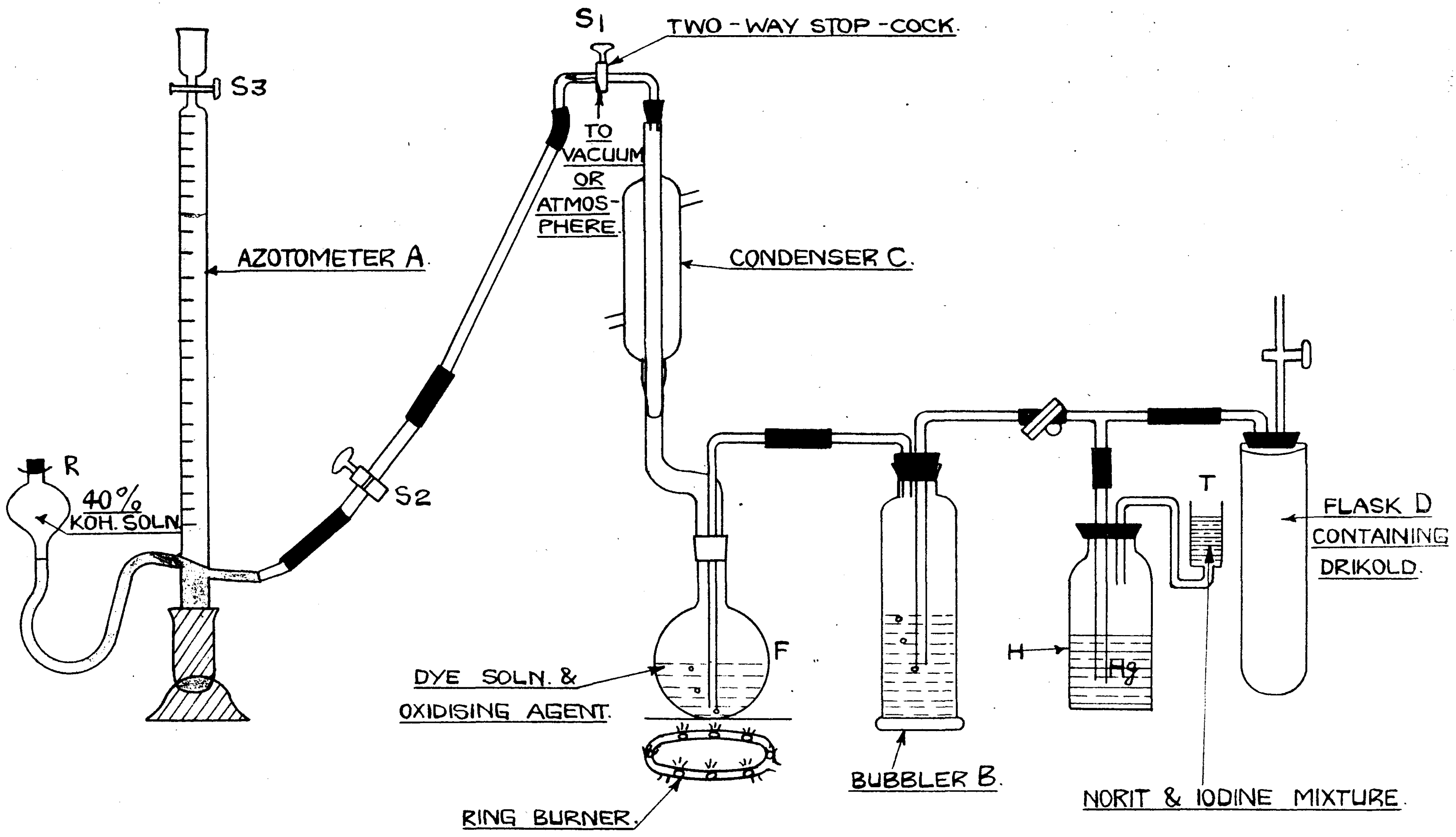
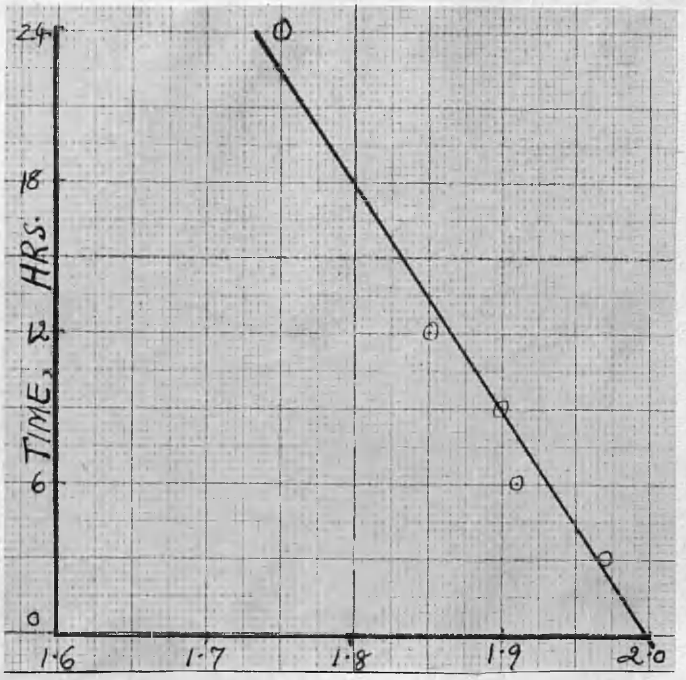
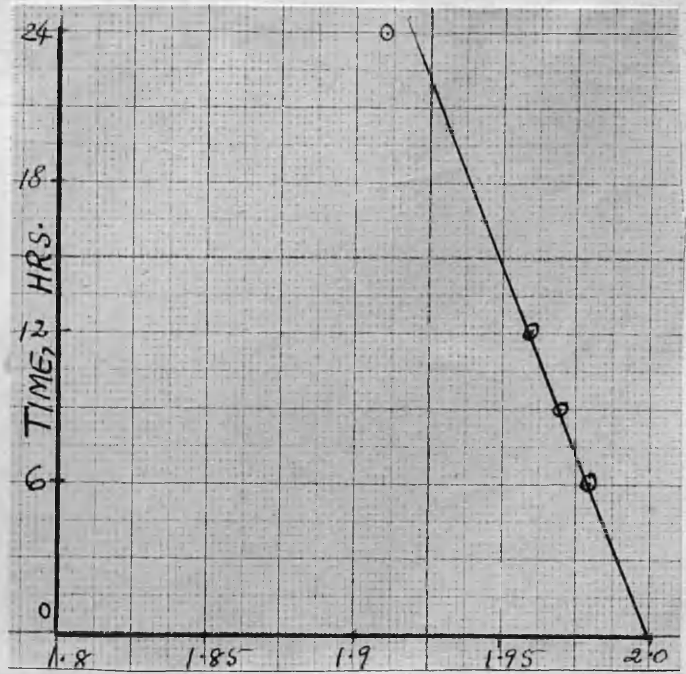


FIG.4 MODIFIED DUMAS' APPARATUS FOR MEASURING NITROGEN.



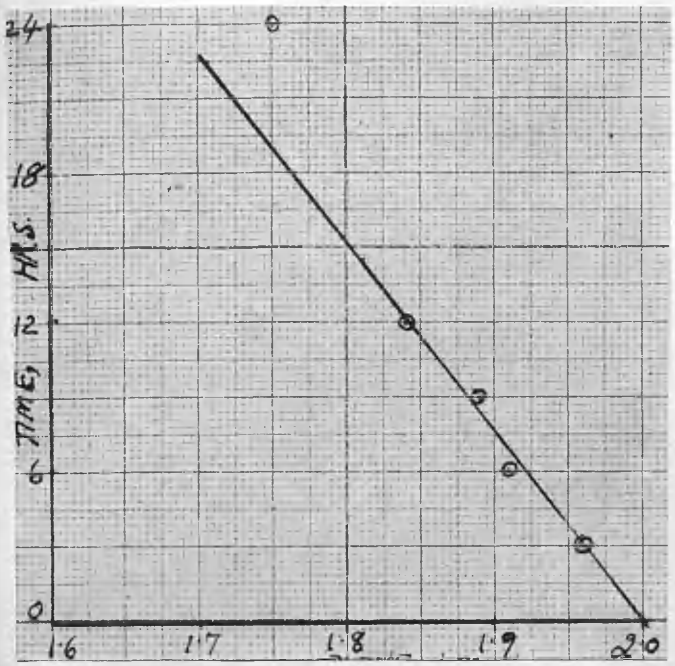
UNOXODISED DYE, LOG %

FIG. 5 - OXIDATION OF ORANGE II WITH NEUTRAL H_2O_2



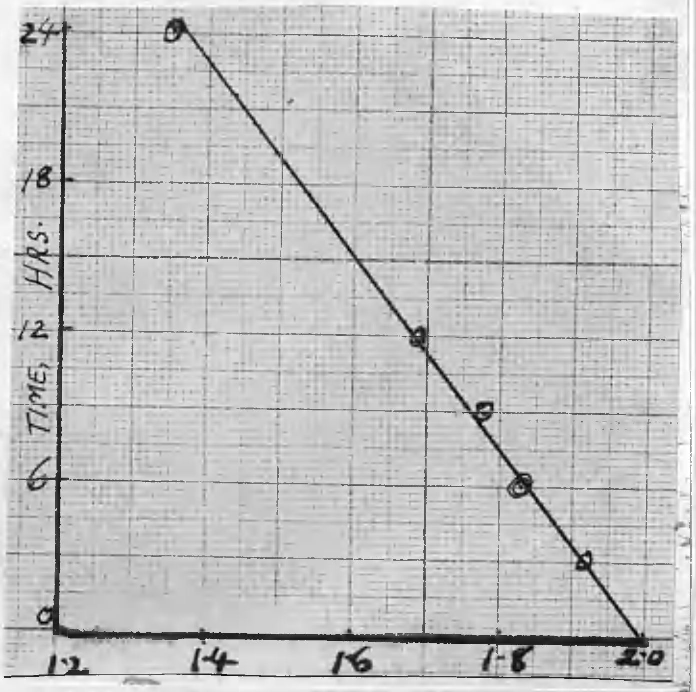
UNOXIDISED DYE, LOG %

FIG. 6 - OXIDATION OF ORANGE I WITH NEUTRAL H_2O_2.



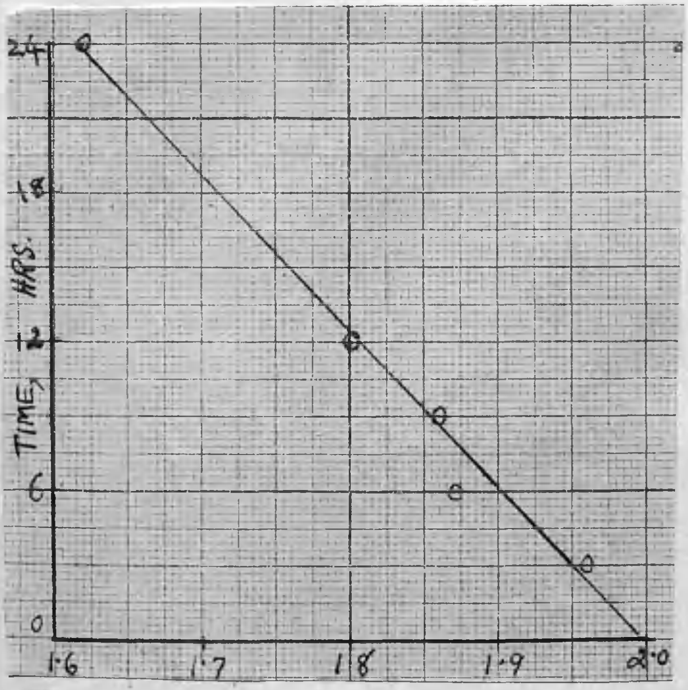
UNOXIDISED DYE, LOG %

FIG. 7 - OXIDATION OF DYE, ANILINE →R-ACID WITH NEUTRAL H_2O_2



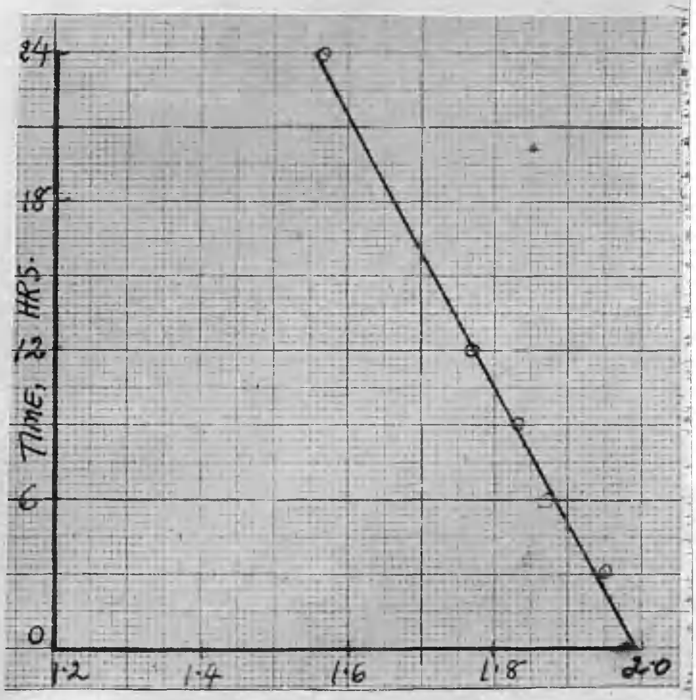
UNOXIDISED DYE, LOG %

FIG. 8 - OXIDATION OF DYE, o-NITROANILINE →R-ACID, WITH NEUTRAL H_2O_2.



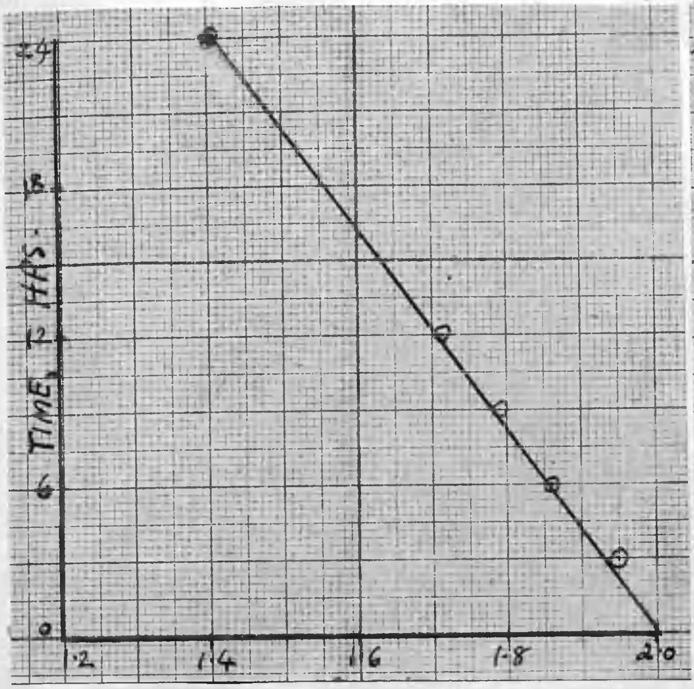
UNOXIDISED DYE, LOG %

FIG. 9 - OXIDATION OF DYE, m-NITROANILINE →R-ACID WITH NEUTRAL H_2O_2



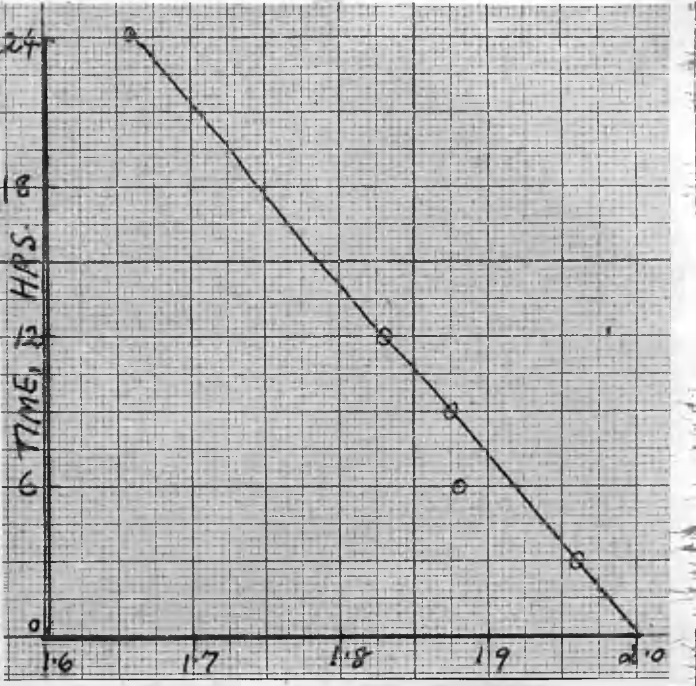
UNOXIDISED DYE, LOG %

FiG 10. OXIDATION OF DYE, p-NITROANILINE →R-ACID WITH NEUTRAL H_2O_2



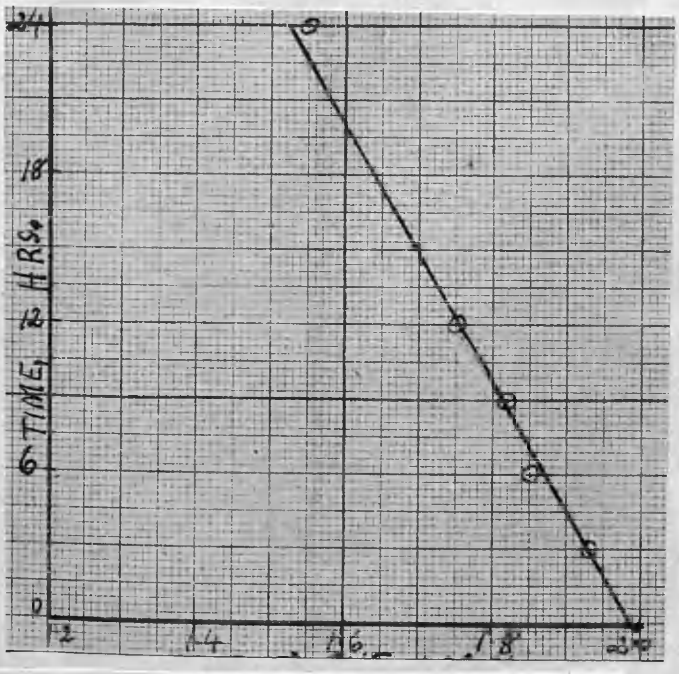
UNOXIDISED DYE, LOG %

FIG. 11 - OXIDATION OF DYE, o-CHLORO-ANILINE → R-ACID, WITH NEUTRAL H_2O_2



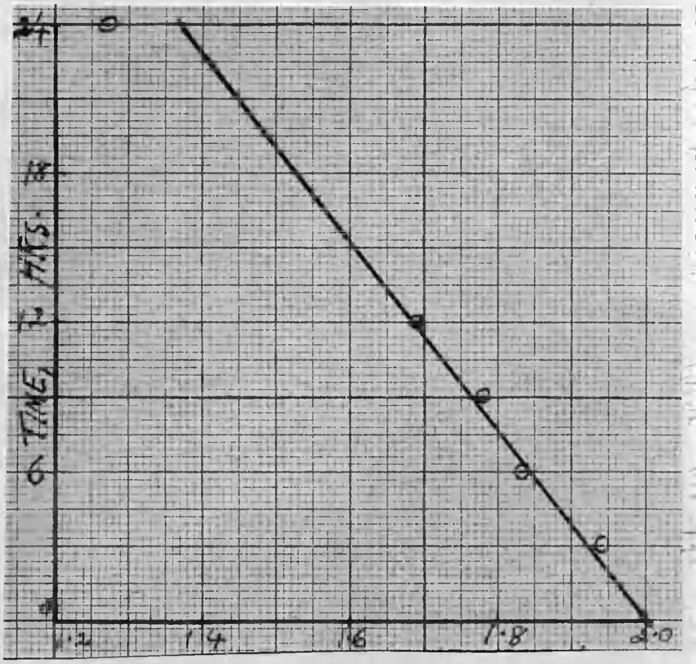
UNOXIDISED DYE, LOG %

FIG. 12 - OXIDATION OF DYE, m-CHLORO-ANILINE → R-ACID, WITH NEUTRAL H_2O_2.



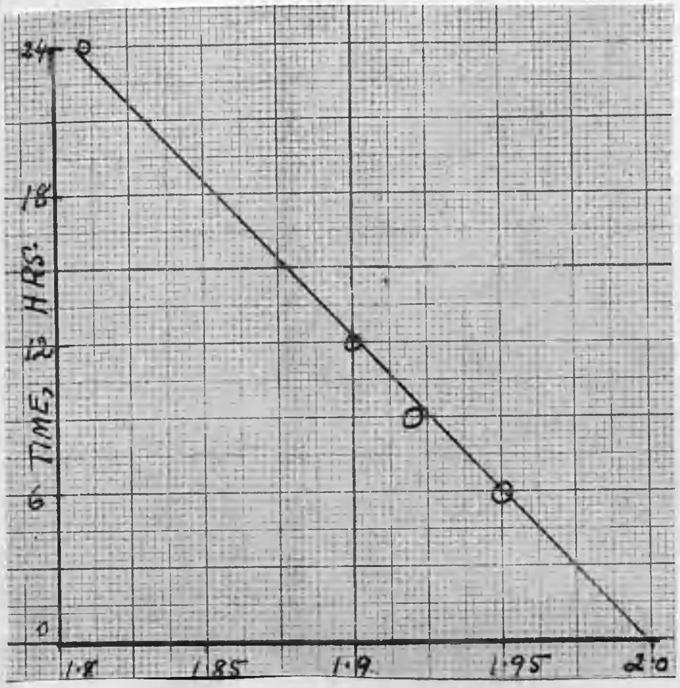
UNOXIDISED DYE, LOG %

FIG. 13 - OXIDATION OF DYE, p-CHLORO-ANILINE → R-ACID WITH NEUTRAL H_2O_2.



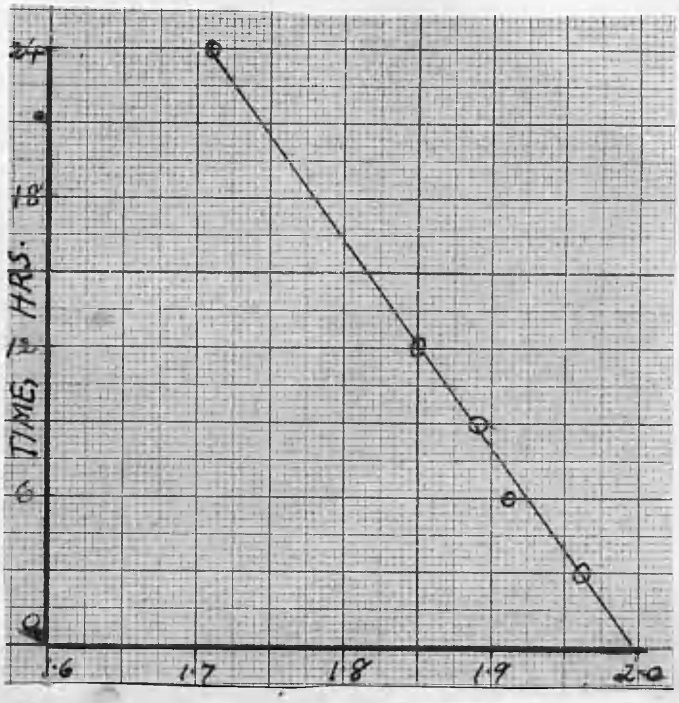
UNOXIDISED DYE, LOG %

FIG. 14 - OXIDATION OF DYE, 2:4-DICHLORO-ANILINE → R-ACID, WITH NEUTRAL H_2O_2.



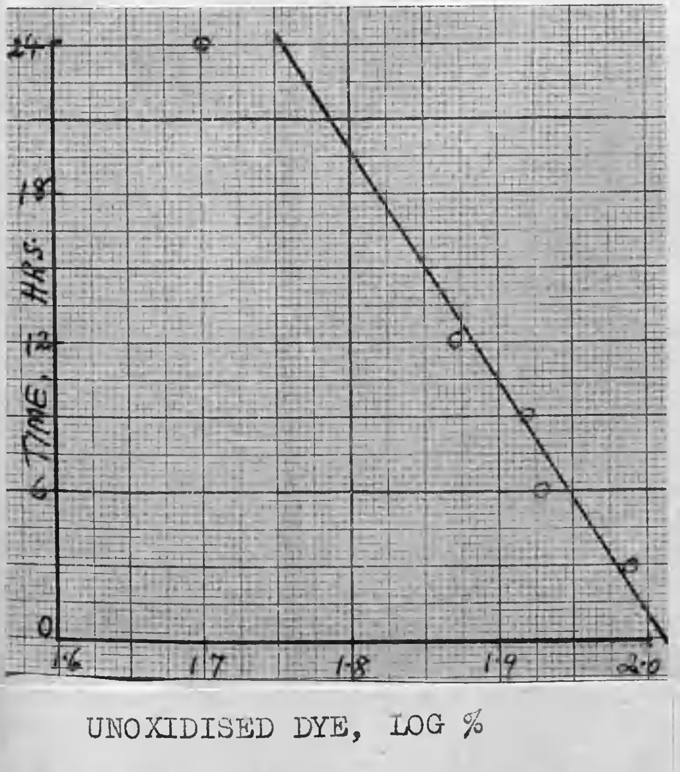
UNOXIDISED DYE, LOG %

FIG. 15 - OXIDATION OF DYE, m-TOLUIDINE → R-ACID, WITH NEUTRAL H_2O_2



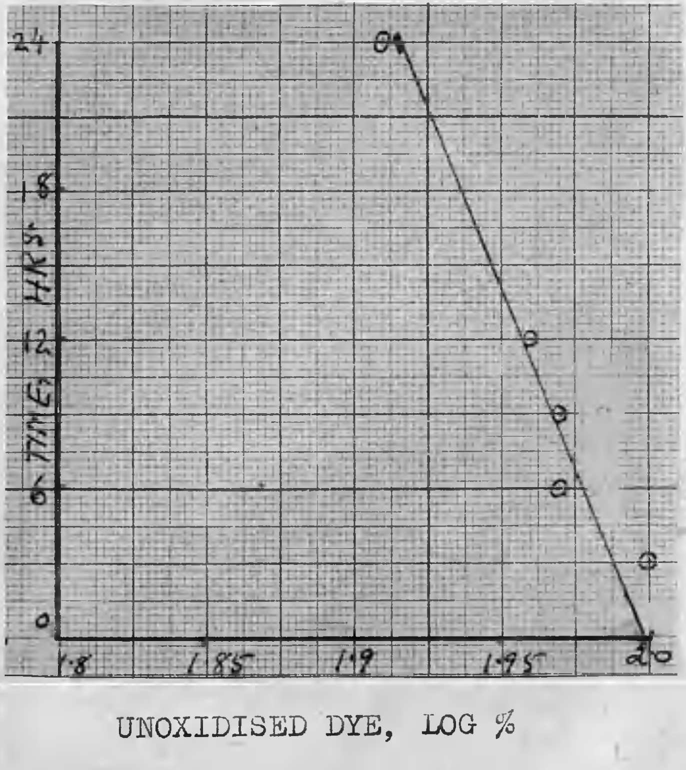
UNOXIDISED DYE, LOG %

FIG. 16 - OXIDATION OF DYE, p-TOLUIDINE →R-ACID, WITH NEUTRAL H_2O_2.



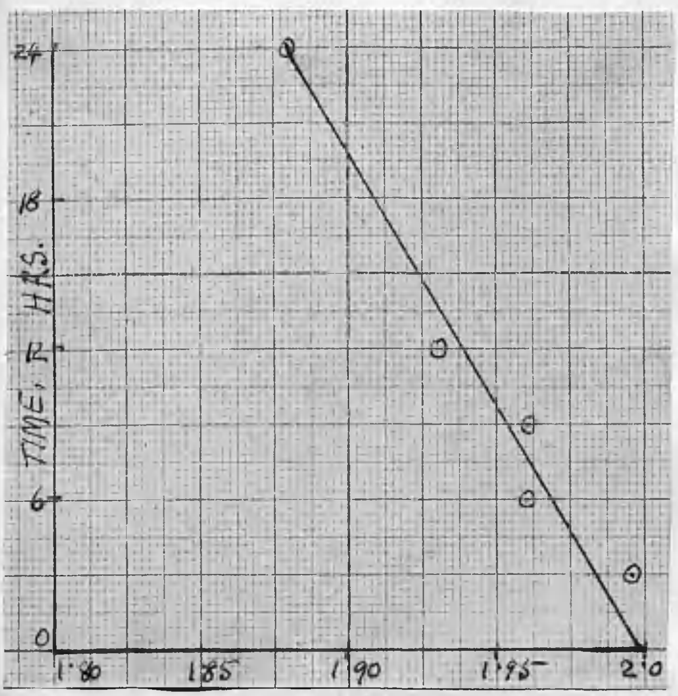
UNOXIDISED DYE, LOG %

FIG. 17 - OXIDATION OF DYE, o-ANISIDINE → R-ACID, WITH NEUTRAL H_2O_2



UNOXIDISED DYE, LOG %

FIG. 18 - OXIDATION OF DYE, p-ANISIDINE →R-ACID, WITH NEUTRAL H_2O_2.



IG.19 - OXIDATION OF DYE, ANTHRANILIC
CID → R-ACID, WITH NEUTRAL H_2O_2.

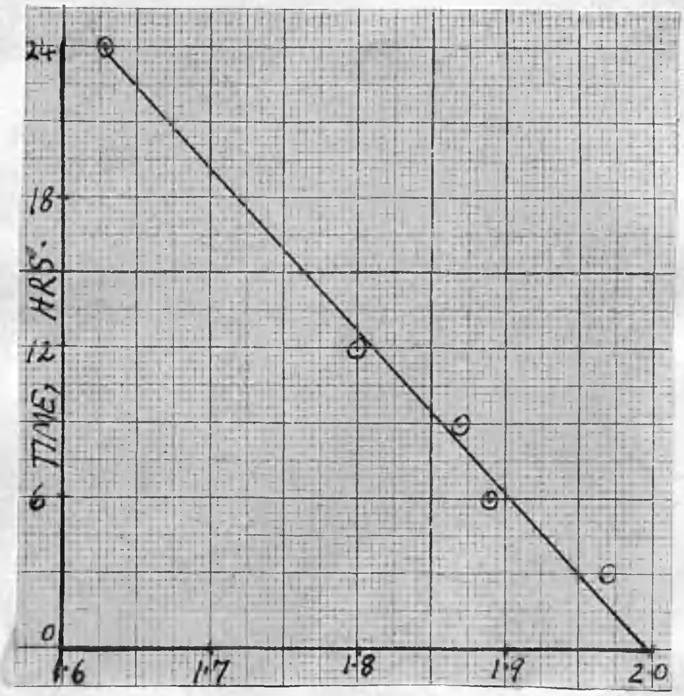


FIG. 20 - OXIDATION OF DYE, p-AMINOBENZOIC ACID → R-ACID, WITH NEUTRAL H_2O_2

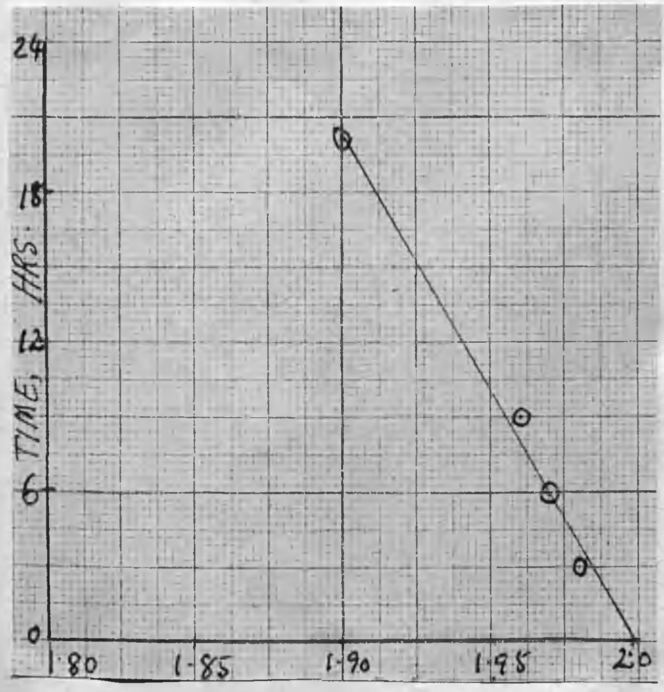


FIG. 21 - OXIDATION OF DYE, METANILIC ACID → R-ACID, WITH NEUTRAL H_2O_2.

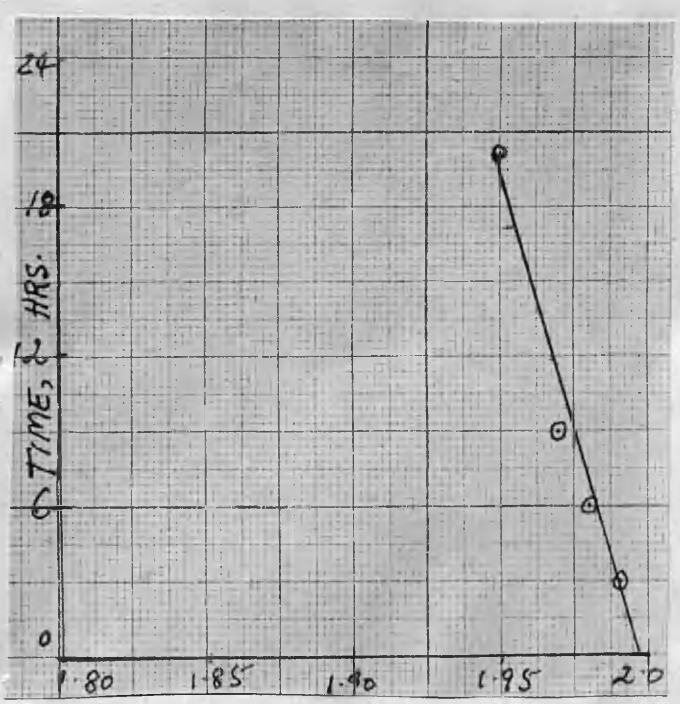


FIG. 22 - OXIDATION OF DYE, SULPHANILIC ACID → R-ACID, WITH NEUTRAL H_2O_2.

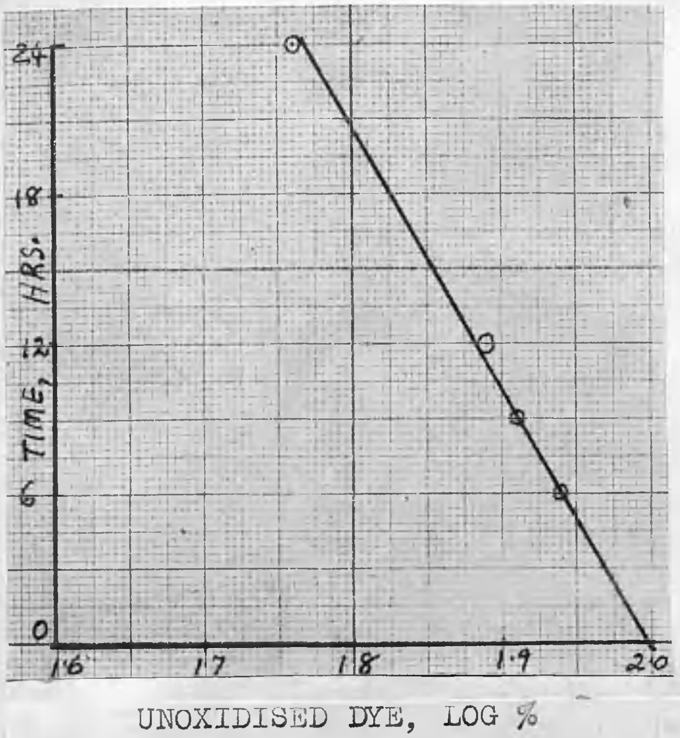


FIG. 23 - OXIDATION OF DYE, ANILINE →OXY-L-ACID, WITH NEUTRAL H_2O_2.

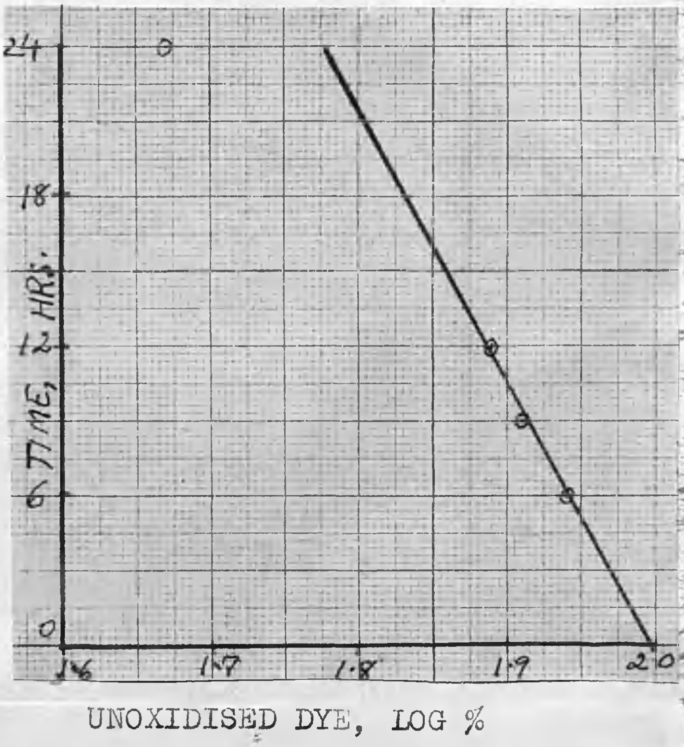


FIG. 24 - OXIDATION OF DYE, o-NITRO-ANILINE →OXY-L-ACID, WITH NEUTRAL H_2O_2

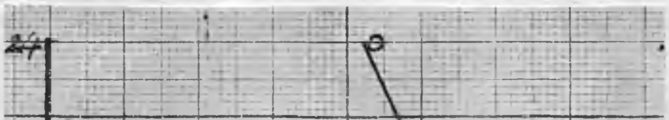


FIG. 25 - OXIDATION OF DYE, m-NITRO-ANILINE → OXY-L-ACID WITH NEUTRAL H_2O_2

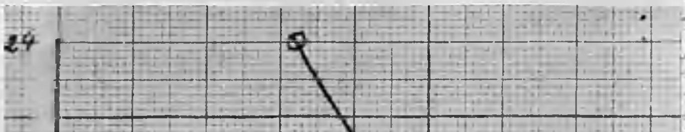
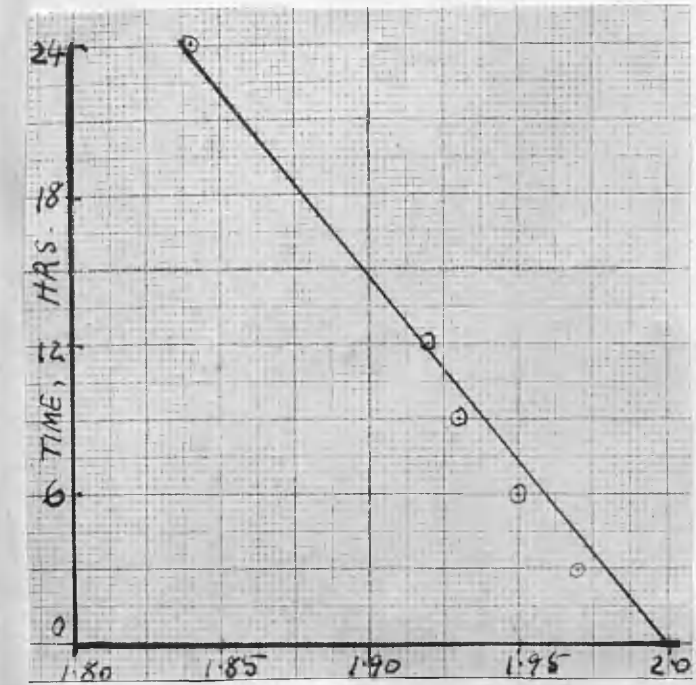
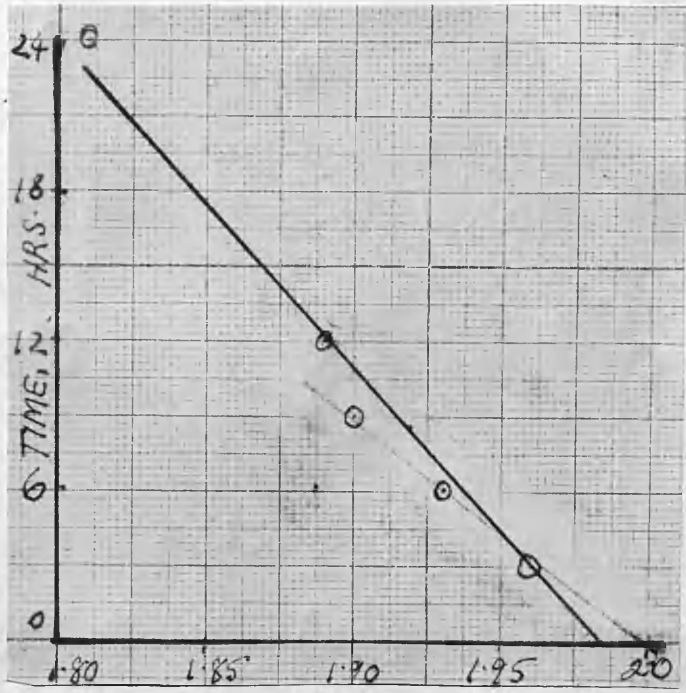


FIG. 26 - OXIDATION OF DYE, p-NITRO-ANILINE →OXY-L-ACID, WITH NEUTRAL H_2O_2.



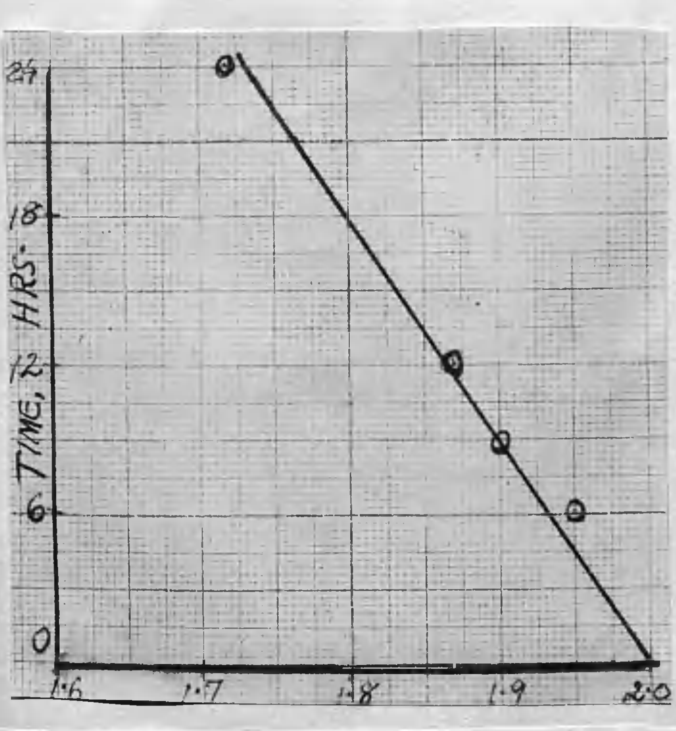
UNOXIDISED DYE, LOG %

FIG. 27 - OXIDATION OF DYE, o-CHLORO-ANILINE → OXY-L-ACID WITH NEUTRAL H_2O_2



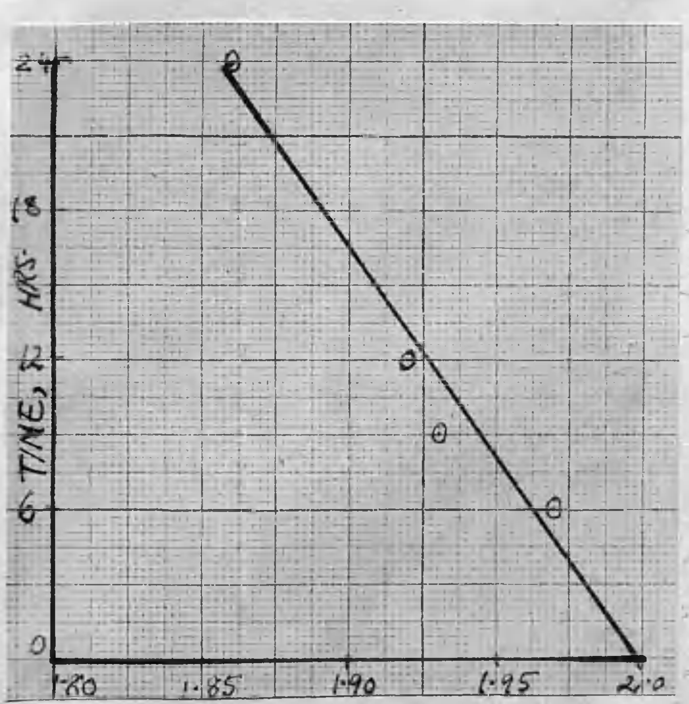
UNOXIDISED DYE, LOG %

FIG. 28 - OXIDATION OF DYE, m-CHLORO-ANILINE → OXY-L-ACID, WITH NEUTRAL H_2O_2.



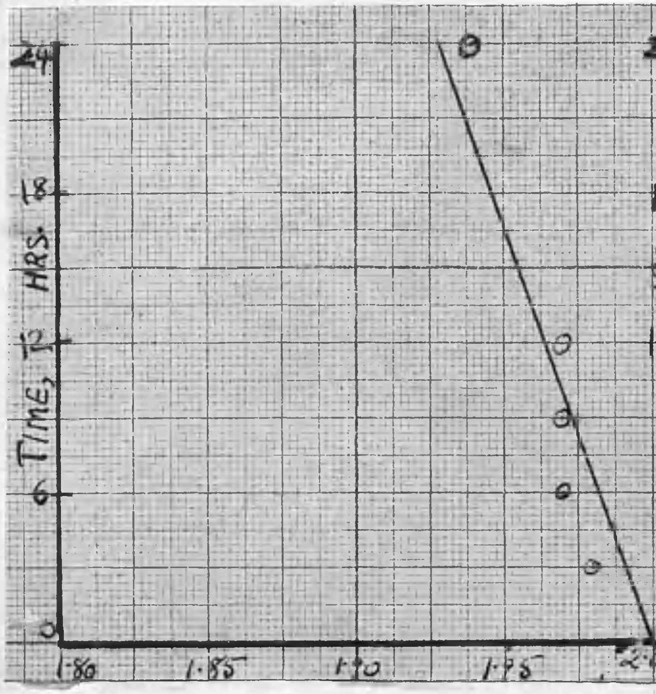
UNOXIDISED DYE, LOG %

IG. 29 - OXIDATION OF DYE, p-CHLORO-ILINE → OXY-L-ACID, WITH NEUTRAL H_2O_2.



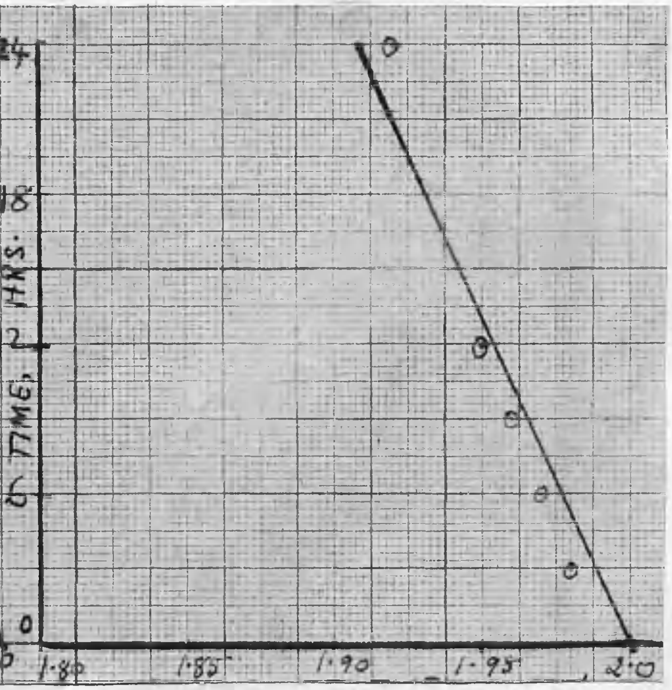
UNOXIDISED DYE, LOG %

FIG. 30 - OXIDATION OF DYE, 2:4-DICHLORO-ANILINE → OXY-L-ACID, WITH NEUTRAL H_2O_2.



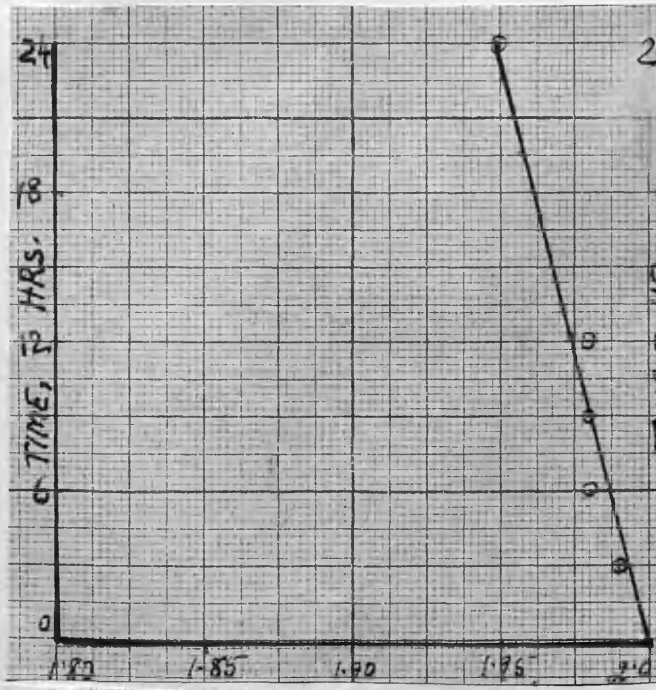
UNOXIDISED DYE, LOG %

FIG. 31 - OXIDATION OF DYE, m-TOLUIDINE
→ OXY-L-ACID, WITH NEUTRAL H_2O_2.



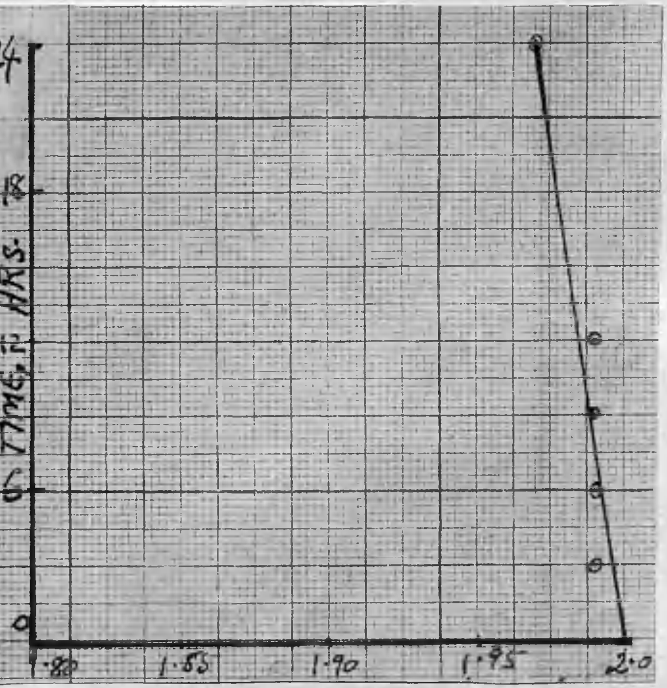
UNOXIDISED DYE, LOG %

FIG. 32 - OXIDATION OF DYE, p-TOLUIDIN
→ OXY-L-ACID, WITH NEUTRAL H_2O_2. -INE



UNOXIDISED DYE, LOG %

FIG. 33 - OXIDATION OF DYE, o-ANISIDINE
→ OXY-L-ACID WITH NEUTRAL H_2O_2.



UNOXIDISED DYE, LOG %

FIG. 34 - OXIDATION OF DYE, p-ANISIDINE
→ OXY-L-ACID, WITH NEUTRAL H_2O_2.

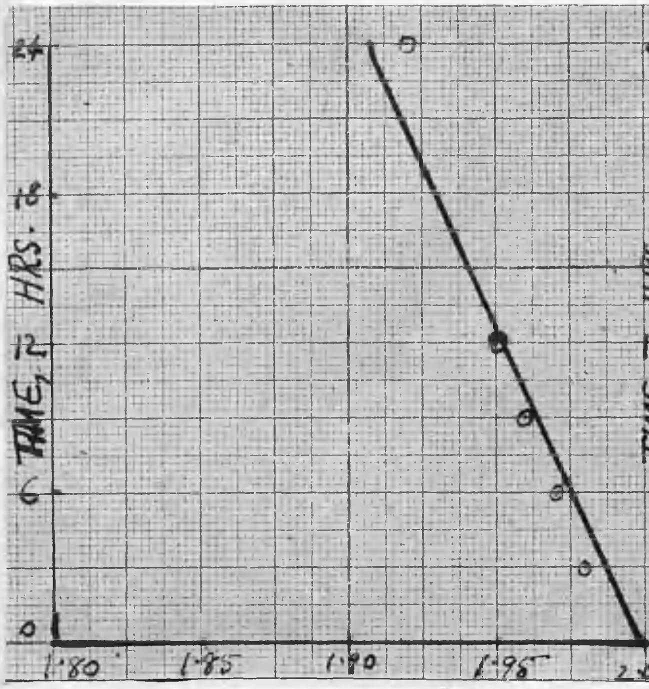


FIG. 35 - OXIDATION OF METANILIC ACID
OXY-L-ACID WITH NEUTRAL H_2O_2

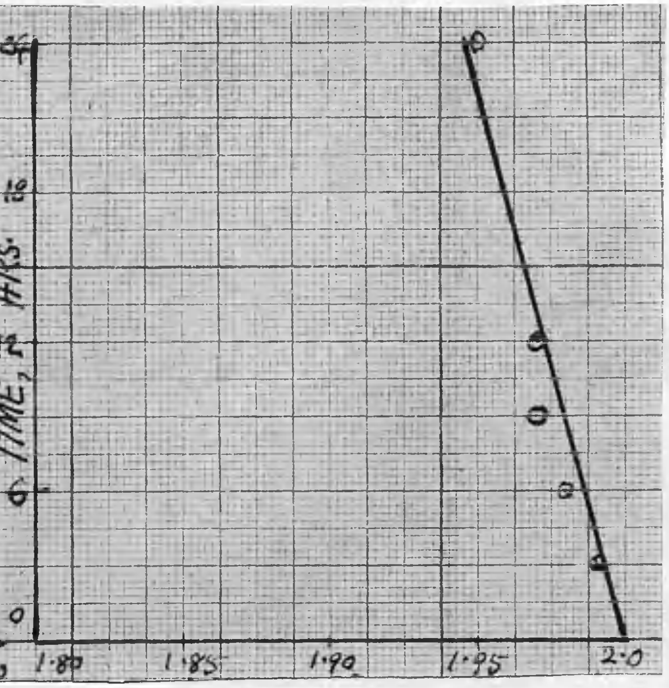


FIG. 36 - OXIDATION OF SULPHANILIC ACID
→ OXY-L-ACID WITH NEUTRAL H_2O_2.

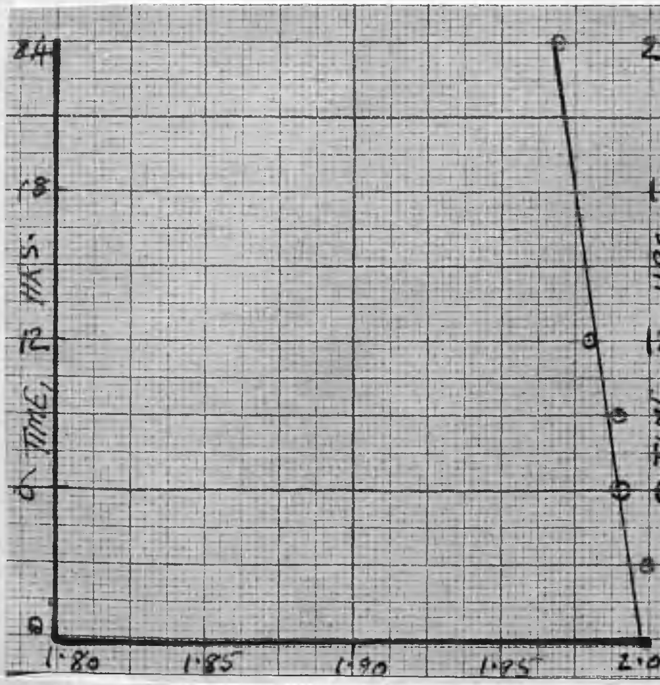


FIG. 37 - OXIDATION OF ANTHRANILIC ACI
→ OXY-L-ACID WITH NEUTRAL H_2O_2

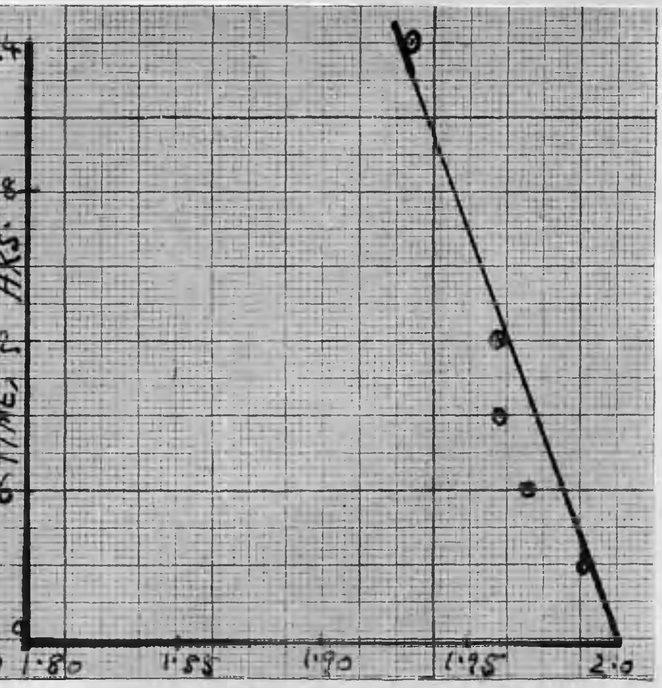


FIG. 38 - OXIDATION OF DYE, p-AMINO
BENZOIC ACID → OXY-L-ACID WITH NEUT

TRAL H_2O_2

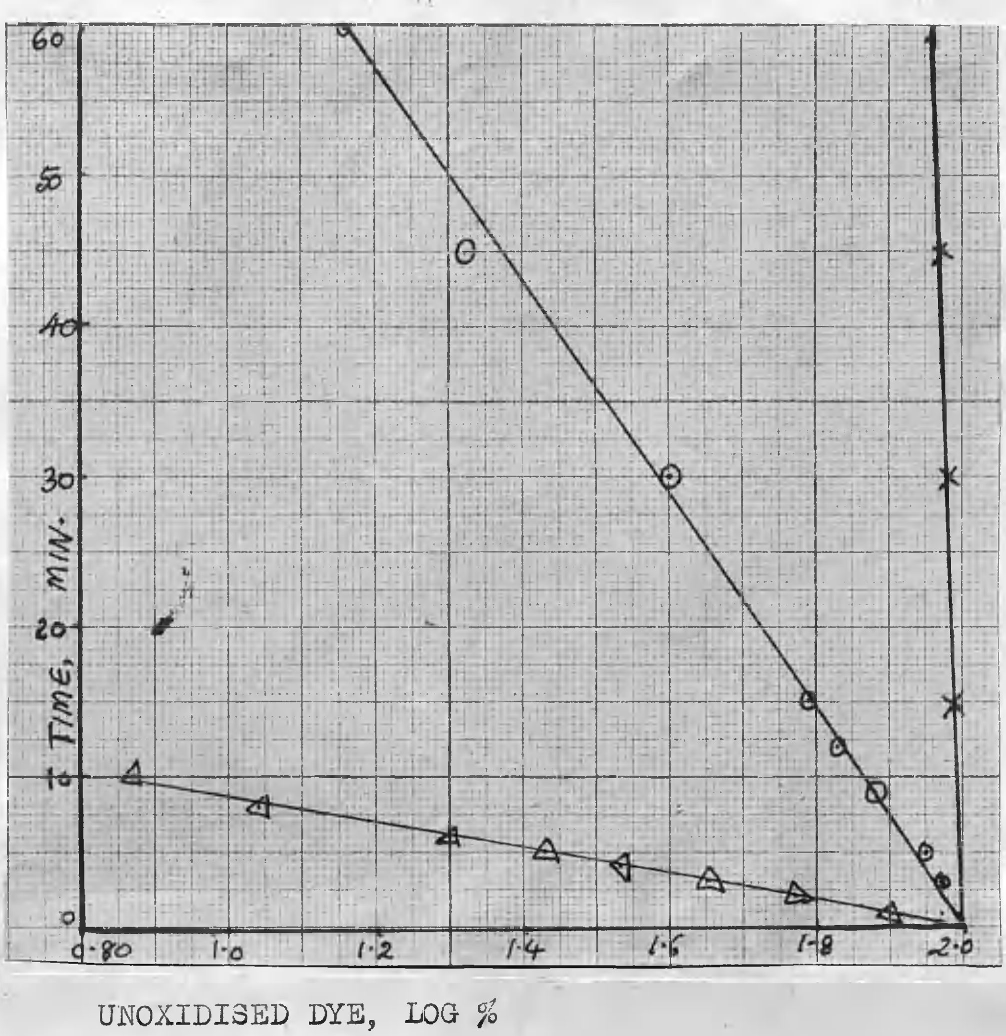


FIG. 39 - OXIDATION OF ORANGE II (△), ORANGE I (⊙), AND O-METHYL ETHER OF ORANGE I WITH ALKALINE H_2O_2. ⓧ

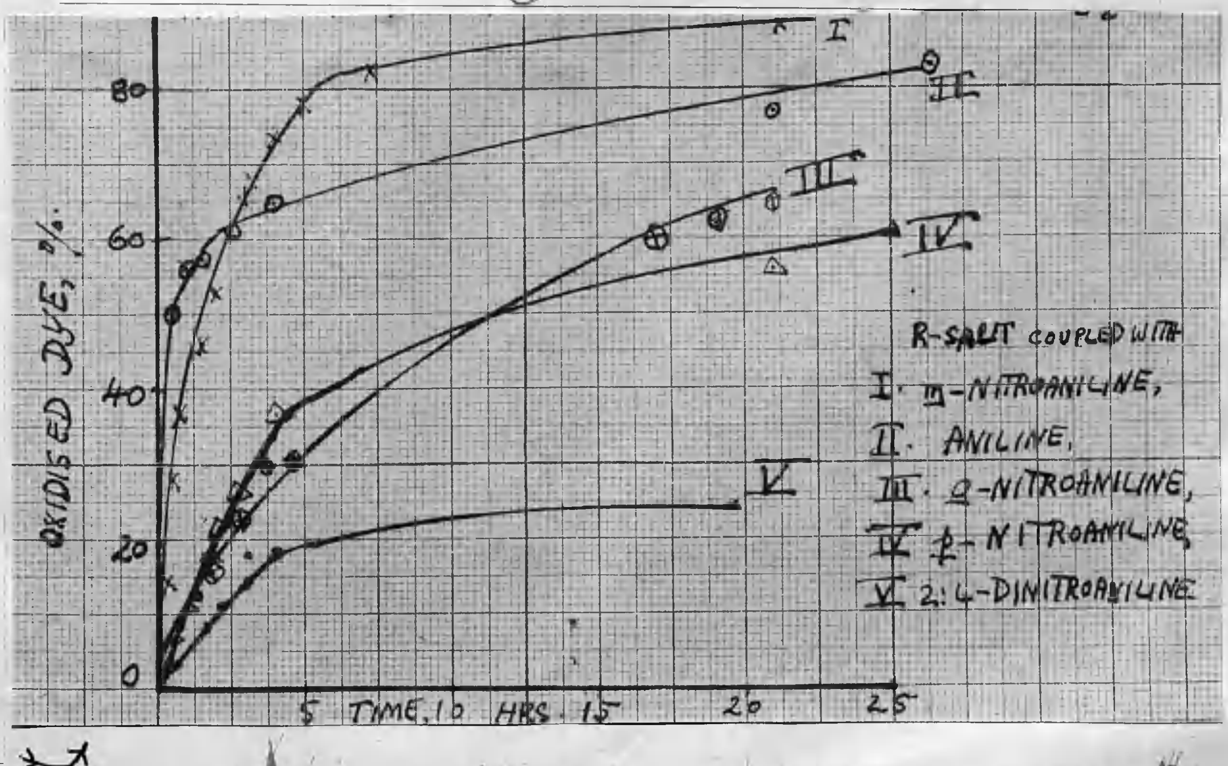
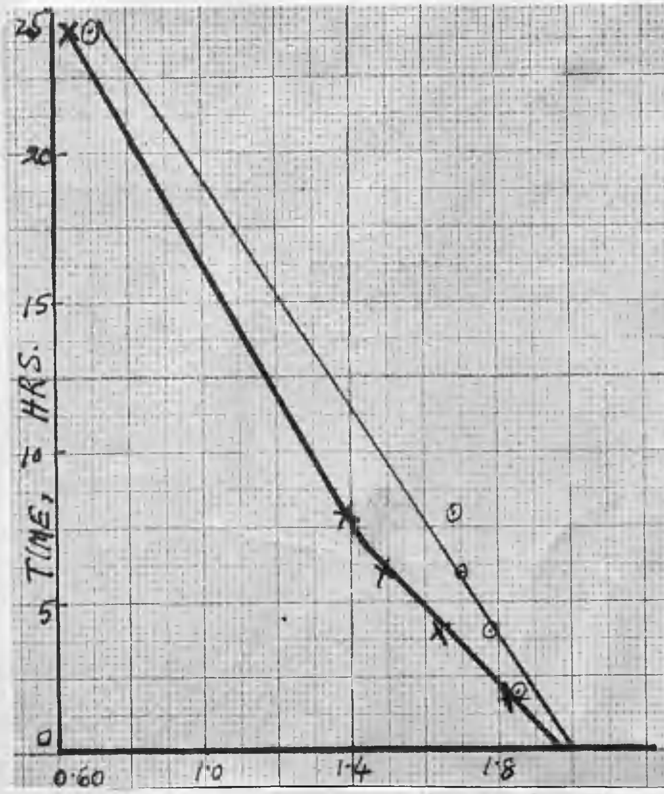


FIG. 40 - OXIDATION OF SOLUBLE DYES WITH ALKALINE H_2O_2.



IG.41 - OXIDATION OF DYES, ANILINE→
-ACID (⊙) AND o-NITROANILINE →
R-ACID (X) with ALKALINE H_2O_2

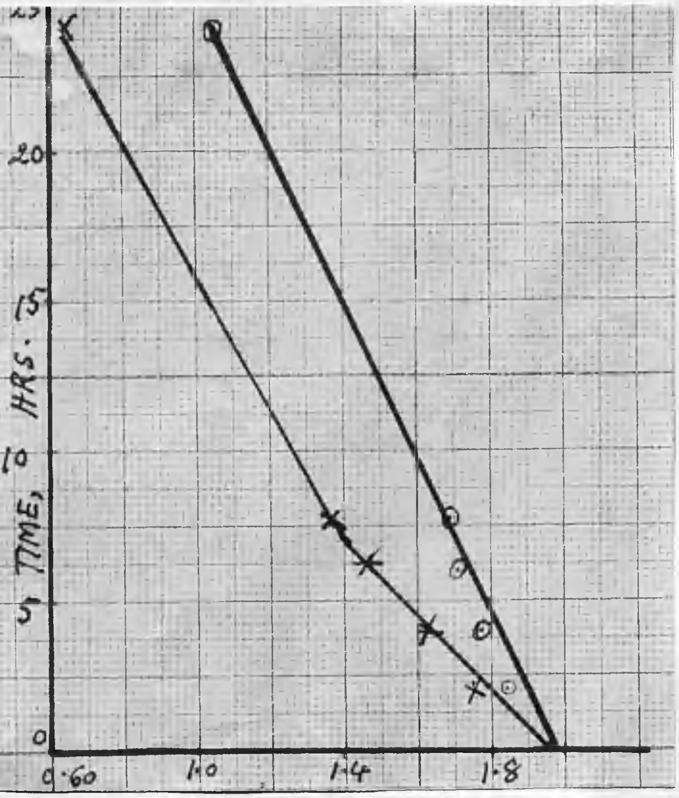


FIG. 42 - OXIDATION OF DYES, m-NITROANILINE →
R-ACID (⊙) AND p-NITROANILINE →
R-ACID (X) WITH ALKALINE H_2O_2.

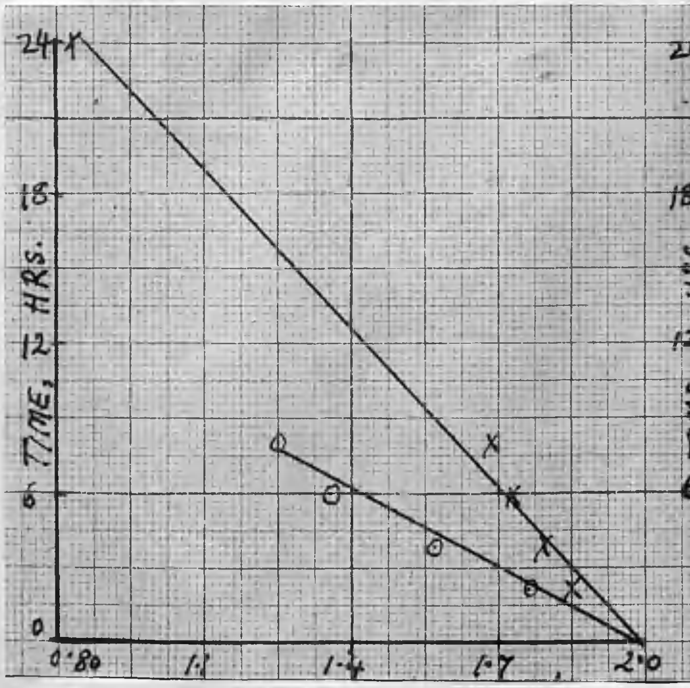


FIG. 43 - OXIDATION OF DYES,
o-CHLOROANILINE → R-ACID (⊙) and
m-CHLOROANILINE → R-ACID (X),
WITH ALKALINE H_2O_2

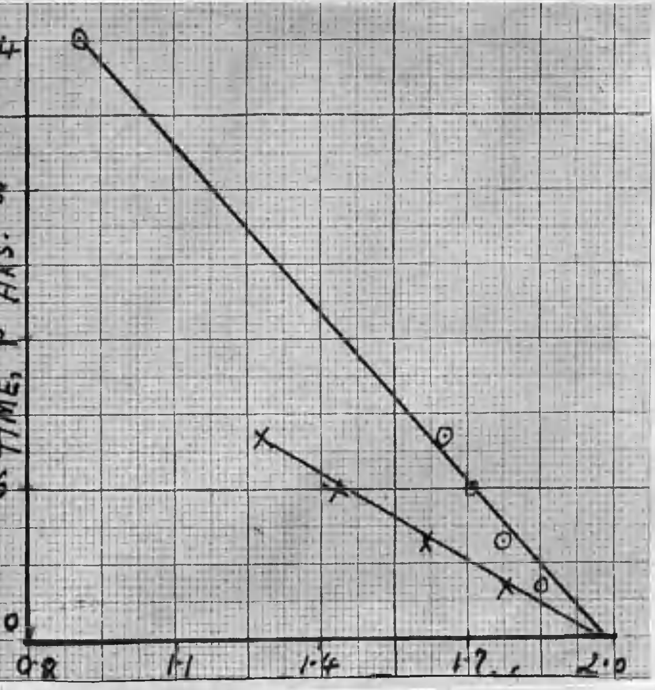


FIG. 44 - OXIDATION OF DYES,
p-CHLOROANILINE → R-ACID(⊙) and
2:4-DICHLOROANILINE →R-ACID (X)
WITH ALKALINE H_2O_2.

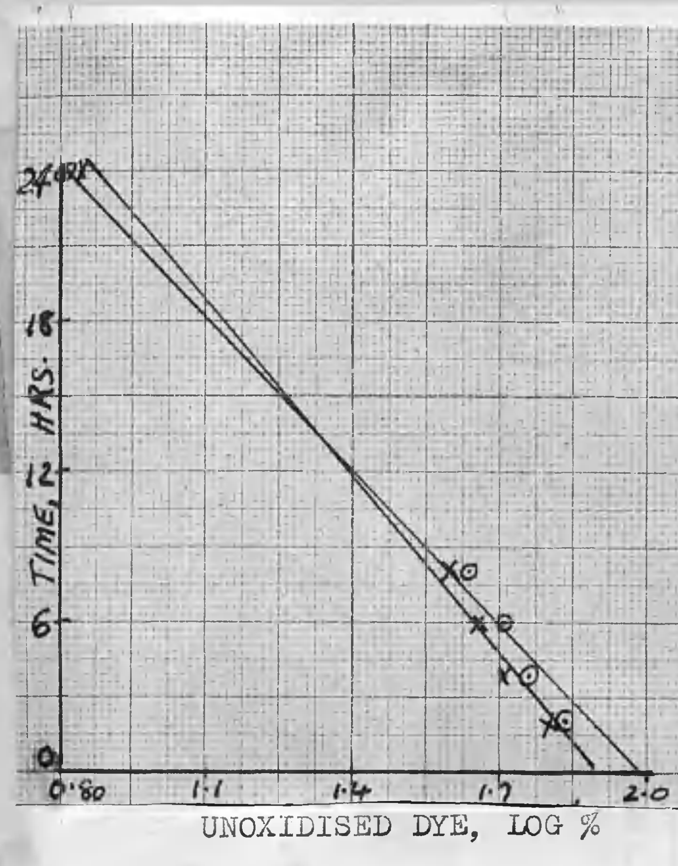


FIG. 45 - OXIDATION OF DYES, m-TOLUIDINE → R-ACID (⊙) and p-TOLUIDINE → R-ACID (×) WITH ALKALINE H_2O_2.

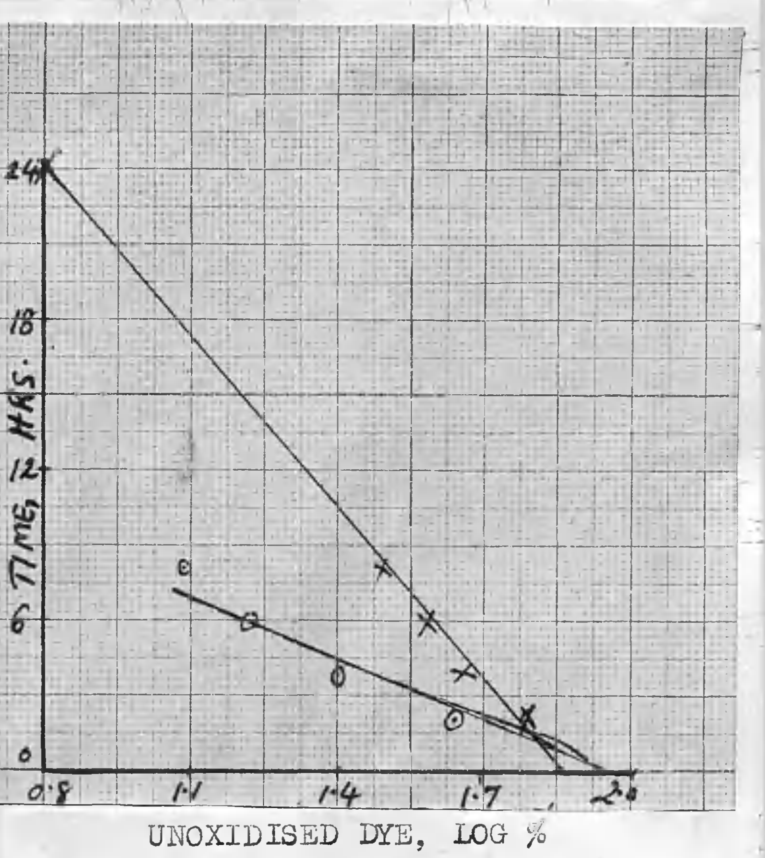


FIG. 46 - OXIDATION OF DYES, o-ANISIDINE → R-ACID (⊙) and p-ANISIDINE → R-ACID (×) WITH ALKALINE H_2O_2.

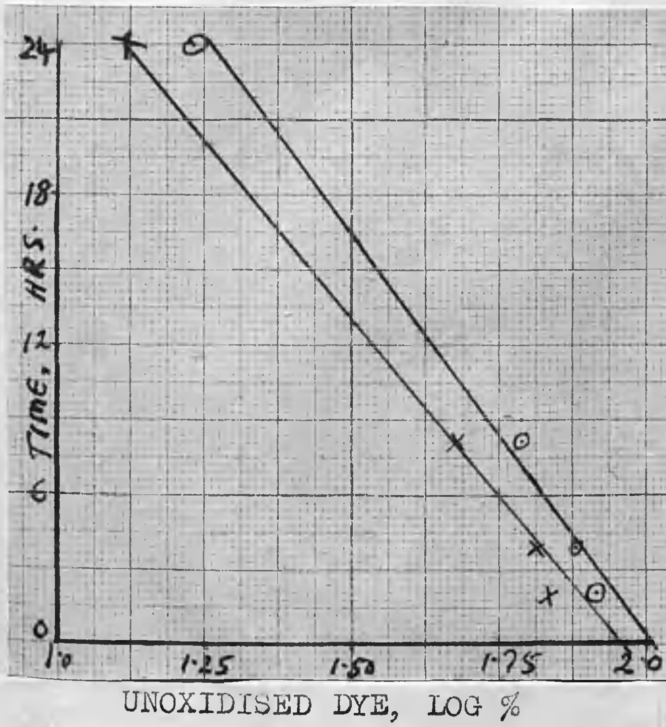


FIG. 47 - OXIDATION OF DYES, METANILIC ACID → R-ACID (⊙) and SULPHANILIC ACID → R-ACID (×) WITH ALKALINE H_2O_2

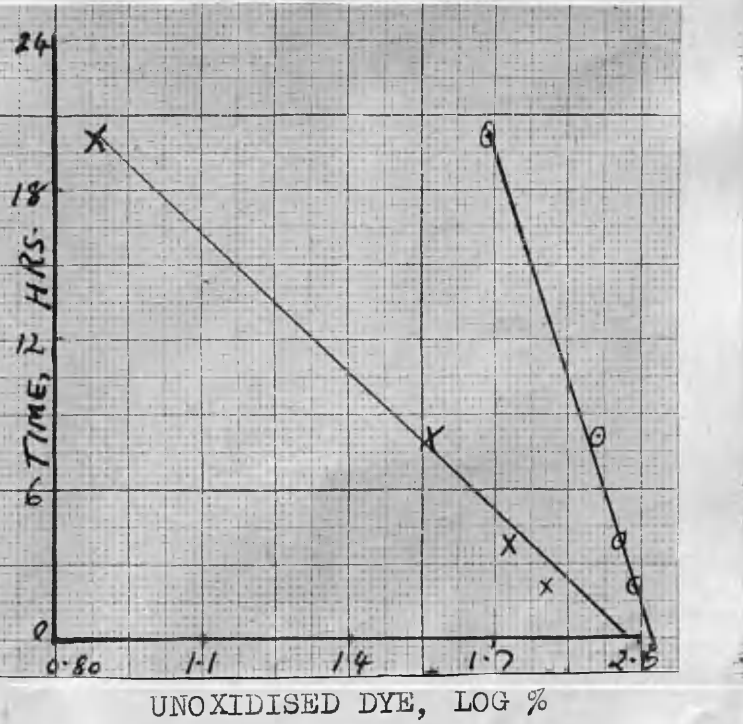
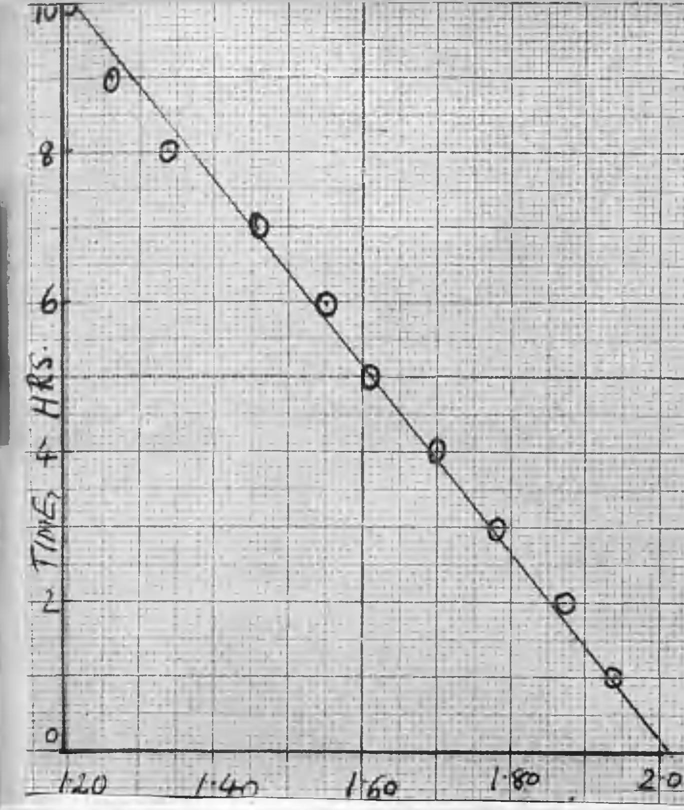
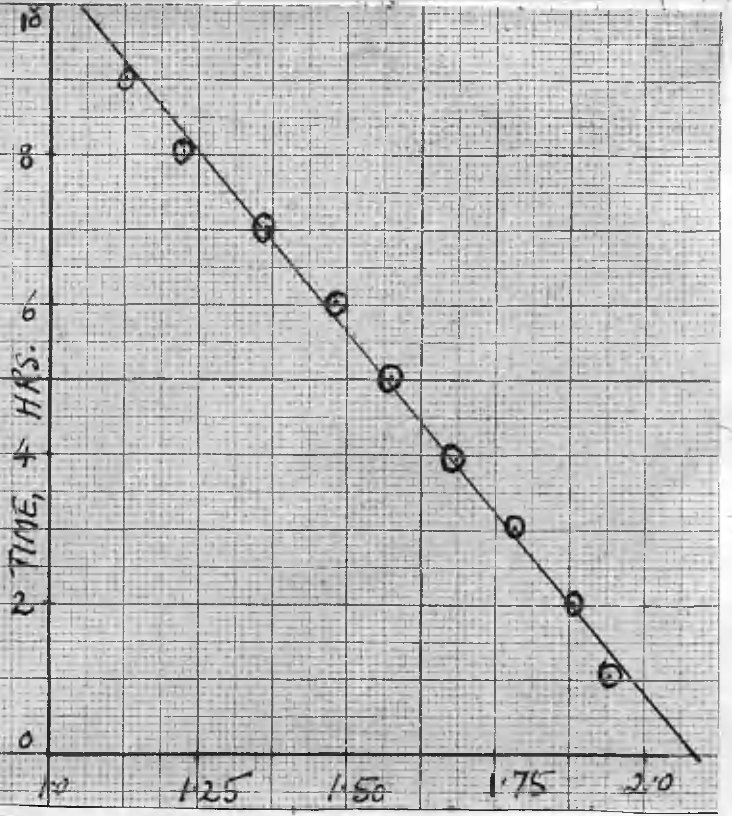


FIG. 48 - OXIDATION OF DYES, ANTHRANILIC ACID → R-ACID (⊙) and p-AMINOBENZOIC ACID → R-ACID (×) WITH ALKALINE H_2O_2



UNOXIDISED DYE, LOG %

FIG. 49 - OXIDATION OF DYE, ANILINE → R-ACID, WITH 0.05 M $K_2S_2O_8$.



UNOXIDISED DYE, LOG %

FIG. 50 - OXIDATION OF DYE, o-NITROANILINE →R-ACID, WITH 0.05M $K_2S_2O_8$.

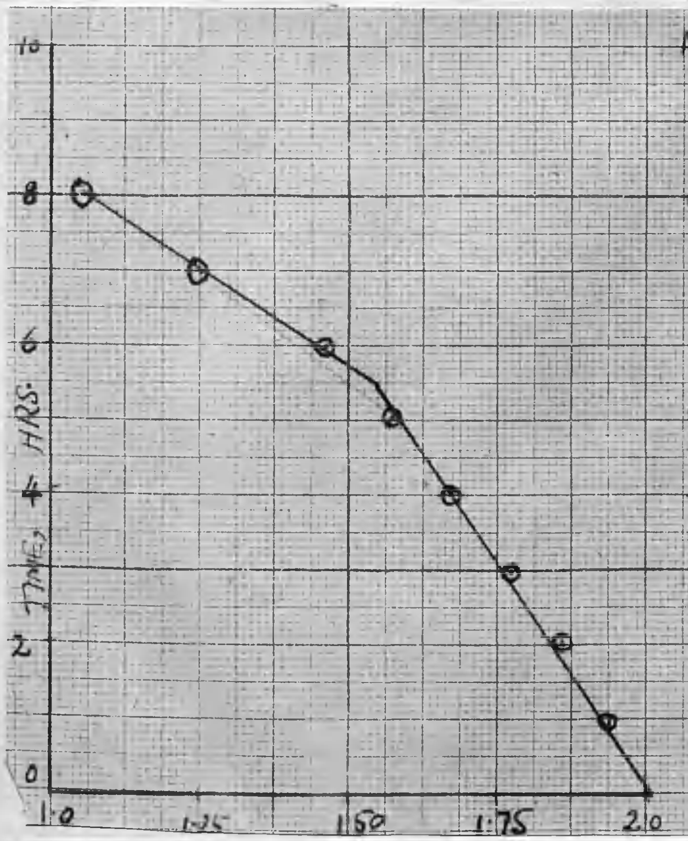


FIG. 51 - OXIDATION OF DYE, m-NITROANILINE →R-ACID WITH 0.05M $K_2S_2O_8$

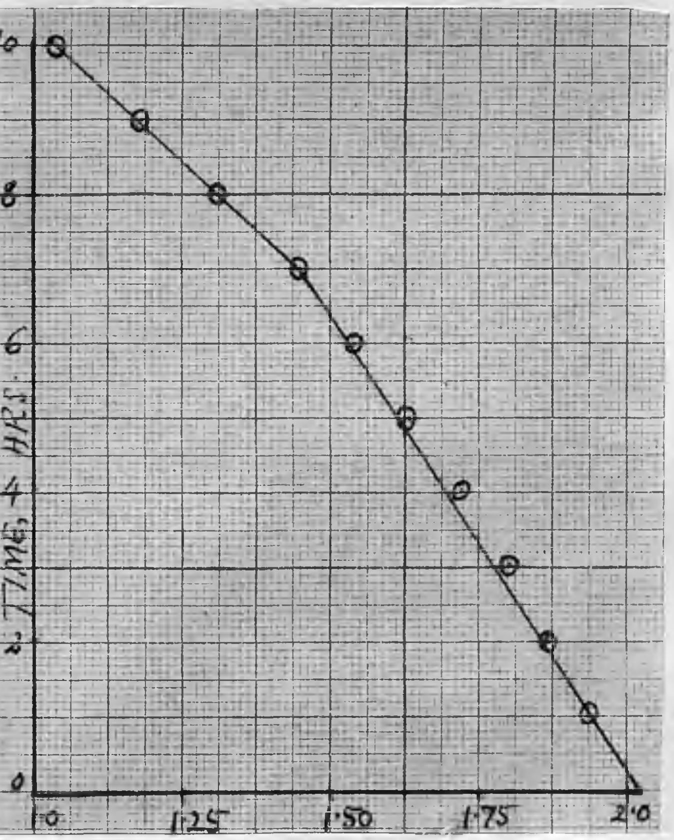
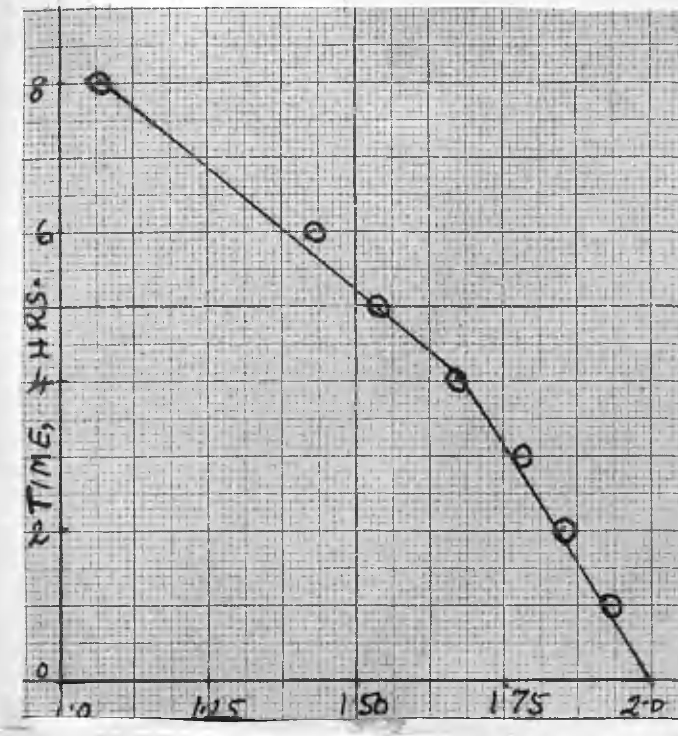
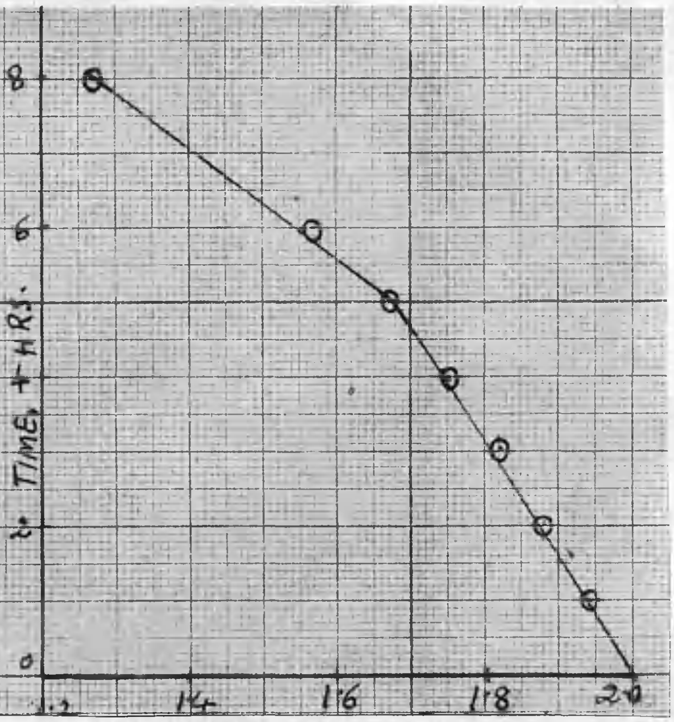


FIG. 52 - OXIDATION OF DYE, p-NITROANILINE →R-ACID WITH 0.05 M $K_2S_2O_8$



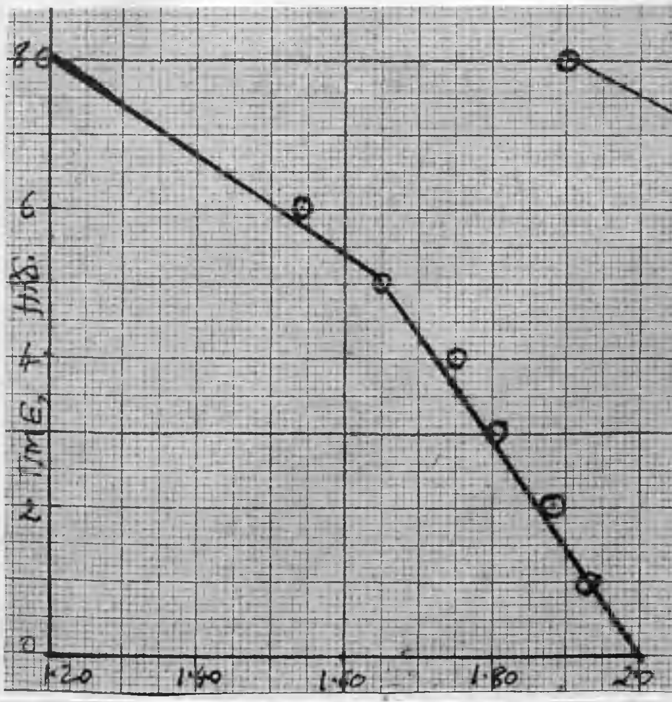
UNOXIDISED DYE, LOG %

FIG. 53 - OXIDATION OF DYE, o-CHLORO-ANILINE → R-ACID, WITH 0.05 M K_2S_2O



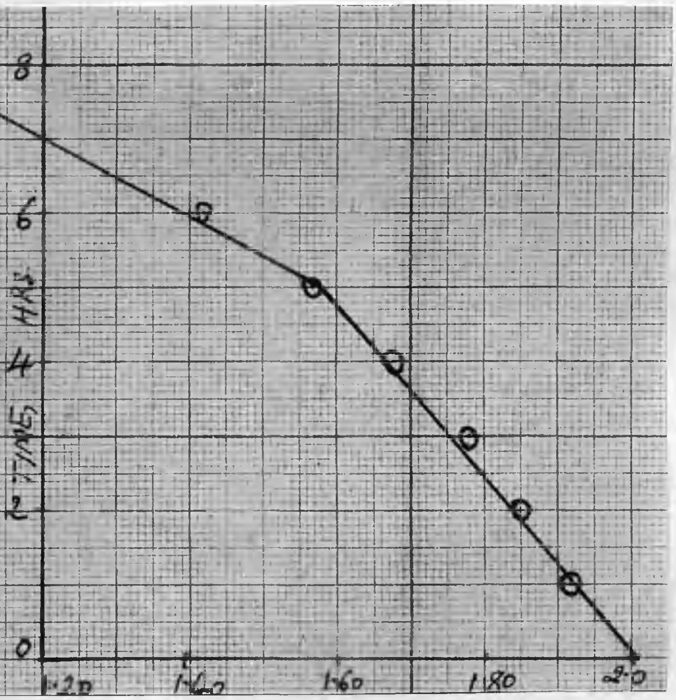
UNOXIDISED DYE, LOG %

FIG. 54 - OXIDATION OF DYE, m-CHLORO-ANILINE → R-ACID, WITH 0.05M $K_2S_2O_8$



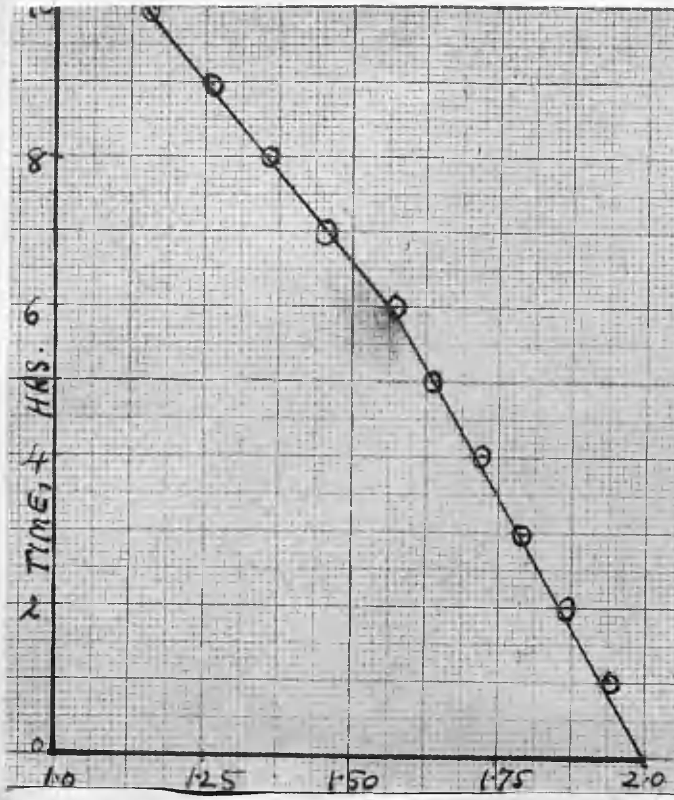
UNOXIDISED DYE, LOG %

FIG. 55 - OXIDATION OF DYE, p-CHLORO-ANILINE → R-ACID, WITH 0.05M $K_2S_2O_8$



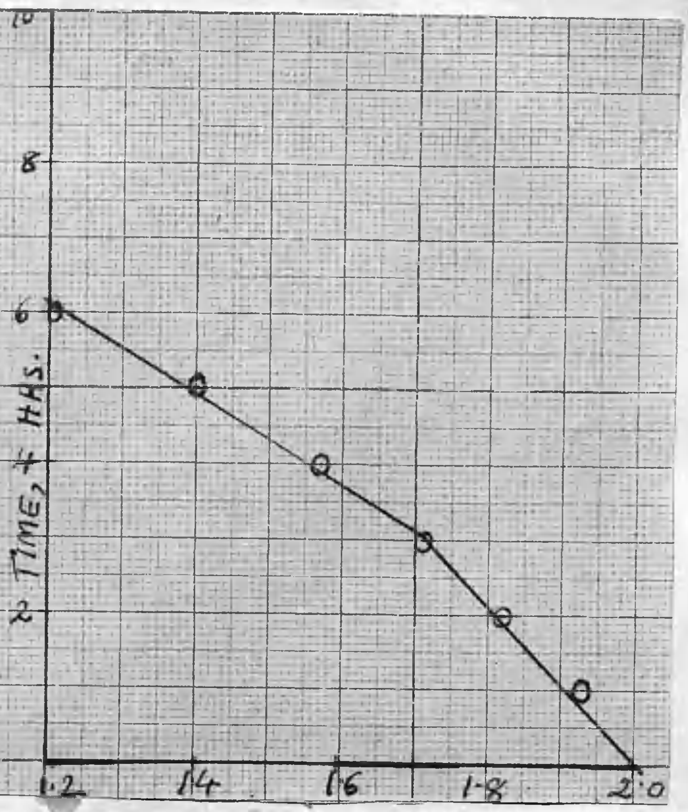
UNOXIDISED DYE, LOG %

FIG. 56 - OXIDATION OF DYE, 2:4-DICHLORO ANILINE → R-ACID, WITH 0.05M $K_2S_2O_8$



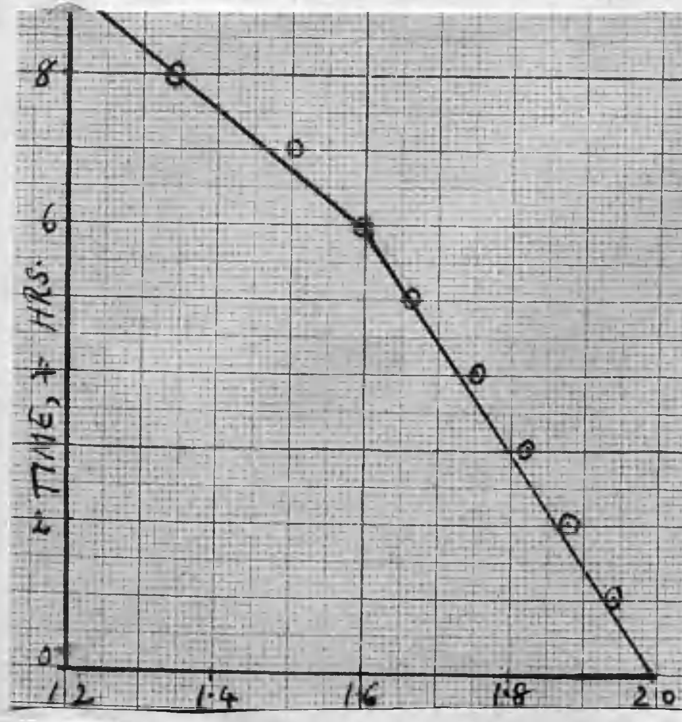
UNOXIDISED DYE,

IG. 57 - OXIDATION OF DYE, m-TOLUIDINE -ACID WITH 0.05 M $K_2S_2O_8$



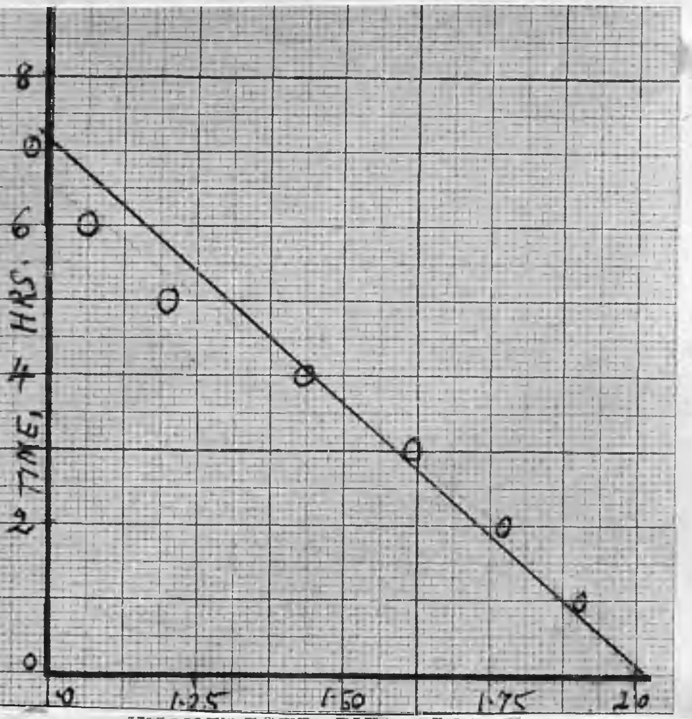
UNOXIDISED DYE, LOG %

FIG. 58 - OXIDATION OF DYE, p-TOLUIDINE R-ACID WITH 0.05 M $K_2S_2O_8$ →



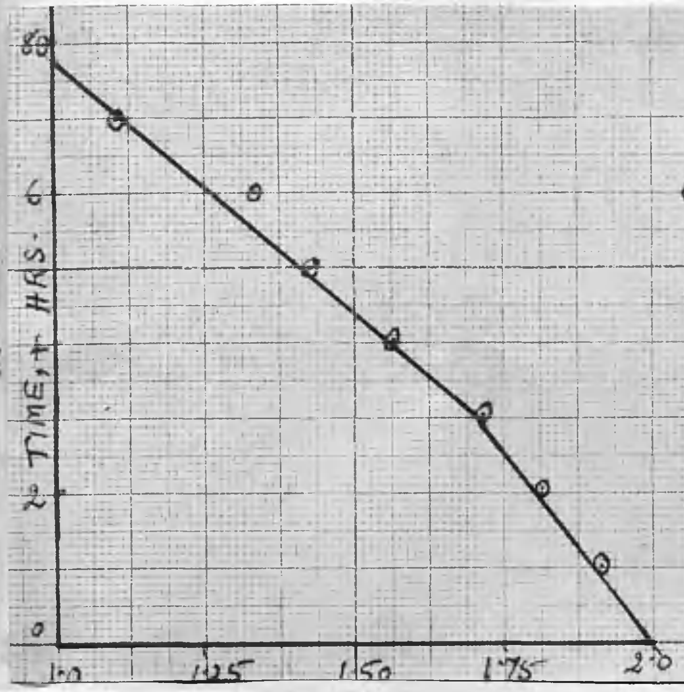
UNOXIDISED DYE, LOG %

FIG. 59 - OXIDATION OF DYE, o-ANISIDINE R-ACID, WITH 0.05M $K_2S_2O_8$. →



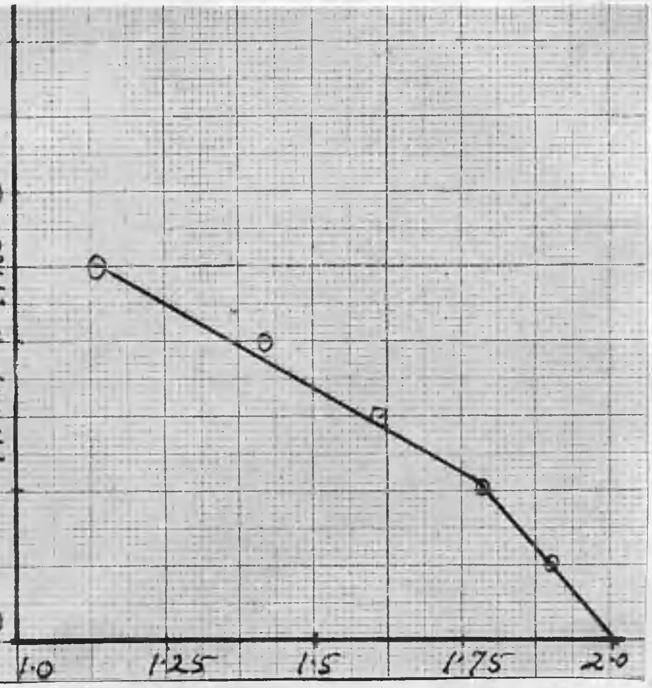
UNOXIDISED DYE, LOG %

FIG. 60 - OXIDATION OF DYE, p-ANISIDINE R-ACID, WITH 0.05M $K_2S_2O_8$. →



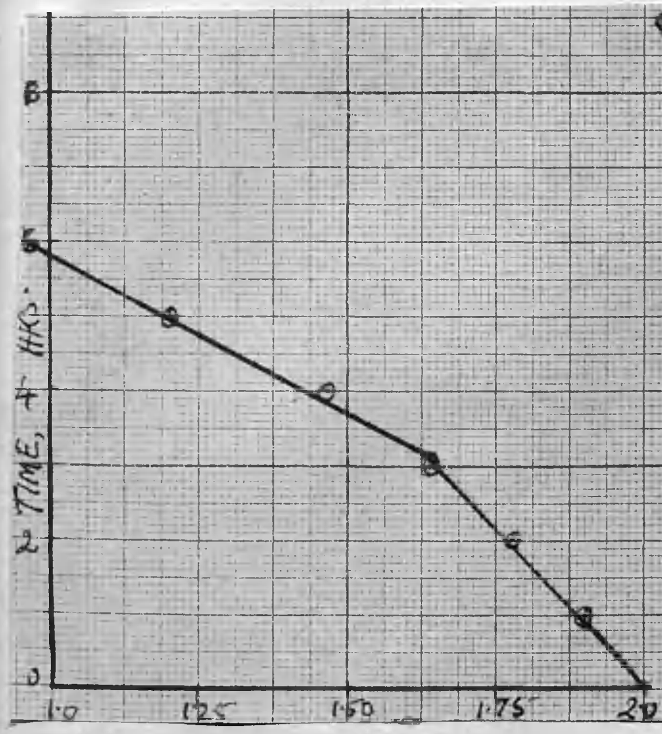
UNOXIDISED DYE, LOG %

FIG. 61 - OXIDATION OF DYE, DIANISIDI INE → R-ACID WITH 0.05 M $K_2S_2O_8$



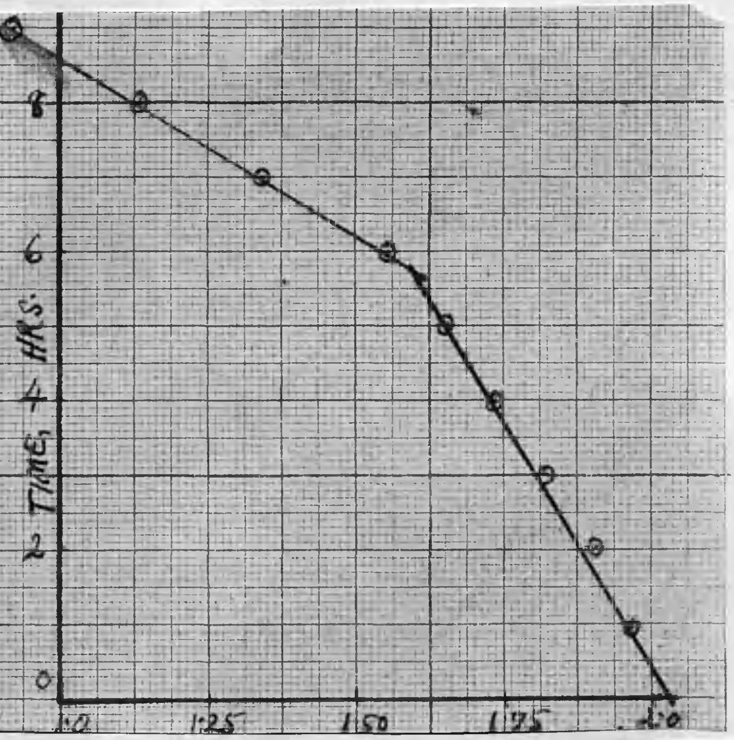
UNOXIDISED DYE, LOG %

FIG. 62 - OXIDATION OF DYE, METANILIC ACID → R-ACID WITH 0.05 M $K_2S_2O_8$



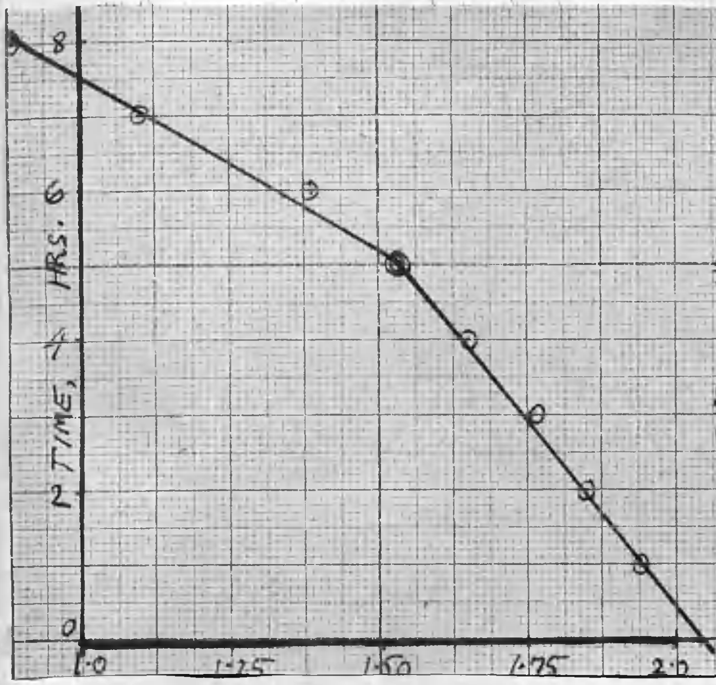
UNOXIDISED DYE, LOG %

FIG. 63 - OXIDATION OF DYE, SULPHANILIC ACID → R-ACID WITH 0.05M $K_2S_2O_8$



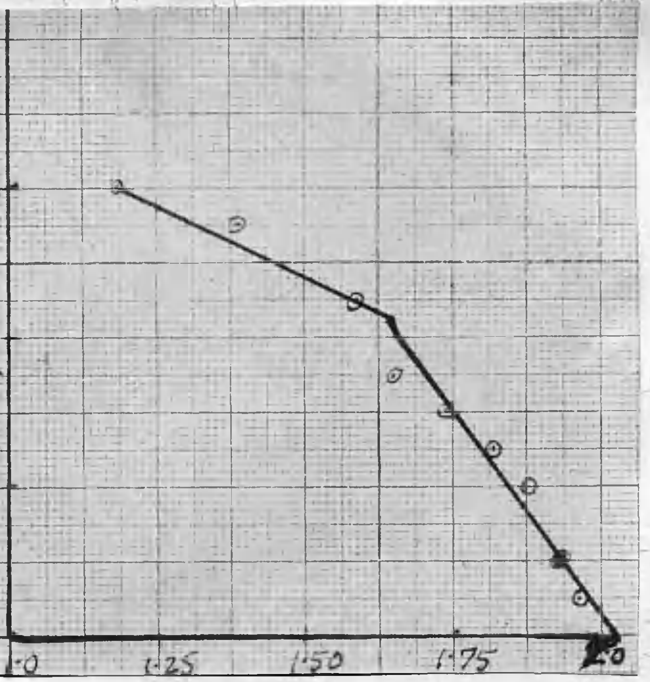
UNOXIDISED DYE, LOG %

FIG. 64 - OXIDATION OF DYE, ANTHRANILIC ACID → R-ACID, WITH 0.05 M $K_2S_2O_8$



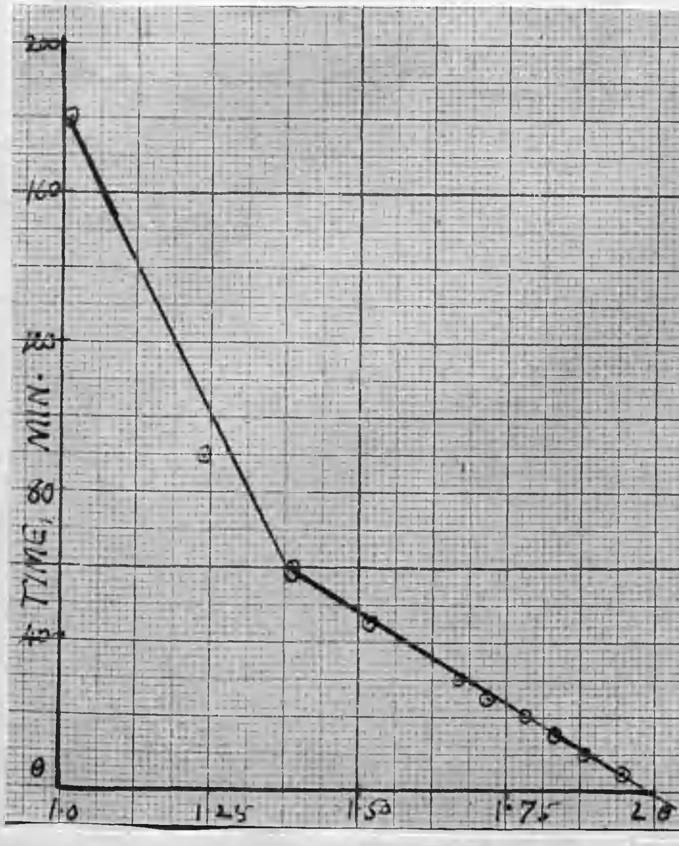
UNOXIDISED DYE, LOG %

IG. 65 - OXIDATION OF DYE, p-AMINOBENZOIC CID →R-ACID WITH 0.05 M $K_2S_2O_8$



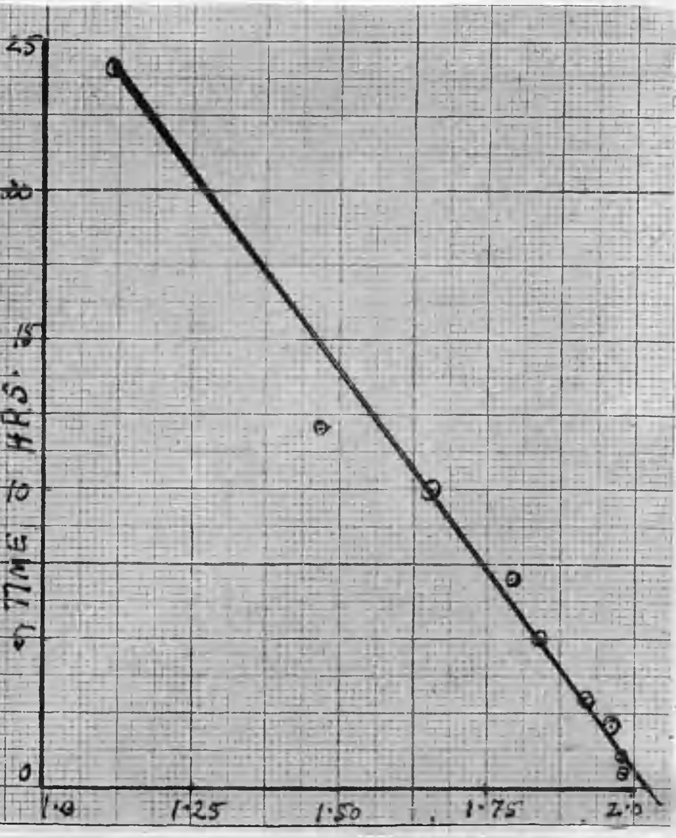
UNOXIDISED DYE, LOG %

- OXIDATION OF ORANGE II WITH 0.05M $K_2S_2O_8$



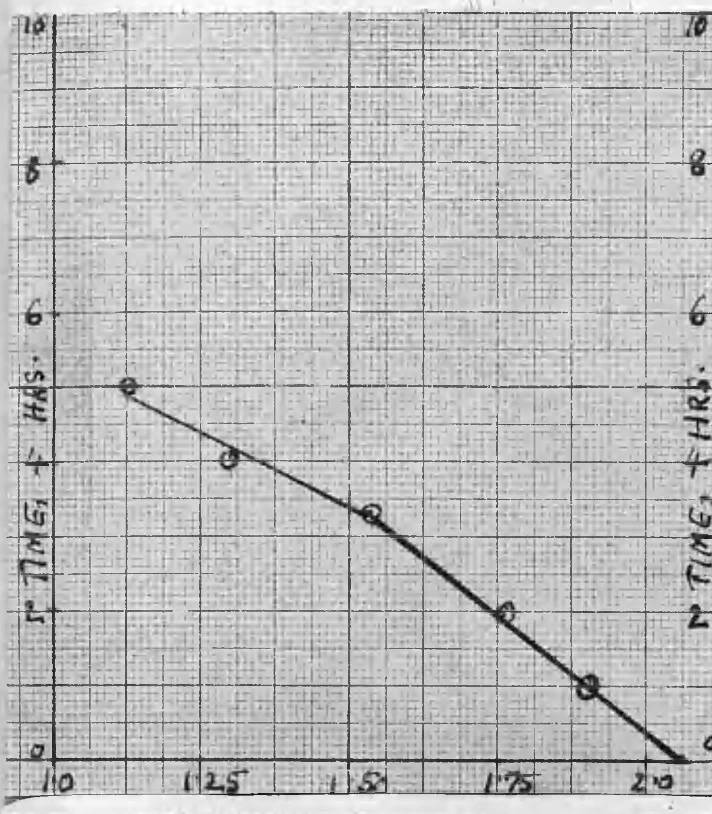
UNOXIDISED DYE, LOG %

67 - OXIDATION OF ORANGE I WITH 0.05M $K_2S_2O_8$



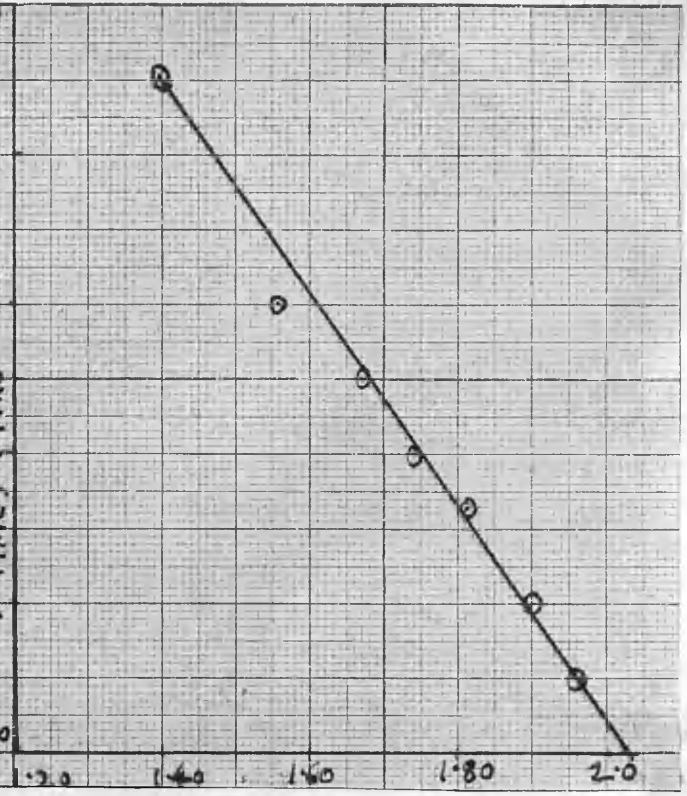
UNOXIDISED DYE, LOG %

FIG. 68 - OXIDATION OF O-METHYL ETHER OF ORANGE I WITH 0.05M $K_2S_2O_8$



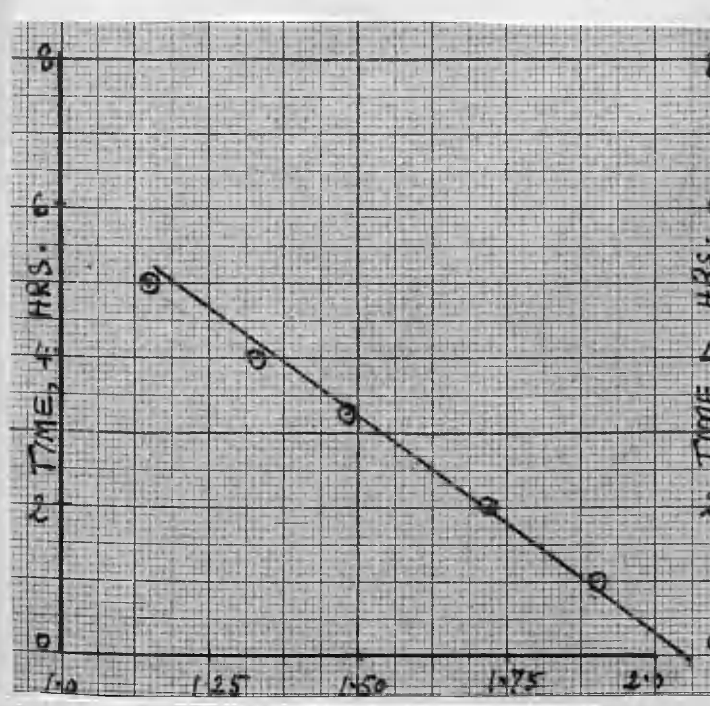
UNOXIDISED DYE, LOG %

FIG. 69 - OXIDATION OF DYE, ANILINE→OXY-L-ACID with 0.05M $K_2S_2O_8$



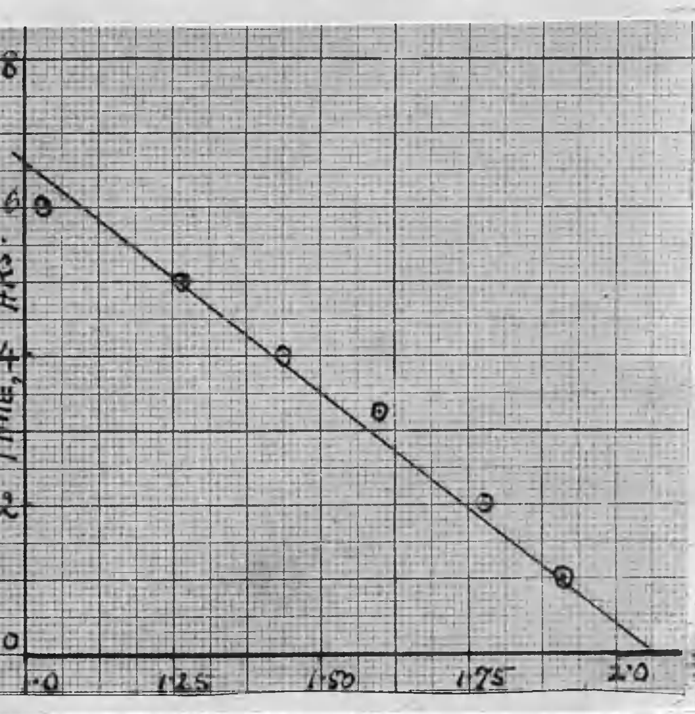
UNOXIDISED DYE, LOG %

FIG. 70 - OXIDATION OF DYE, o-NITROANILINE→OXY-L-ACID WITH 0.05M $K_2S_2O_8$



UNOXIDISED DYE, LOG %

FIG. 71 - OXIDATION OF DYE, m-NITRO ANILINE →OXY-L-ACID WITH 0.05 M $K_2S_2O_8$



UNOXIDISED DYE, LOG %

FIG 72. - OXIDATION OF DYE, p-NITROANILINE →OXY-L-ACID, WITH 0.05M $K_2S_2O_8$

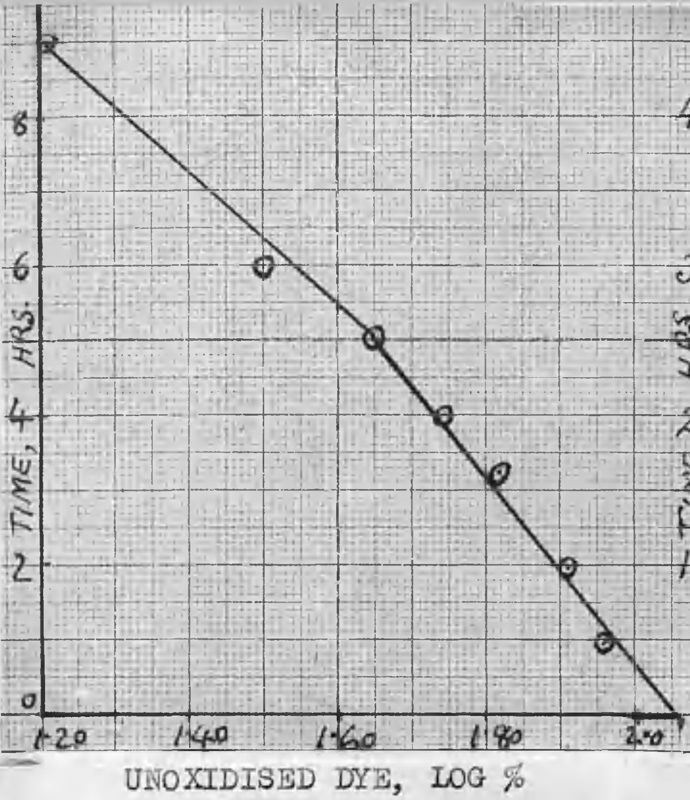


FIG. 73 - OXIDATION OF DYE, o-CHLORO-ANILINE →OXY-L-ACID WITH 0.05M $K_2S_2O_8$

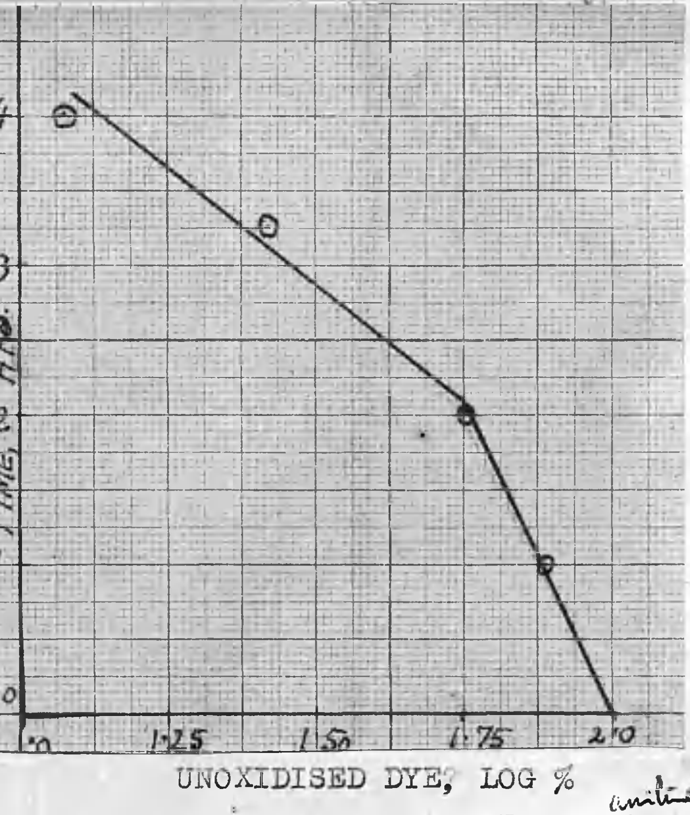


FIG. 74 - OXIDATION OF DYE, m-CHLORO aniline → OXY-L-ACID WITH 0.05M $K_2S_2O_8$

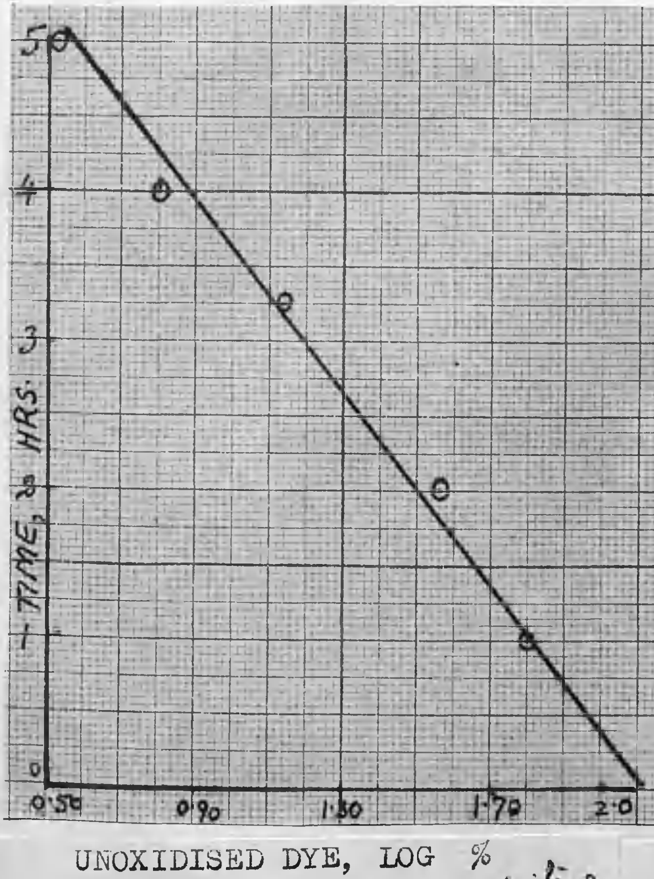


FIG. 75 - OXIDATION OF DYE, p-CHLORO- aniline ANILINE →OXY-L-ACID WITH 0.05 M K_2S_2 $K_2S_2O_8$

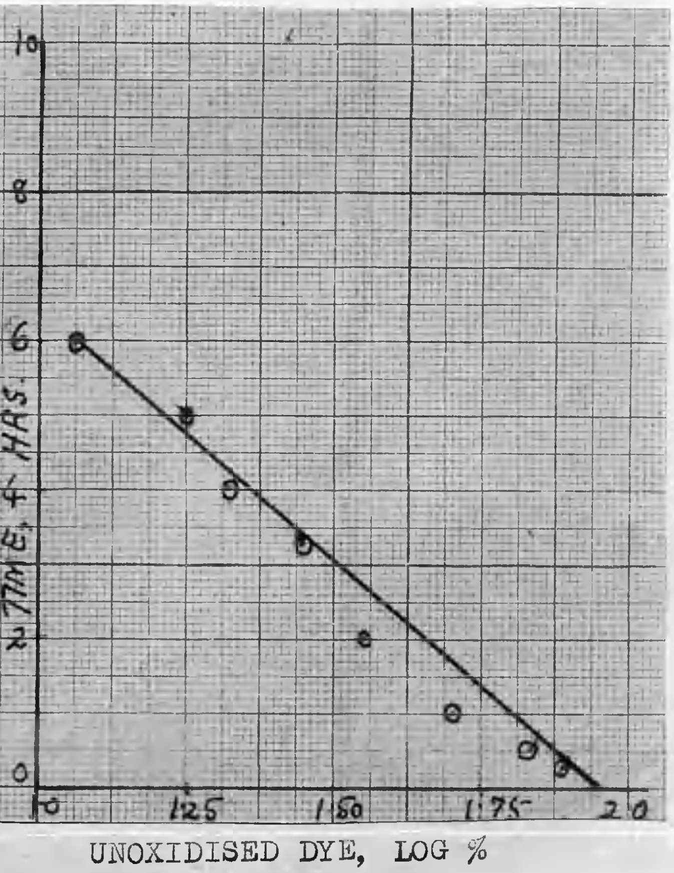


FIG. 76 - OXIDATION OF DYE, 2:4-DICHLORO-ANILINE →OXY-L-ACID WITH 0.05M $K_2S_2O_8$

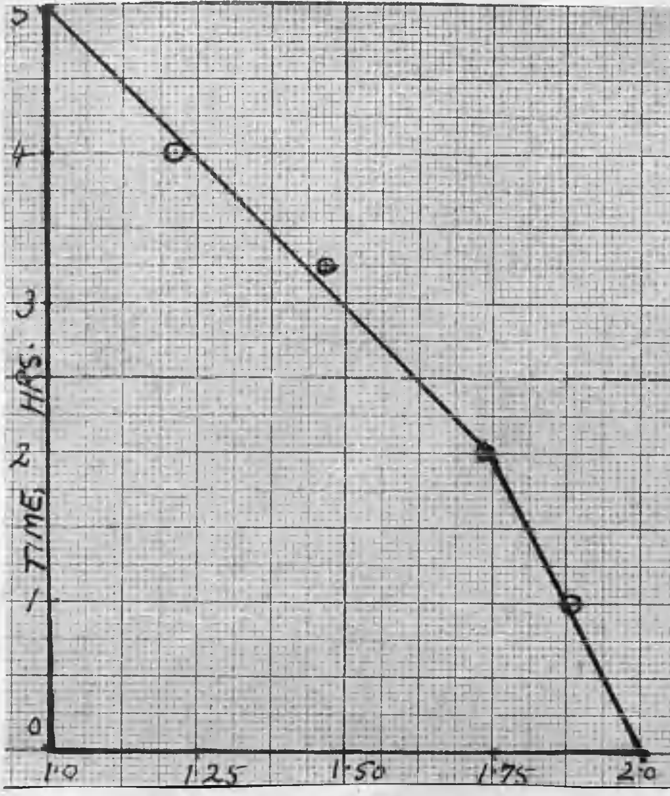


FIG. 77 - OXIDATION OF DYE, m-TOLUIDINE → OXY-L-ACID, WITH 0.05 M $K_2S_2O_8$

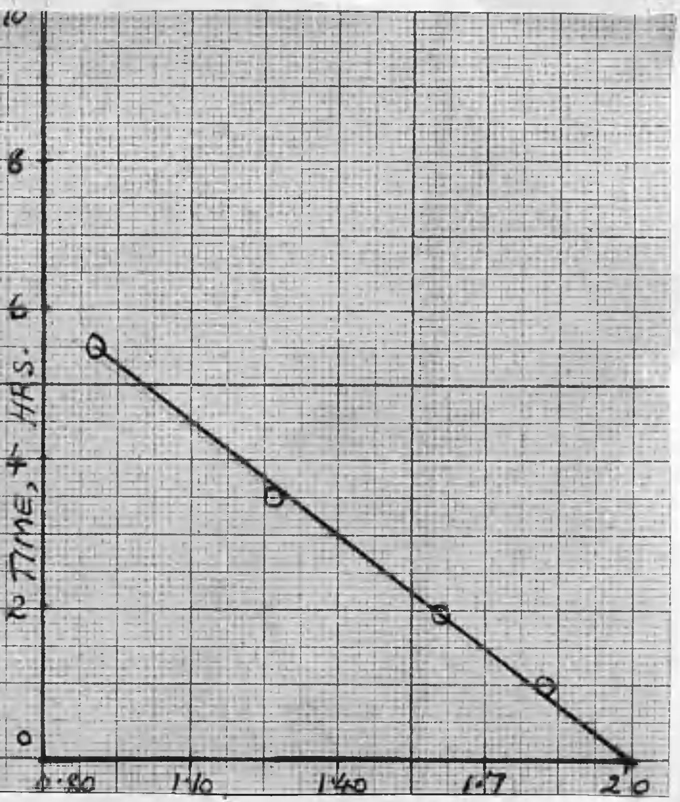


FIG. 78 - OXIDATION OF DYE, p-TOLUIDINE → OXY-L-ACID WITH 0.05M $K_2S_2O_8$

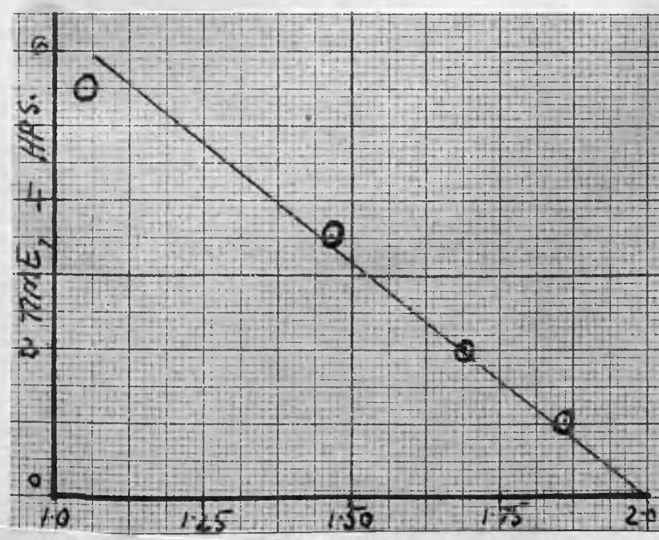


FIG. 79 - OXIDATION OF DYE, o-ANISIDINE → OXY-L-ACID WITH 0.05 M $K_2S_2O_8$

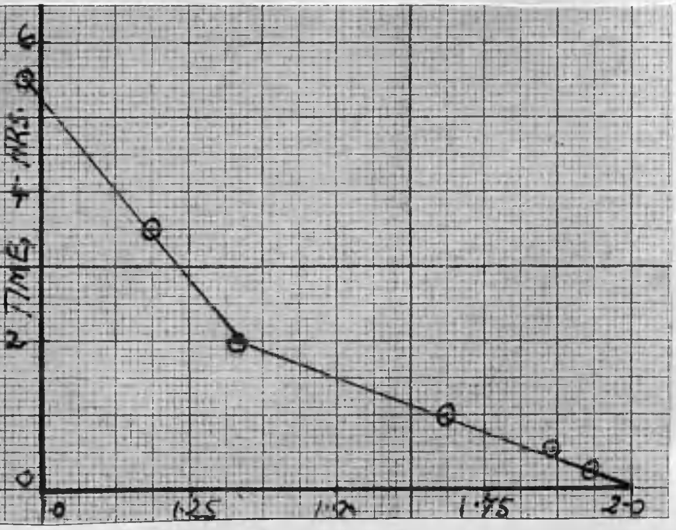
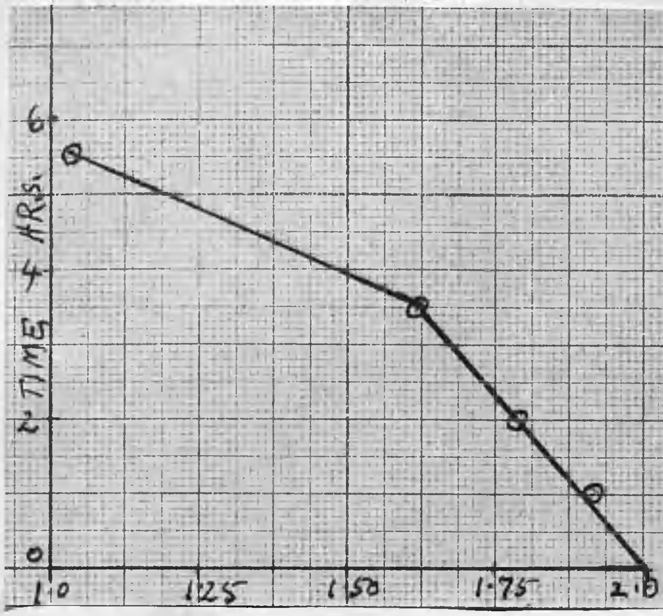
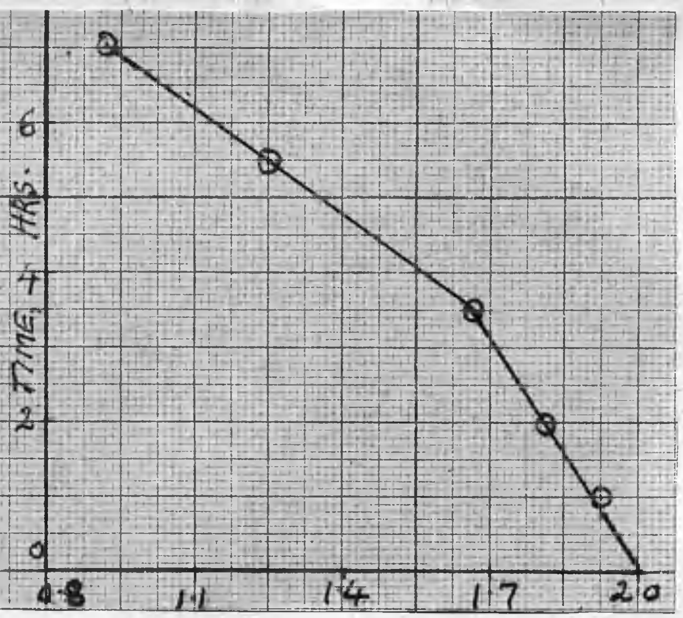


FIG. 80 - OXIDATION OF DYE, p-ANISIDINE → OXY-L-ACID WITH 0.05M K S O



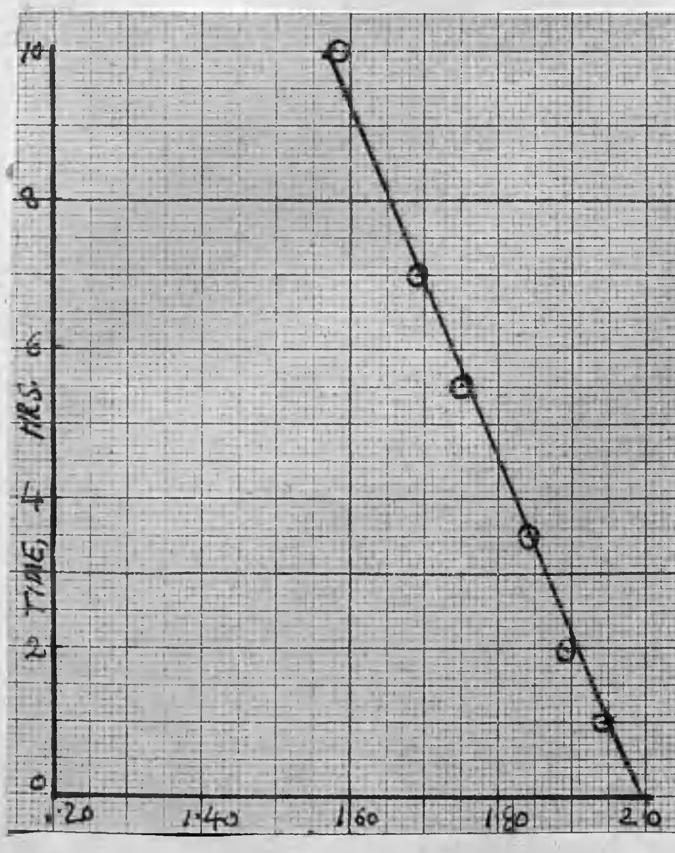
UNOXIDISED DYE, LOG %

FIG. 81 - OXIDATION OF DYE, METANILIC ACID → OXY-L-ACID, WITH 0.05 M $K_2S_2O_8$



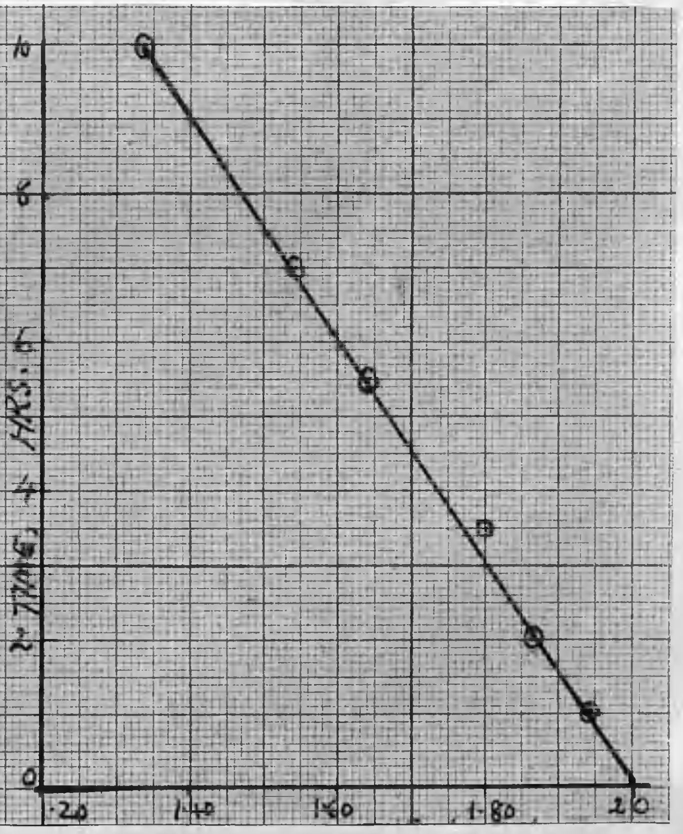
UNOXIDISED DYE, LOG %

FIG. 82 - OXIDATION OF DYE, SULPHANILIC ACID→OXY-L-ACID WITH 0.05M $K_2S_2O_8$



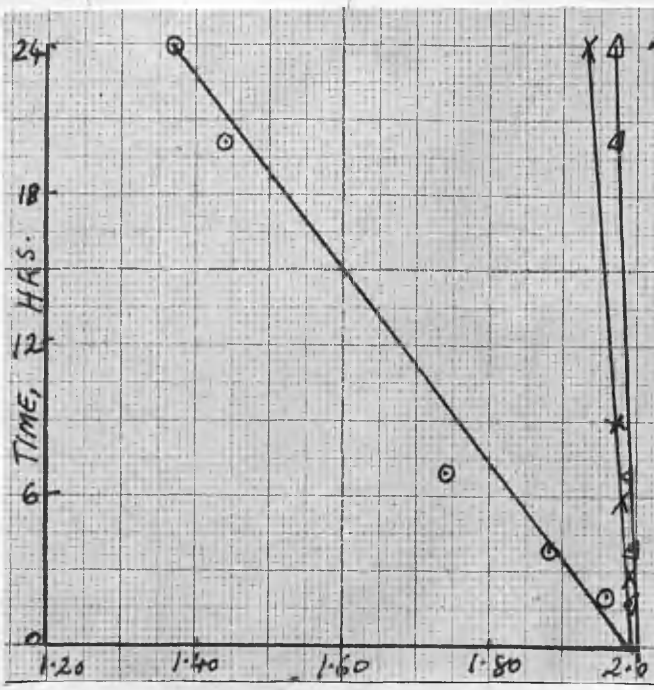
UNOXIDISED DYE, LOG %

FIG. 83 - OXIDATION OF DYE, ANTHRANILIC ACID →OXY-L-ACID WITH 0.05M $K_2S_2O_8$



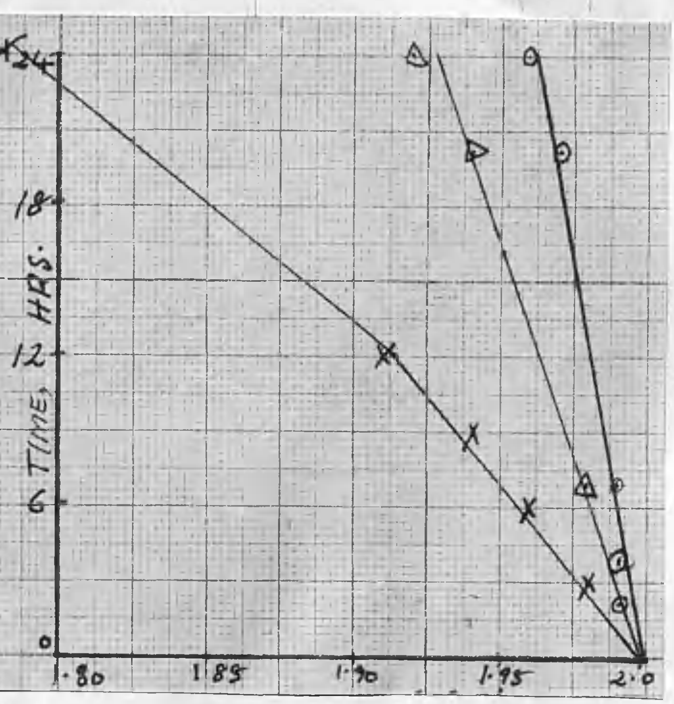
UNOXIDISED DYE, LOG %

FIG. 84 - OXIDATION OF DYE, p-AMINOBenzoic ACID →OXY-L-ACID WITH 0.05M $K_2S_2O_8$



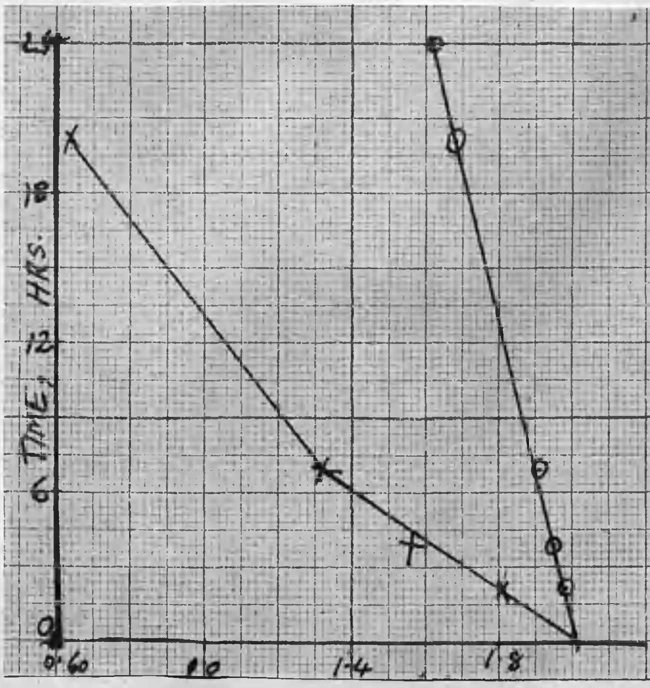
UNOXIDISED DYE, LOG %

FIG. 85 - OXIDATION OF DYES,
ANILINE → R-ACID (⊙)
m-NITROANILINE → " (X)
p " → " (△)
WITH IN HNO_3



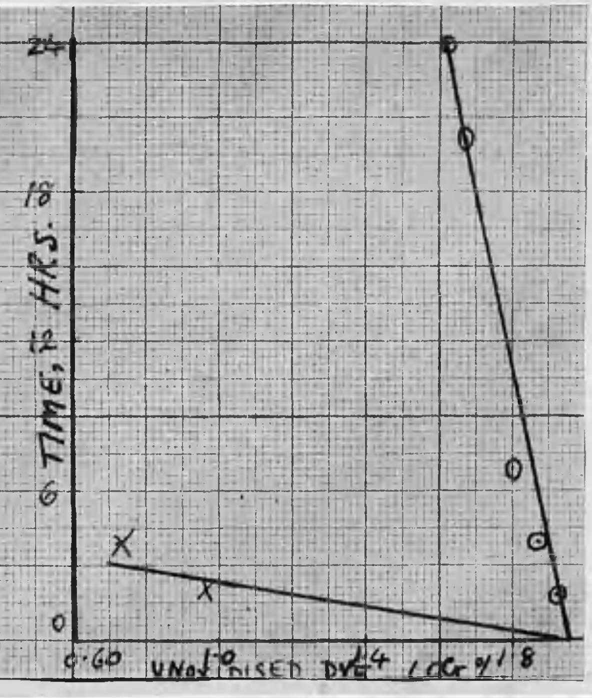
UNOXIDISED DYE, LOG %

FIG. 86 - OXIDATION OF DYES,
o-CHLOROANILINE → R-ACID (⊙)
m- " → " (X)
p- " → " (△)



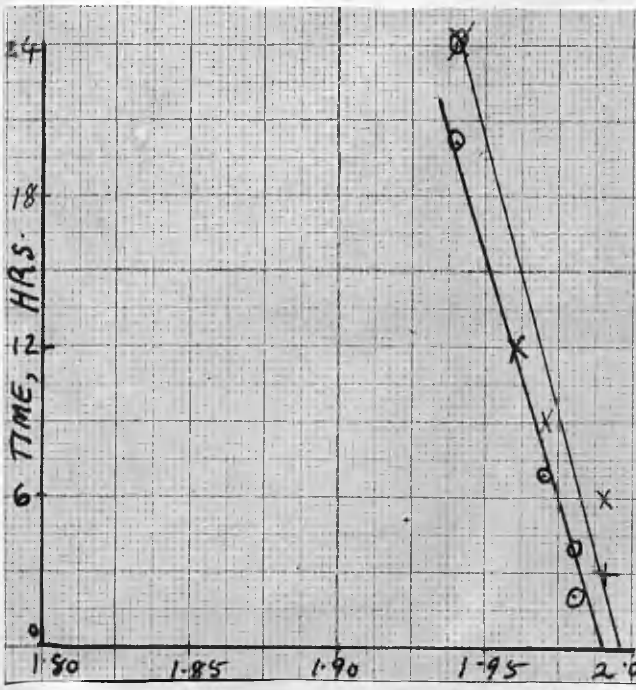
UNOXIDISED DYE, LOG % idine

FIG. 87 - OXIDATION OF DYES, m-TOLU
→ R-ACID (⊙) and p-TOLUIDINE → R-
(X) WITH IN HNO_3 acid

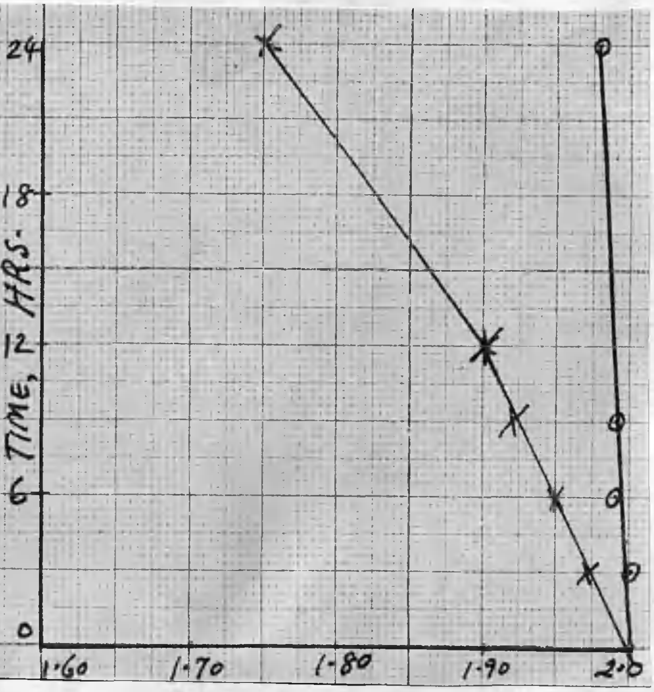


UNOXIDISED DYE, LOG %

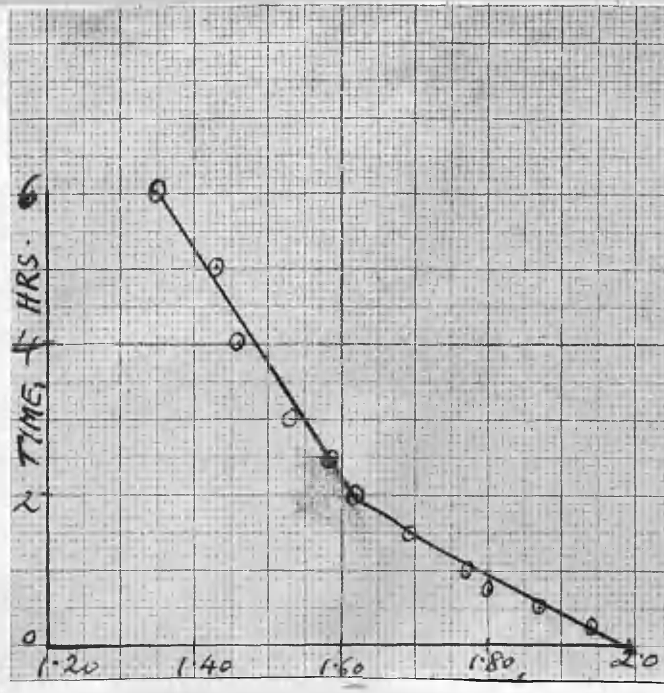
88 - OXIDATION OF DYES, o-ANISIDINE →
R-ACID (⊙) AND p-ANISIDINE → R-ACID
(X) WITH IN HNO_3



UNOXIDISED DYE, LOG %
FIG. 89 - OXIDATION OF DYES,
METANILIC ACID → R-ACID (⊙)
and SULPHANILIC ACID → R-ACID (X)
WITH IN HNO_3

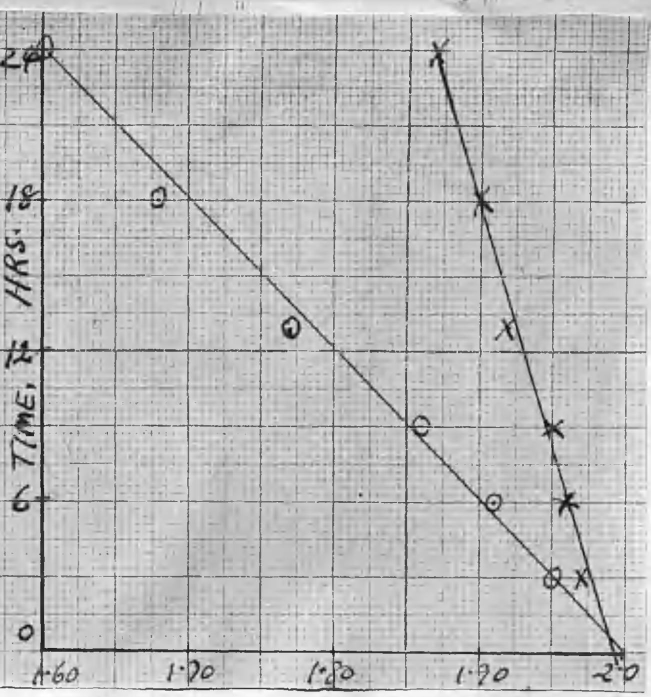


UNOXIDISED DYE, LOG %
FIG. 90 - OXIDATION OF DYES,
ANTHRANILIC ACID → R-ACID (⊙)
p-AMINOBENZOIC ACID → R-ACID (X)
WITH IN HNO_3



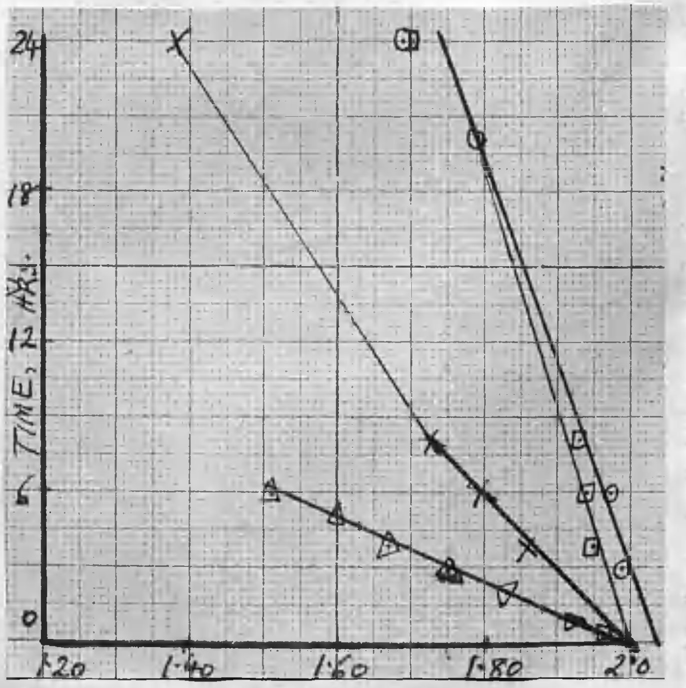
UNOXIDISED DYE, LOG %

FIG. 91 - OXIDATION OF DYE, ANILINE → R-ACID WITH IN HNO_3(d)



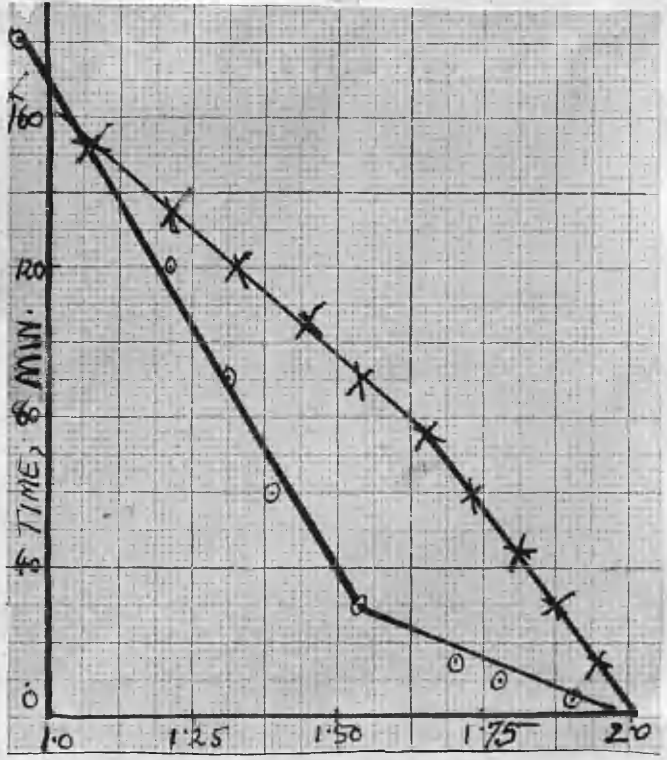
UNOXIDISED DYE, LOG %

FIG. 92 - OXIDATION OF DYES,
m-NITROANILINE → R-ACID (⊙)
p " → " (X)
WITH IN HNO_3(d)



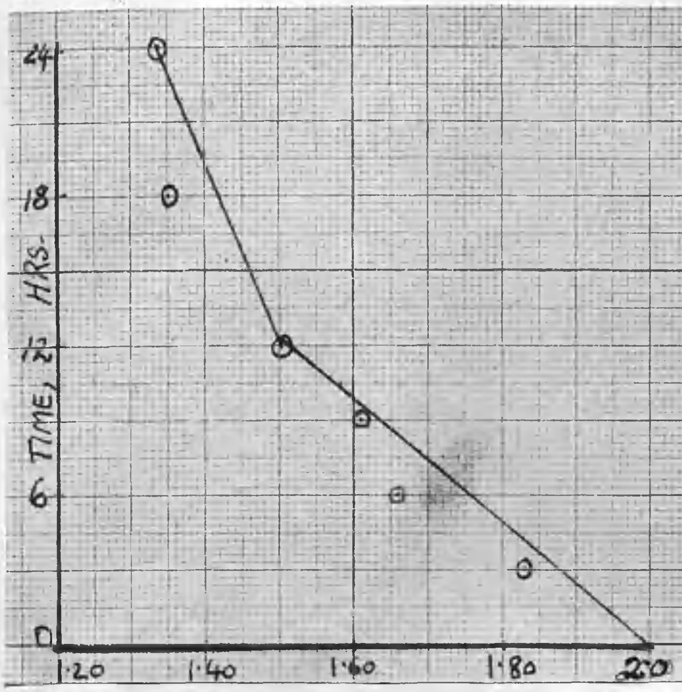
UNOXIDISED DYE, LOG %

FIG. 93 - OXIDATION OF DYES,
o-CHLOROANILINE → R-ACID (⊙)
m " → " (X)
p " → " (△)
2:4-DICHLOROANILINE → " (⊡)
WITH IN HNO_3(d)



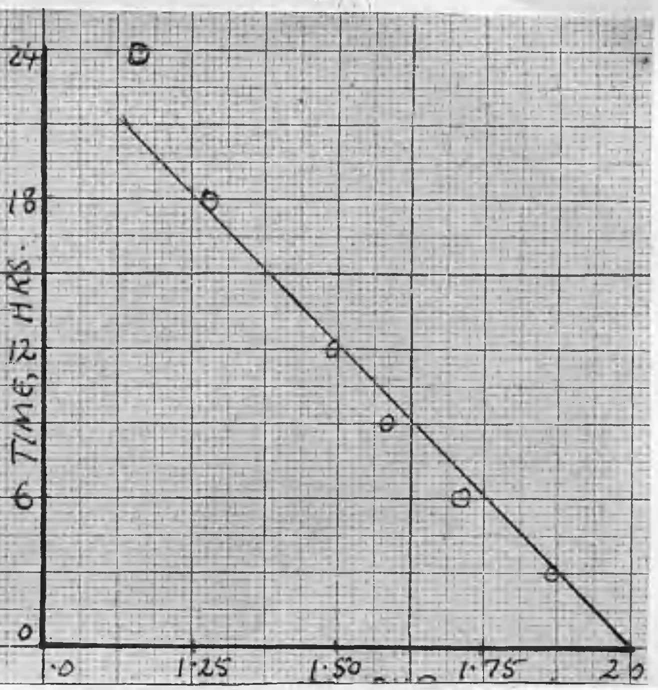
UNOXIDISED DYE, LOG %

FIG. 94 - OXIDATION OF DYES, p-TOLUIDINE → R-ACID (⊙) and ORANGE II (X)
WITH IN HNO_3(d)



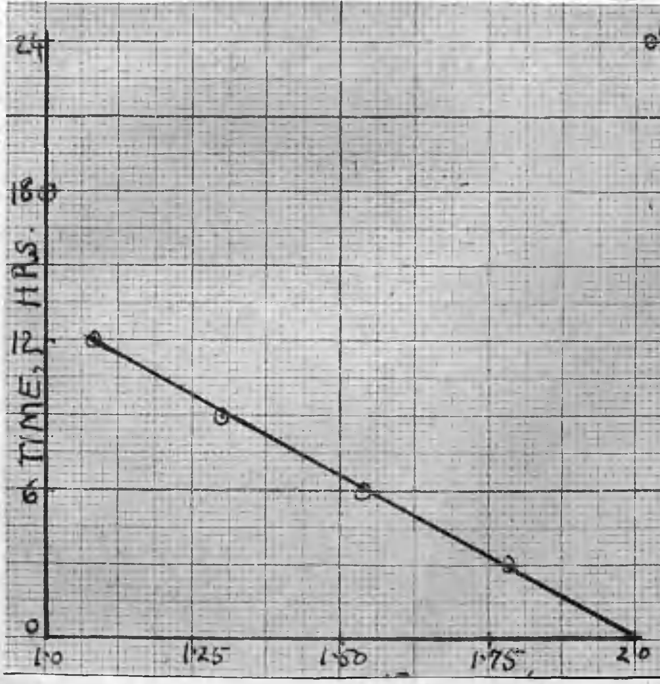
UNOXIDISED DYE, LOG %

FIG. 95 - OXIDATION OF ORANGE I on WOOL WITH 0.05N CERIC SULPHATE.



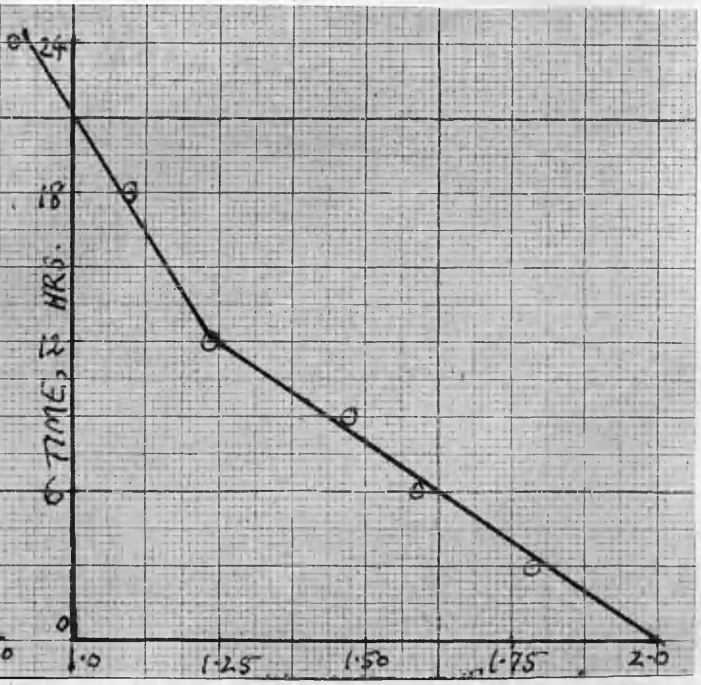
UNOXIDISED DYE, LOG %

FIG. 96 - OXIDATION OF O-METHYL ETHER OF ORANGE I (1%) ON WOOL WITH 0,05N CERIC SULPHATE.



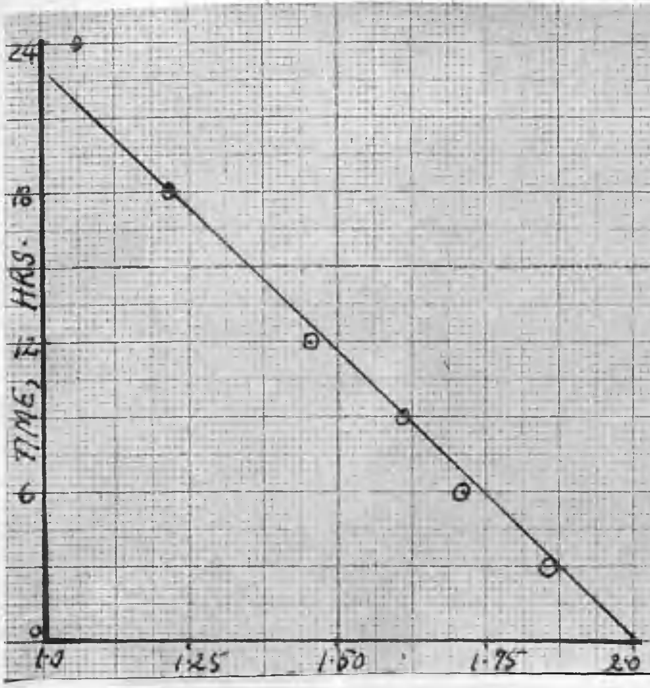
UNOXIDISED DYE, LOG %

FIG. 97 - OXIDATION OF ORANGE II on WOOL WITH 0.05N CERIC SULPHATE.



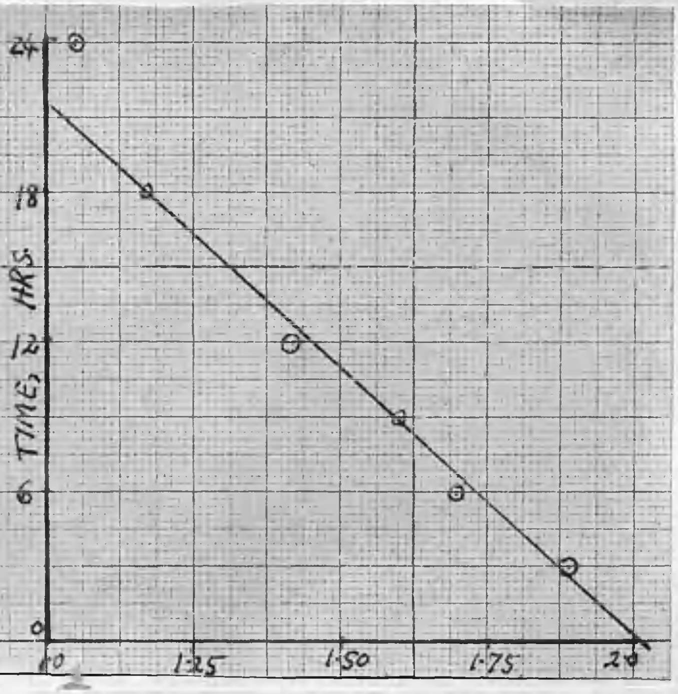
UNOXIDISED DYE, LOG %

FIG 98 - OXIDATION OF DYE, ANILINE (1%)R-ACID ON WOOL WITH 0.05N CERIC SULPHATE



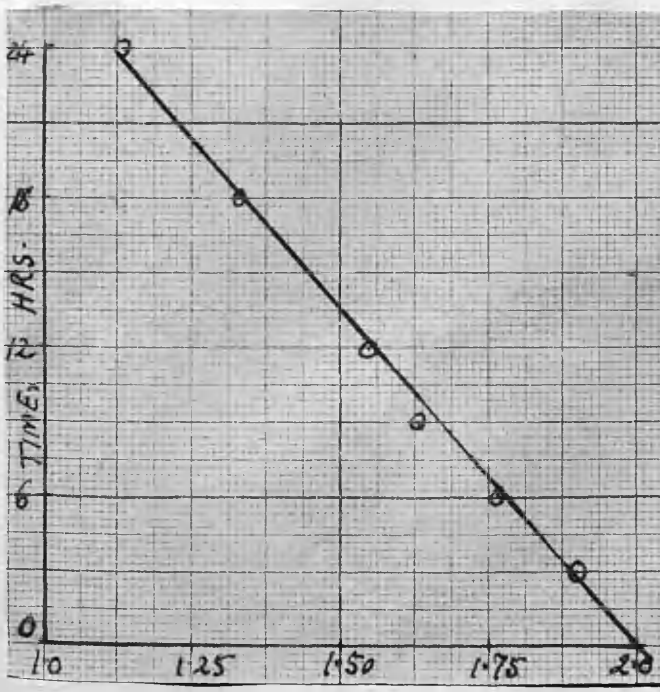
UNOXIDISED DYE, LOG %

FIG. 99 - OXIDATION OF DYE, o-CHLORO ANILINE → R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.



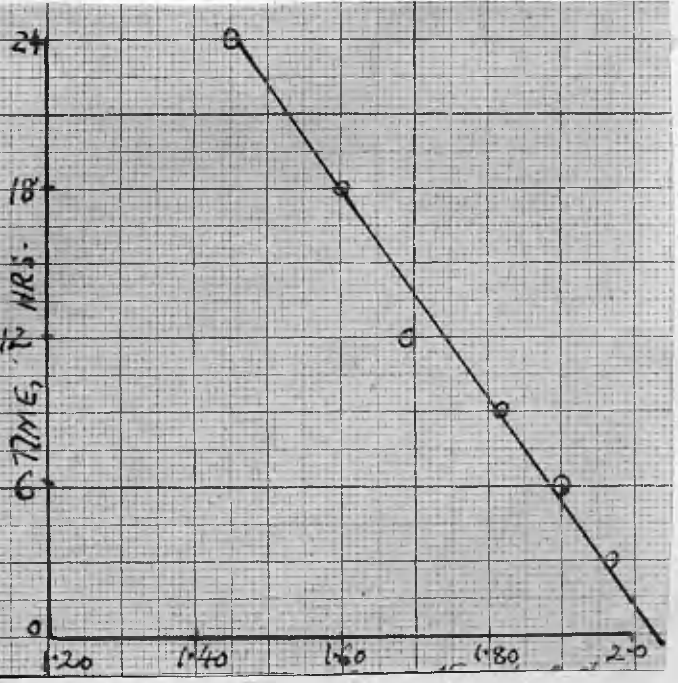
UNOXIDISED DYE, LOG %

FIG. 100 - OXIDATION OF DYE, m-CHLORO-ANILINE → R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.



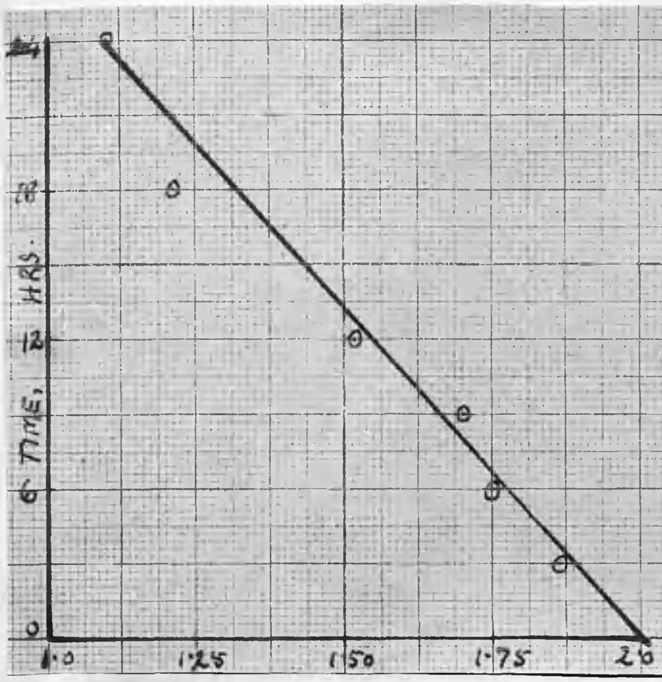
UNOXIDISED DYE, LOG %

FIG. 101 - OXIDATION OF DYE, p-CHLORO-ANILINE → R-ACID (1%) ON WOOL, WITH 0.05 N CERIC SULPHATE.



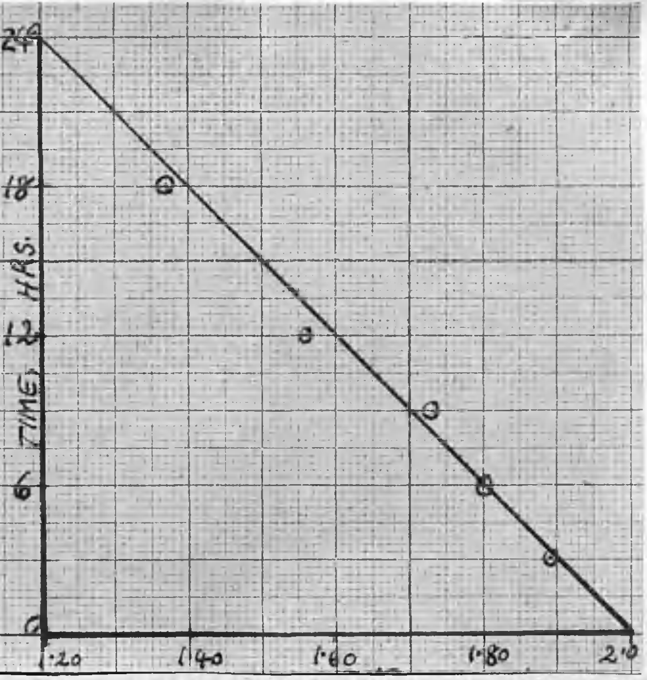
UNOXIDISED DYE, LOG %

FIG. 102 - OXIDATION OF DYE, 2:4-DICHLOROANILINE → R-ACID (1%) ON WOOL WITH 0.05 N CERIC SULPHATE



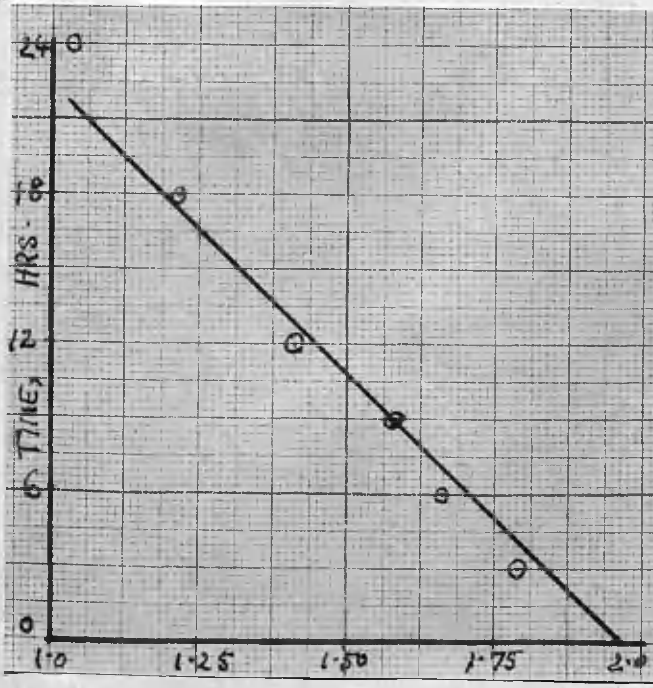
UNOXIDISED DYE, LOG %

FIG. 103 - OXIDATION OF DYE, o-NITRO-ANILINE → R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.



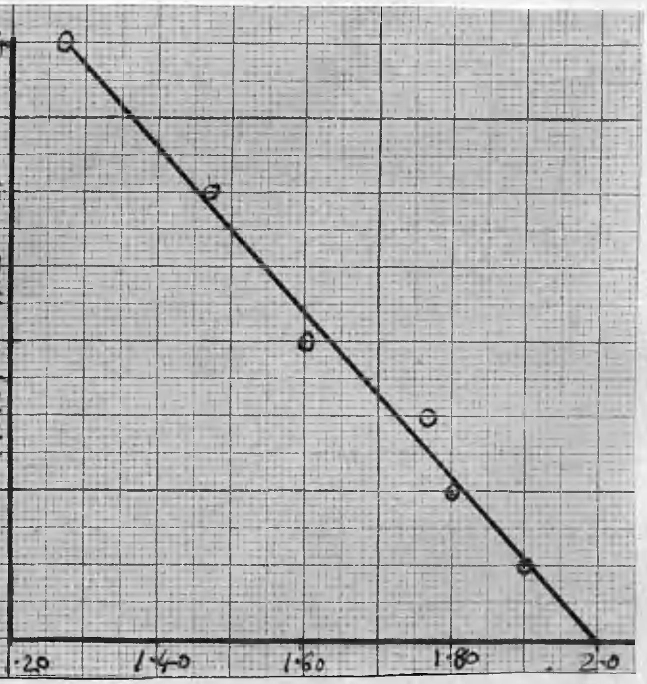
UNOXIDISED DYE, LOG %

FIG. 104 - OXIDATION OF DYE, m-NITRO-ANILINE → R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.



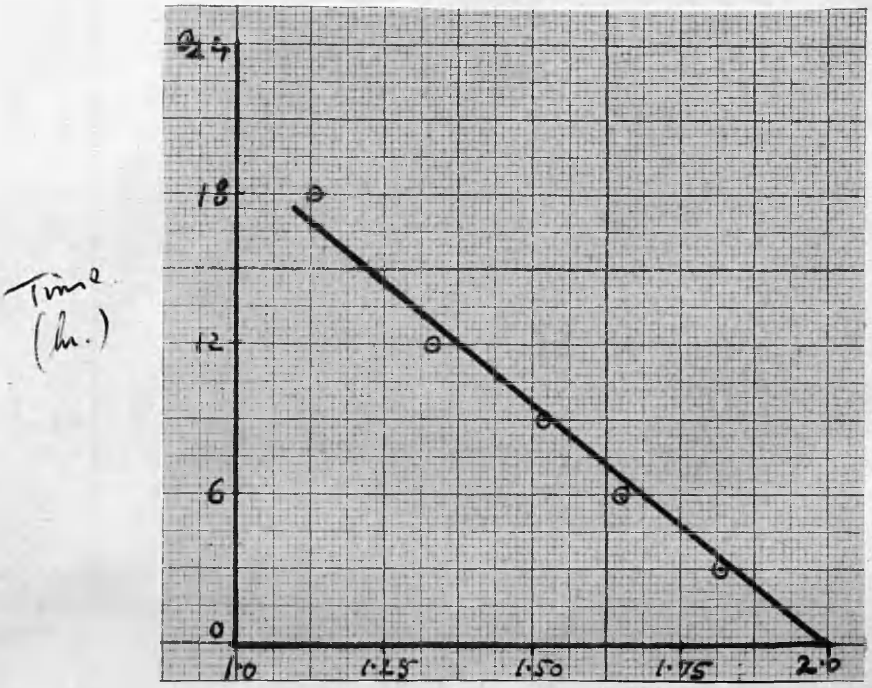
UNOXIDISED DYE, LOG %

FIG. 105 - OXIDATION OF DYE, p-NITRO-ANILINE →R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.



UNOXIDISED DYE, LOG %

FIG. 106 - OXIDATION OF DYE, pTOLUIDine → R-ACID(1%) ON WOOL WITH 0.05N CERIC SULPHATE.



UNOXIDISED DYE, LOG %

FIG. 107 - OXIDATION OF DYE, p-ANISIDINE →R-ACID (1%) ON WOOL WITH 0.05N CERIC SULPHATE.

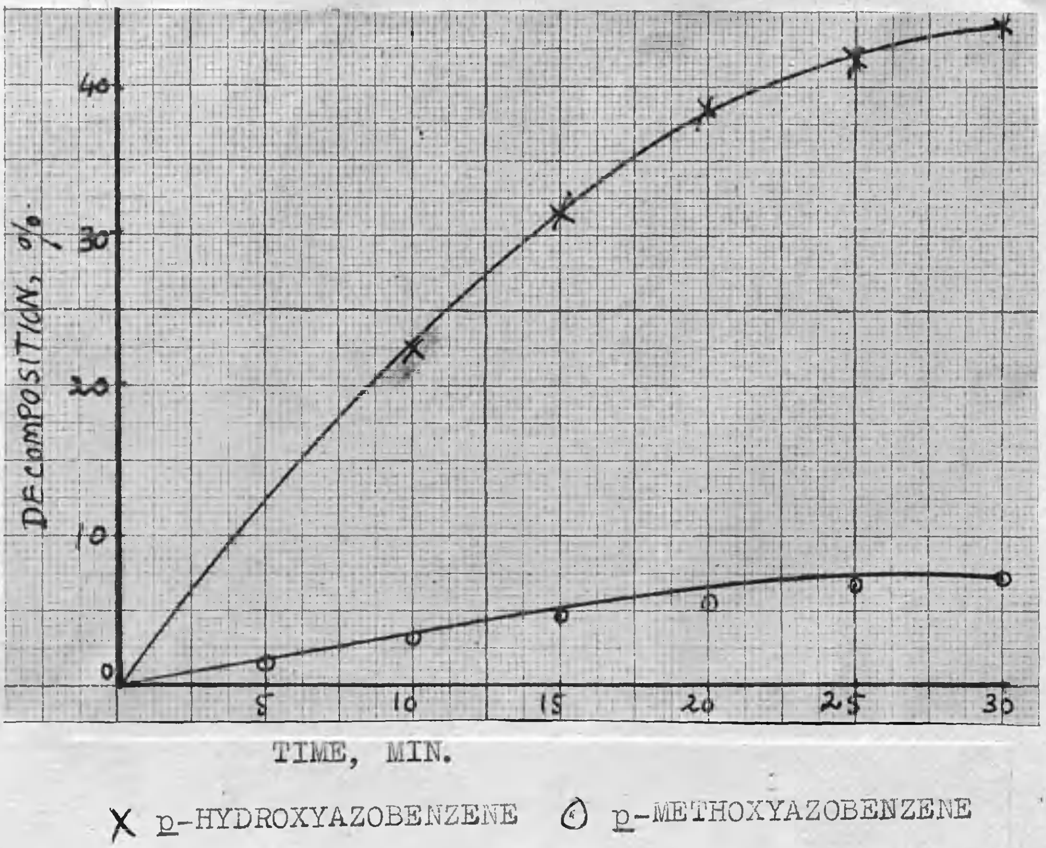


FIG. 108 -RATE OF DECOMPOSITION OF INSOLUBLE DYES IN ACID DICHROMATE SOLUTION.

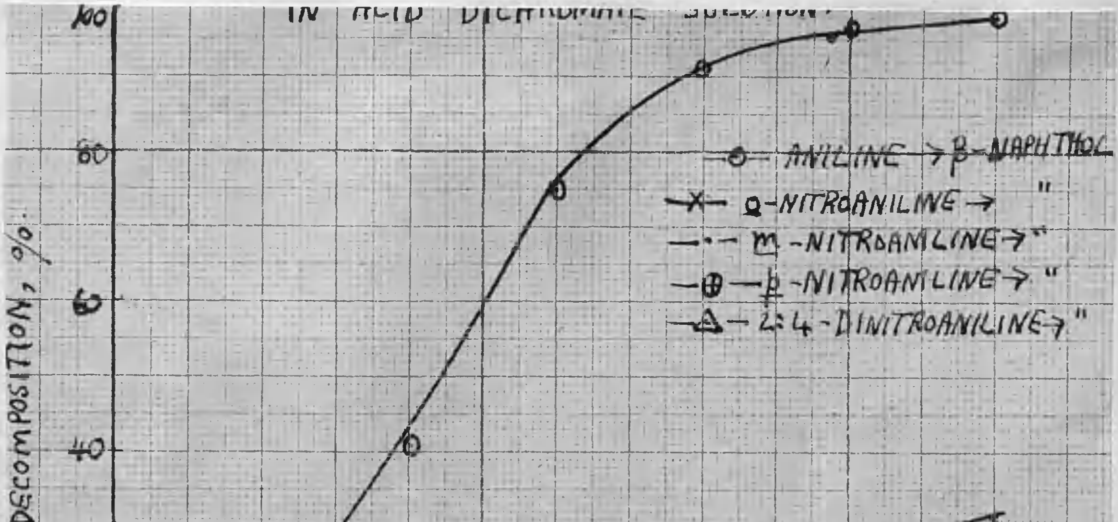
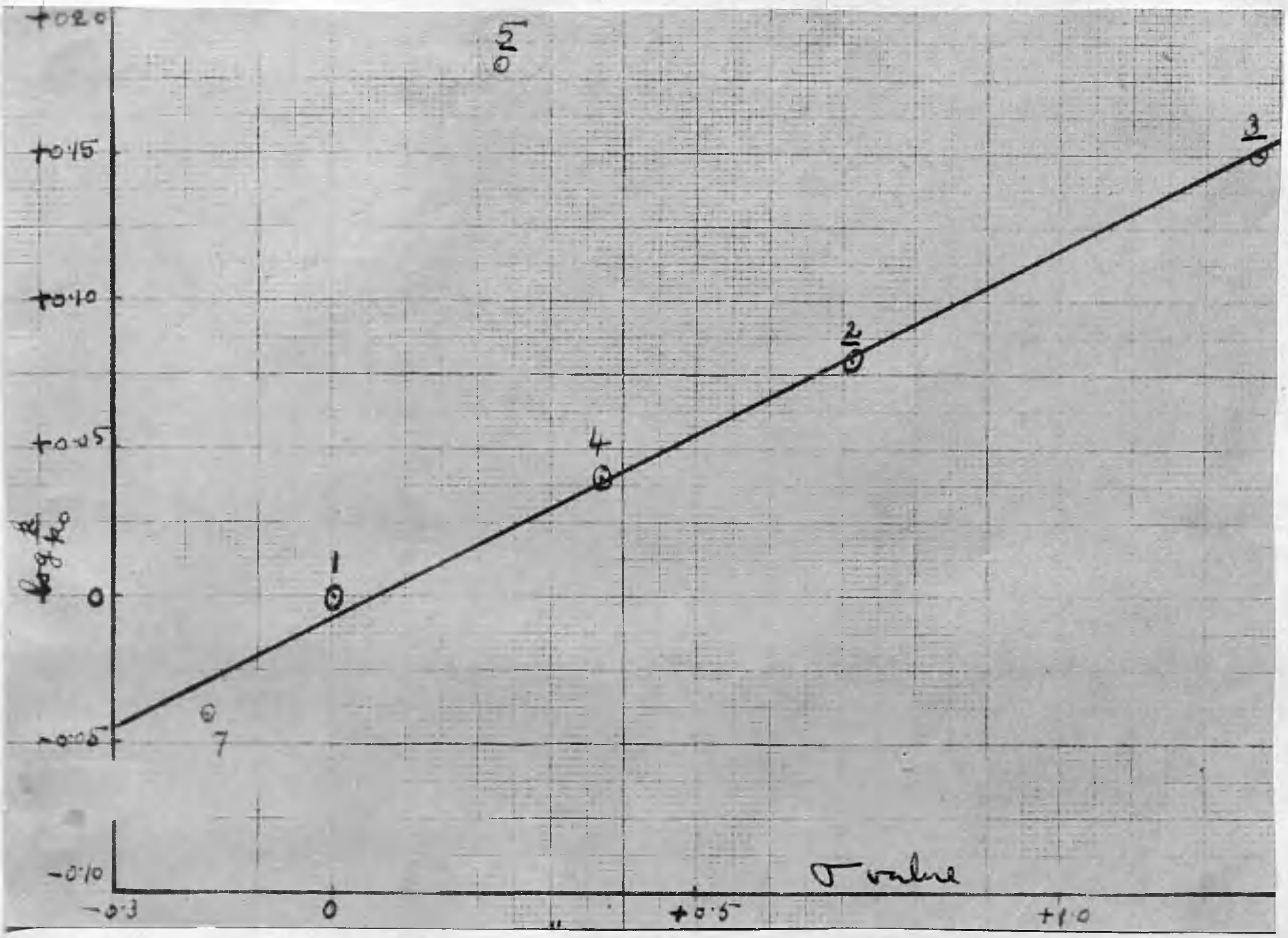
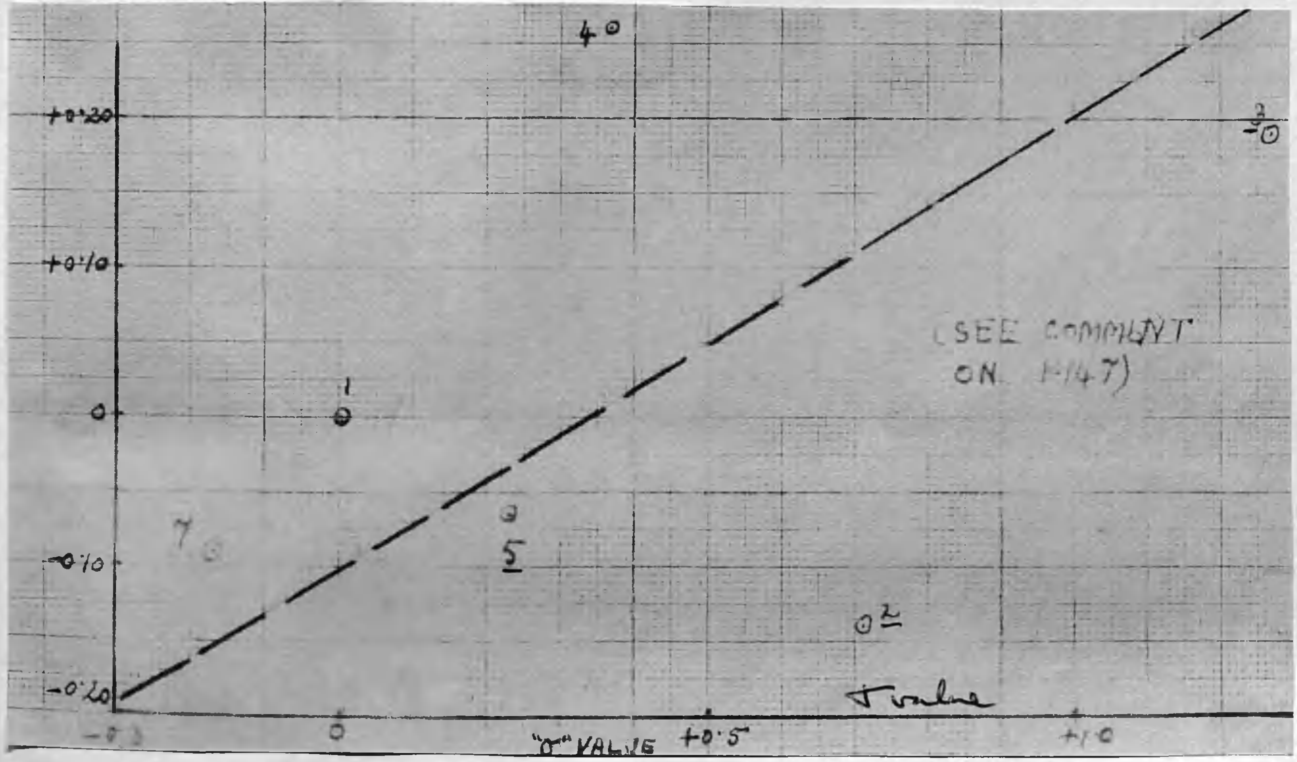


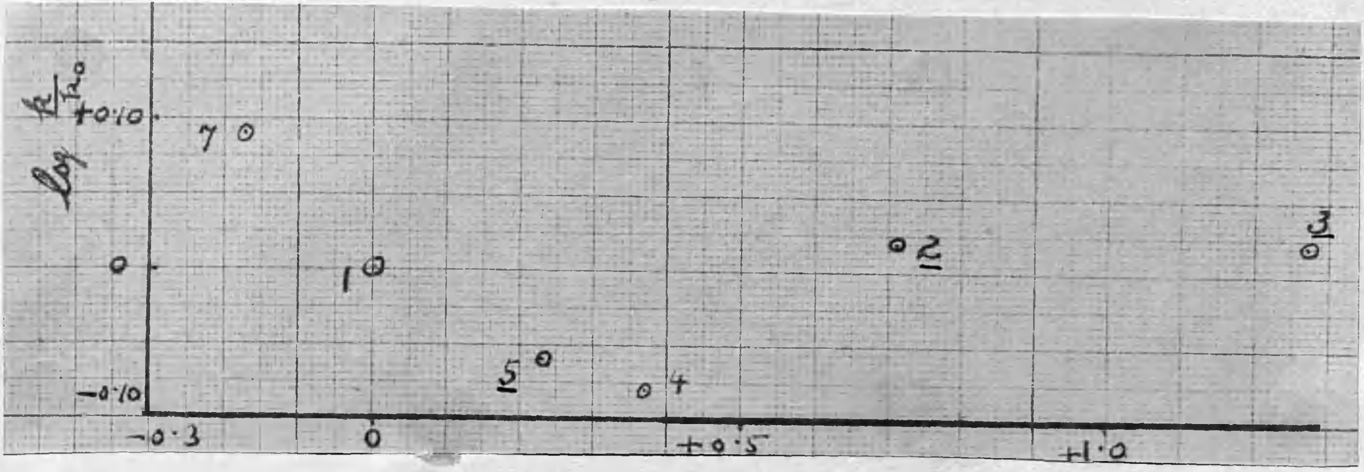
FIG. 109 - RATE OF DECOMPOSITION OF INSOLUBLE DYES IN ACID DICHROMATE SOLUTION.



110
110 Oxidation of R-acid dyes with H_2O_2

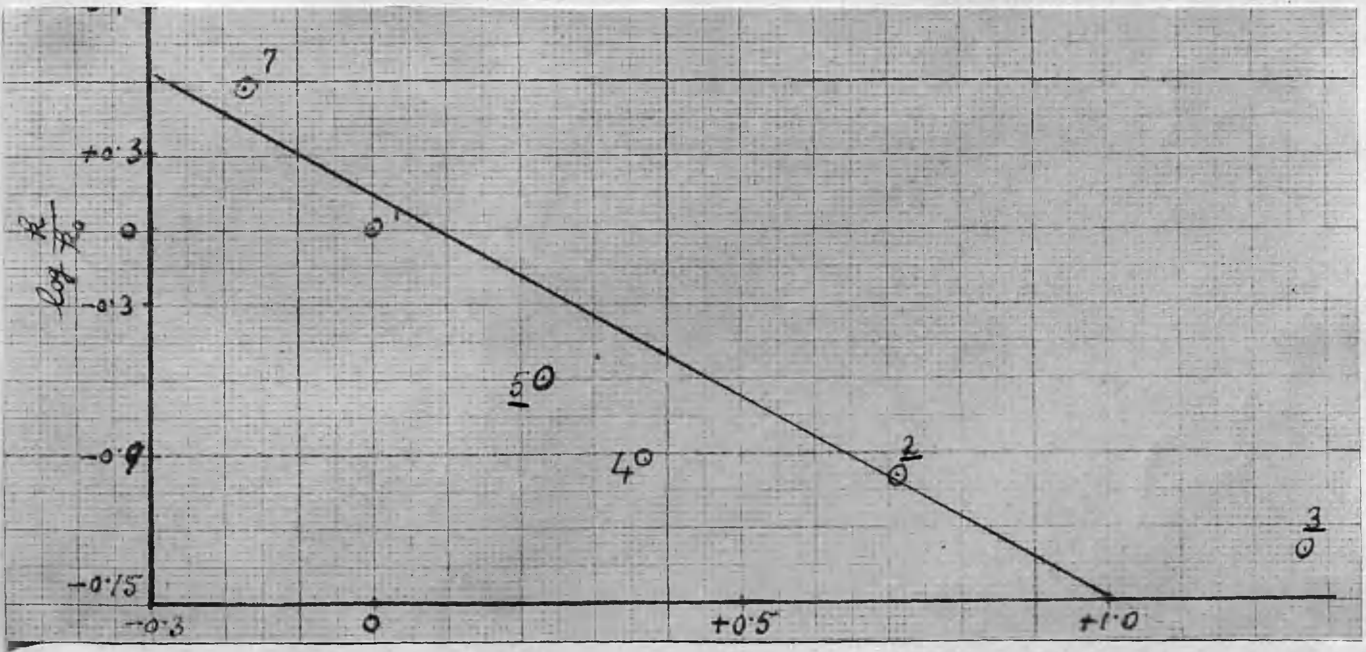
neutral ↑
acid ↓





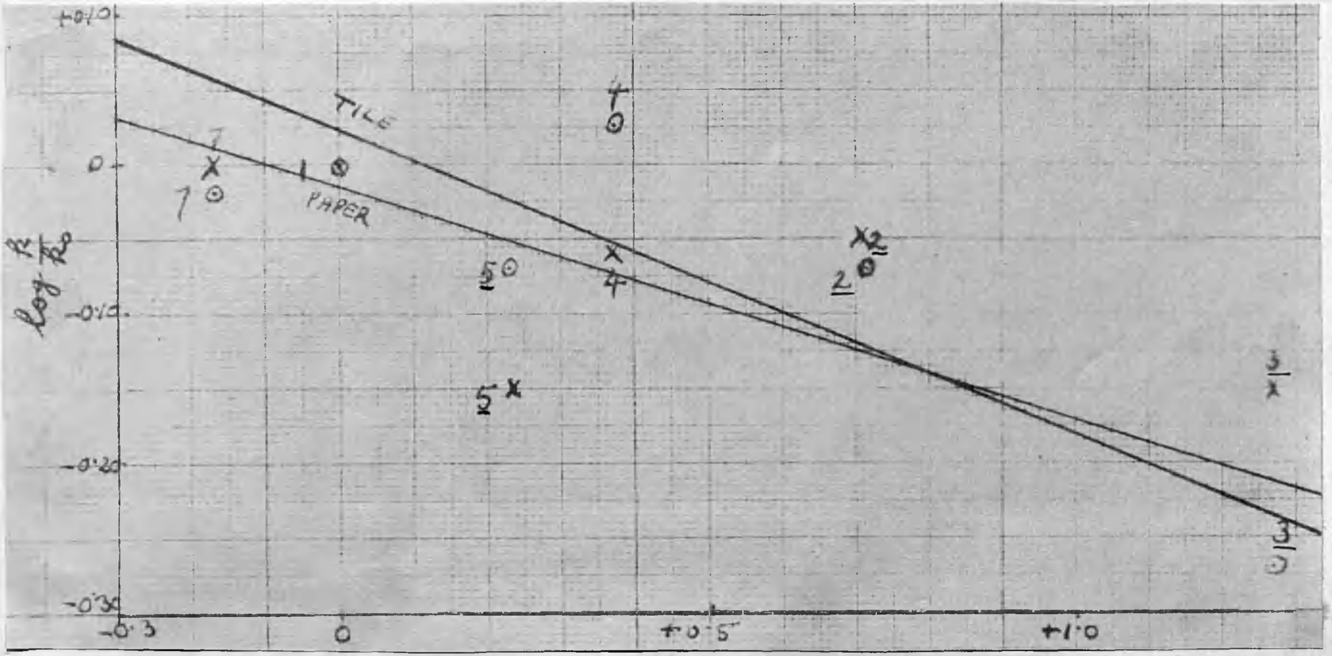
"σ" VALUE

FIG. 112 - OXIDATION OF R-ACID DYES WITH $K_2S_2O_8$

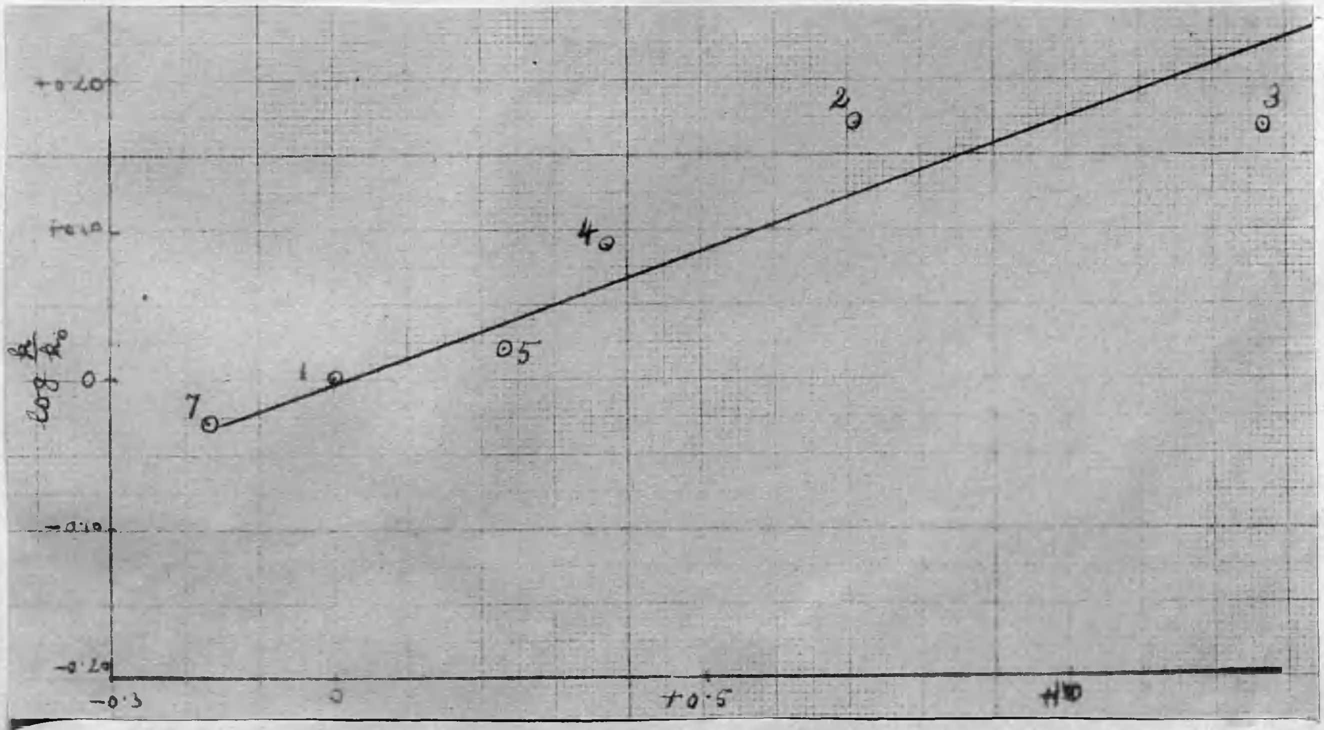


"σ" VALUE

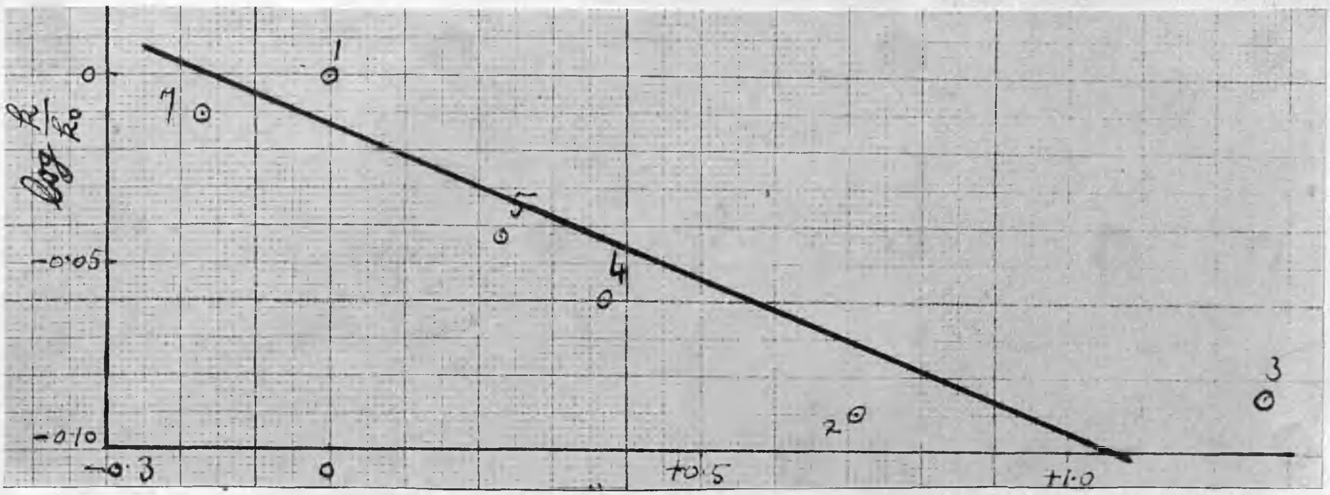
FIG. 113 - OXIDATION OF R-ACID DYES WITH DILUTE HNO_3.



"σ" VALUE.
FIG. 114 ⊙ R-ACID DYES ON TILE.
× R-ACID DYES ON PAPER.

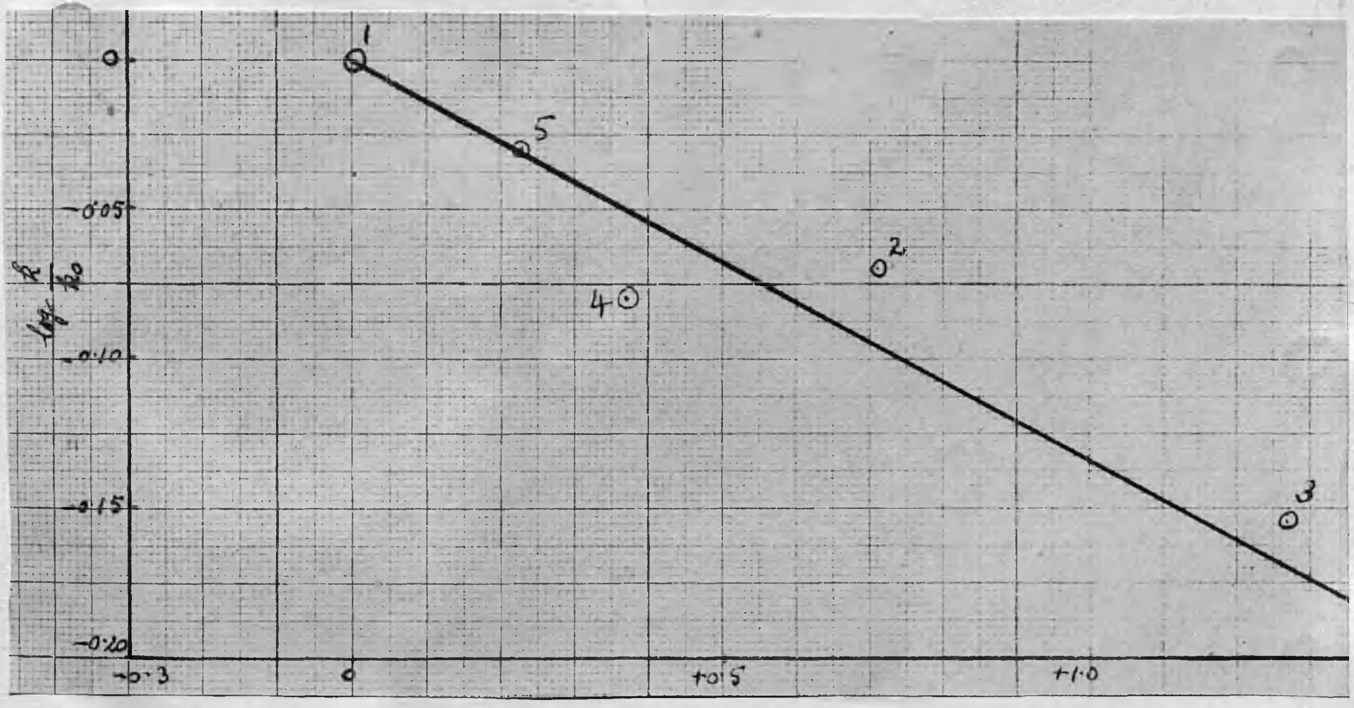


"σ" VALUE
FIG. 115 - R-ACID DYES ON WOOL



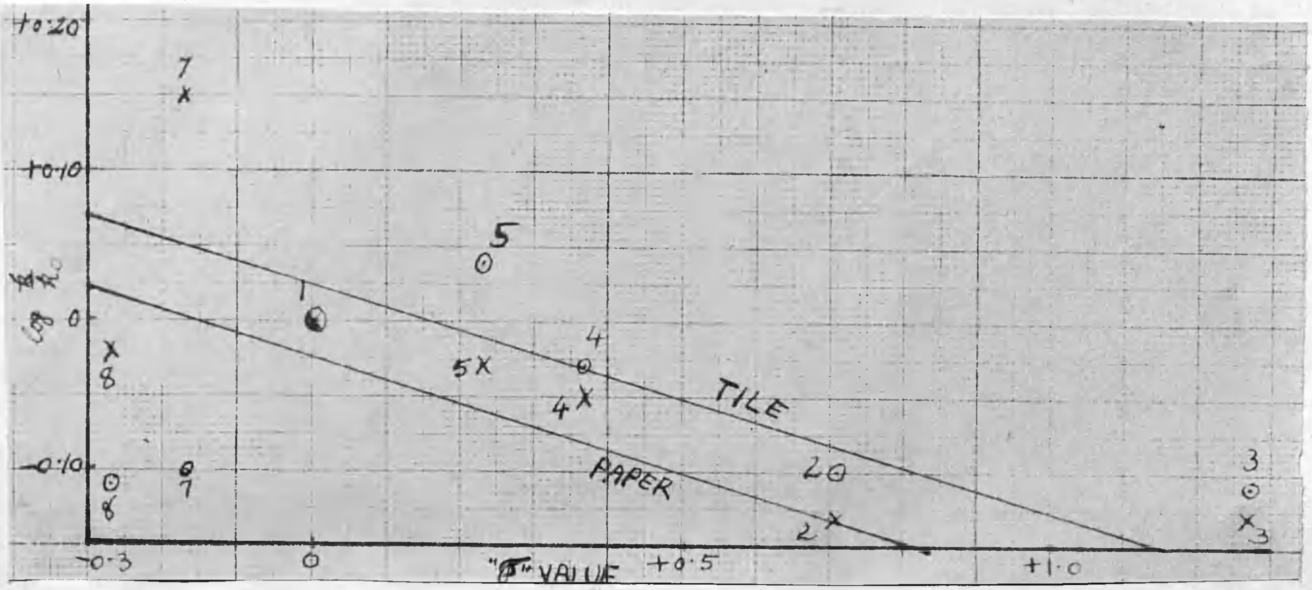
"σ" VALUE

FIG. 116 - MEAN LIGHT FASTNESS FIGURES FOR SIXTEEN COMMERCIAL BRENTHOLS ON COTTON (I.C.I. PAMPHLET (105)).

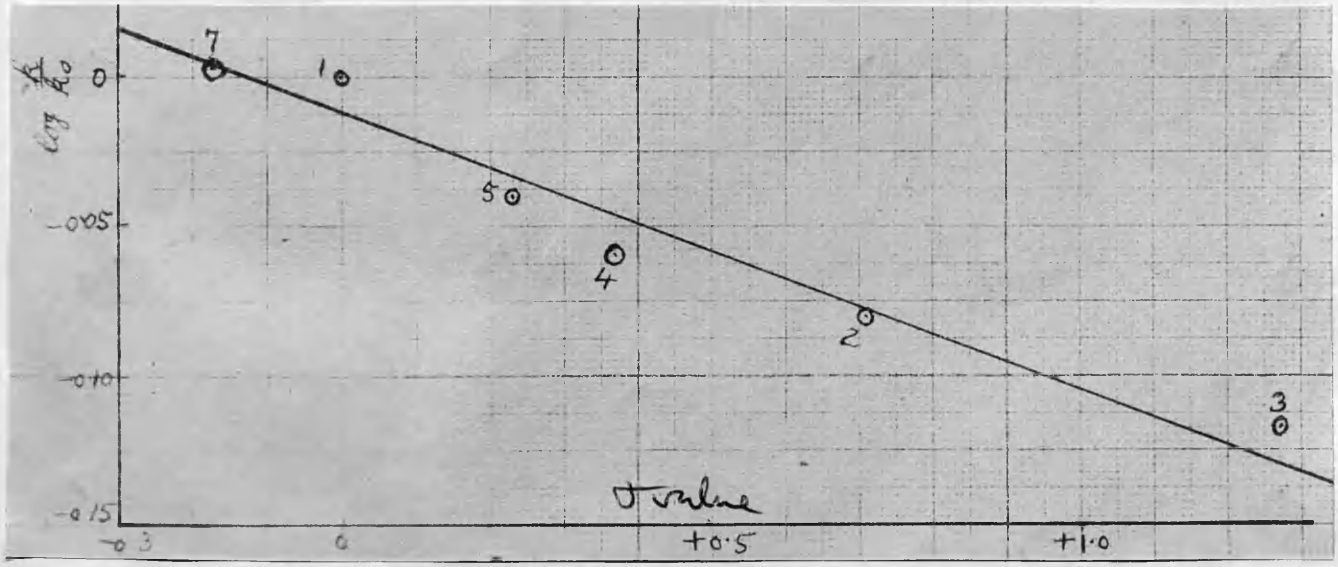


"σ" VALUE

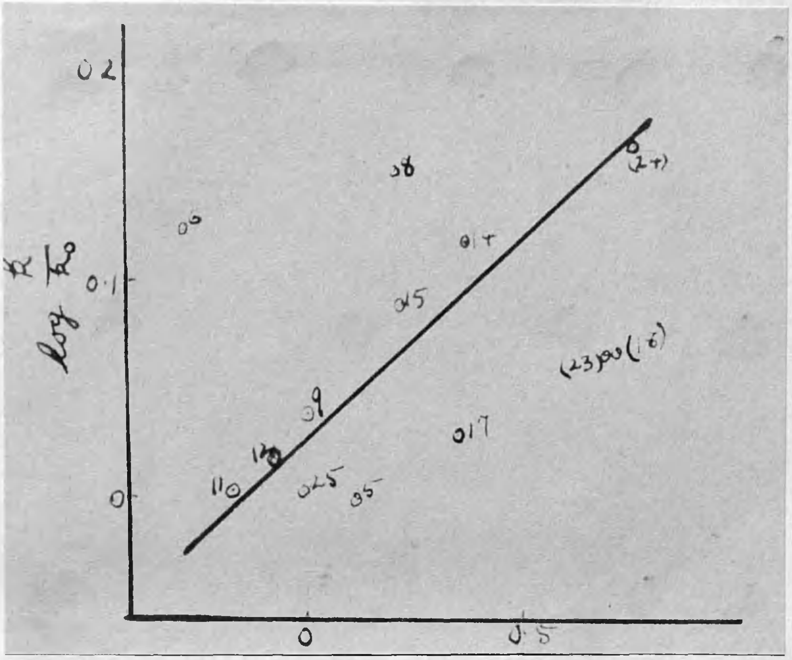
FIG. 117 - BRENTHOL DYEINGS ON MERCERISED COTTON SATEEN (Present Work).



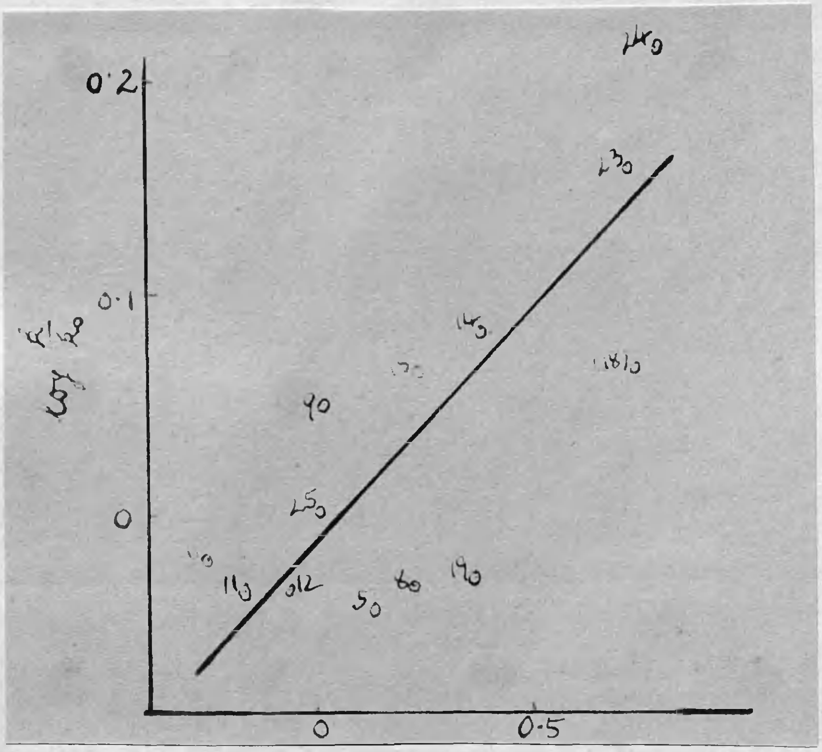
118 β-napthol dyes on paper ⊙ and tile ⊗
Light fastness data



119. Grand mean light fastness data – o-hydroxyazo dyes – all substrates except wool



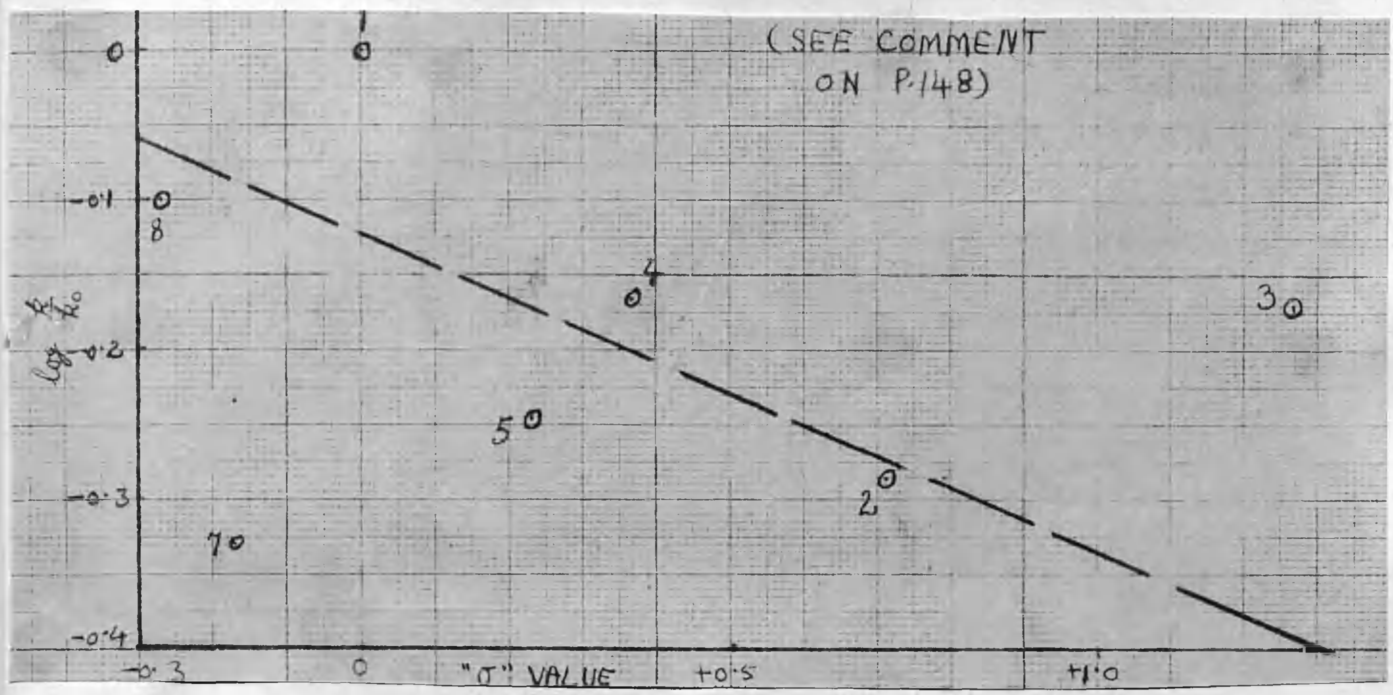
120. Wool



121 Gelatin.

Curves from Kienle *et al* (39)

R-acid dyes
- light fading data



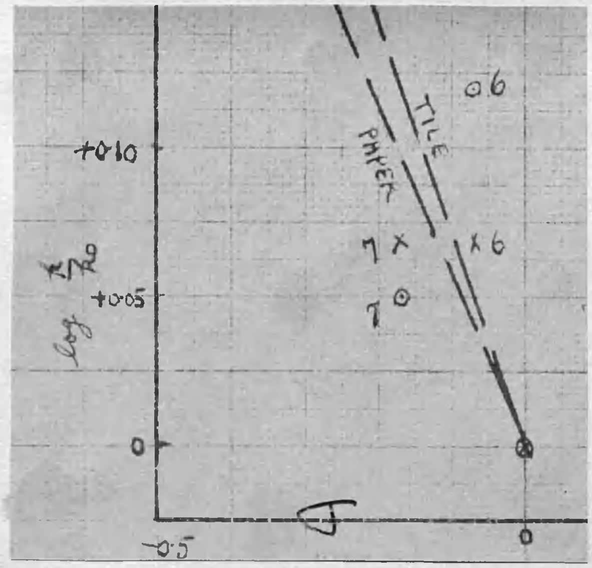
122. R-acid dyes on wool – ceric sulphate

123. Oxy-L-acid dyes

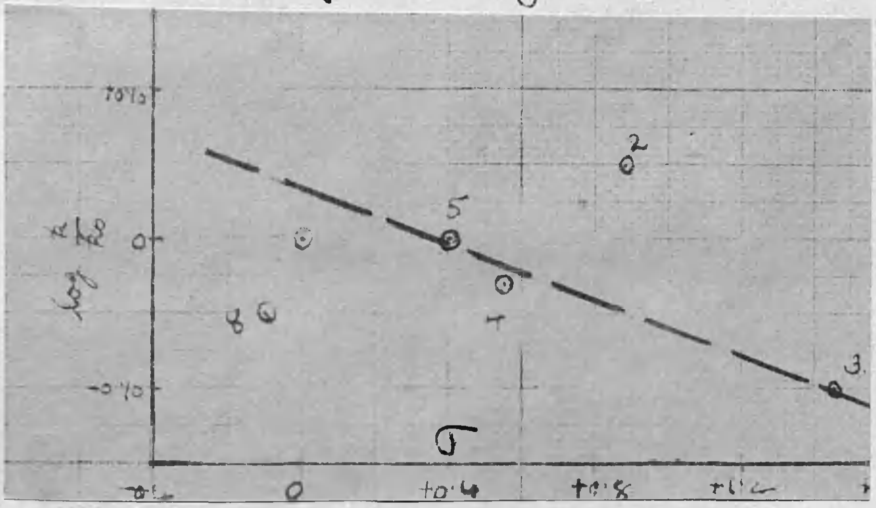
⊙ neutral H_2O_2

X $K_2S_2O_8$

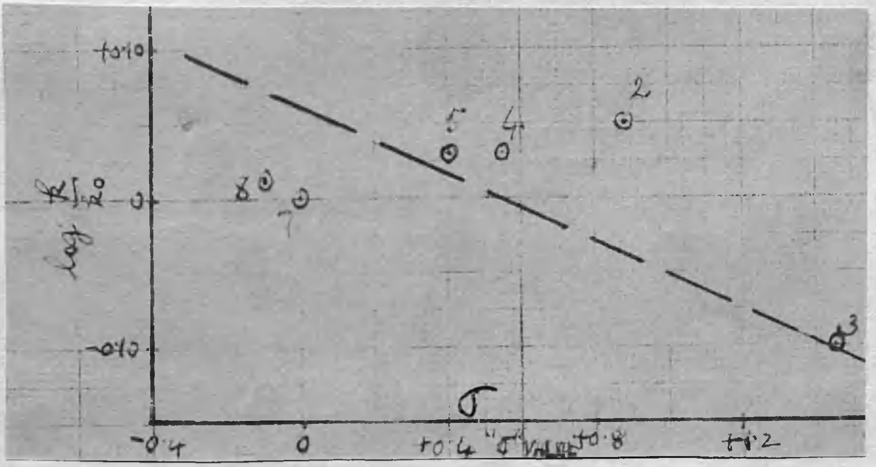
Light fastness data



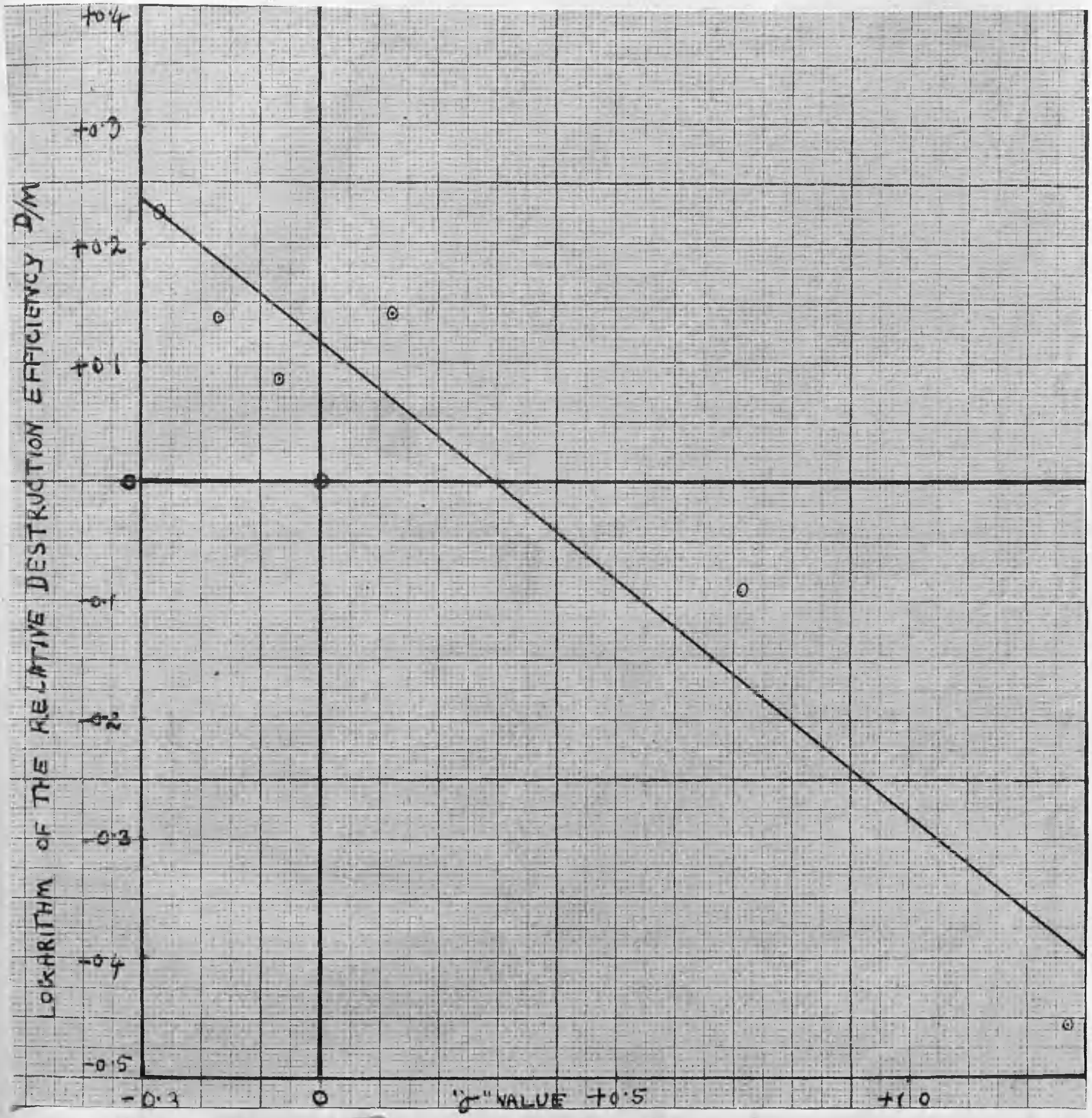
124 Oxy-L-acid dyes ⊙ tile × paper



125 α-naphthol dyes on tile (p-toluidine std.)



126. mean: α-naphthol dyes on tile and paper (p-toluidine standard)



		p-OCH$_3$	p-CH$_3$	m-CH$_3$	m-OCH$_3$	m-NO$_2$	p-NO$_2$
σ	...	−0·27	−0·17	−0·07	+0·12	+0·71	+1·27
$\log_{10}(D/M)_{rel}$	...	+0·226	+0·138	+0·084	+0·139	−0·092	−0·455

127. α-Naphthylamine dyes on cellulose acetate
Fading data curve from Atherton + Seltzer (41)

ABSTRACT OF A THESIS ON

"THE OXIDATION OF AZO DYES AND ITS RELATION TO LIGHT FADING"

submitted for the Ph.D. Degree of
Glasgow University

by

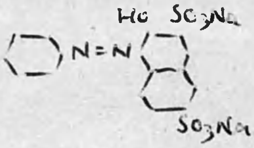
N. F. DESAI. (APRIL 1951)

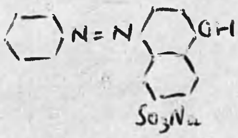
The action of light on dyed fibres in air appears in many cases to involve an oxidation of the dye. The present work has been a preliminary to the fuller investigation of the photochemistry of azo dyes. Several series of simple monoazo dyes have been examined. A study of thermal oxidation in solution by common oxidising agents was followed by comparison with a series of measurements of relative light fastness in an attempt to elucidate the mechanism of the light fading process.

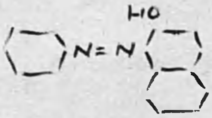
The work has confirmed that oxidation of azo dyes in aqueous media, with several common reagents, e.g., ceric sulphate, potassium dichromate or hydrogen peroxide, disrupts the azo group and leads to the formation of a diazo compound and a quinone. Subsequently, these further decompose to give, respectively, a phenol and nitrogen (in acid media), and phthalic acid. The reaction thus appears to be common to many types of oxidising agent, since previous workers have observed similar effects with, e.g., sodium hypochlorite, lead dioxide and ozone. An acceptor has been used to combine with the quinone formed and thus enable it to be identified without danger of its further oxidation. By boiling the acid solution after oxidising the dye a quantitative yield of nitrogen from the/

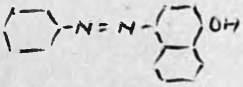
the azo group is obtained, except when free amino groups are also present. This procedure could be used in quantitative analysis.

An hypothesis is put forward suggesting that the initial step in such chemical oxidation is one of hydrolytic attack on the -C = N- bond of the dye, when it is present as the hydrazone and not the azo tautomer. In order to confirm or disprove the postulated hypothesis, several dyes containing nitro, chloro, methyl, methoxy or sulphonic and carboxylic acid groups in various positions in the phenyl nucleus in the following parent dyes, were prepared:-









The rates of oxidation of the water-soluble dyes in presence of various oxidising agents, such as neutral and alkaline hydrogen peroxide, potassium persulphate and dilute nitric acid were studied quantitatively. In the case of the insoluble dyes the rate of nitrogen evolution was examined as a measure of ease of oxidation. To correlate the oxidation of azo dyes with their relative light fastness, the above dyes were exposed in graded depths on substrates of wool, cellulose (cotton and filter paper), unglazed tile, and anodised aluminium. The last two materials were/

were chosen in the hope they might be inert substrates.

Fading and oxidation data were plotted against Hammett *sigma* values to determine the effect of substituents in the phenyl nucleus. The results appear to show that fading on wool is caused by hydrogen peroxide, which it is suggested may be produced by photolysis of the fibre itself, whereas on other substrates some other disruption process of the dye molecule occurs, perhaps by attack of atmospheric oxygen. The results also signify that the initial step in fading is a simple reaction involving attack at one of the unsaturated centres of the dye molecule.

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