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THE PHOTOCHEMISTRY OF

AMINOANTHRAQUINONE COMPOUNDS

IN ORGANIC SOLVENTS.

C O N T E N T S

AUTOBIOGRAPHY

The author was awarded a Sir Richard Arkwright Scholarship in 1955 and entered the Department of Textile Chemistry in the University of Manchester to study for the degree of Bachelor of Technical Science, with honours. He graduated in 1958 and in the same year commenced research under the supervision of Dr. G. S. Egerton. He was also appointed to a Half Demonstratorship in the Department of Textile Chemistry in the Manchester College of Science & Technology. In 1960 he was appointed Demonstrator in Textile Chemistry in the University and in the College.

ABSTRACT

The fading by light of anaerobic solutions of some simple amino-anthraquinone compounds in ethanol and in ethyl acetate and for 1-amino-anthraquinone also in carbon tetrachloride and in n-hexane has been followed spectrophotometrically. Two light sources have been used, one emitting short-wave ultra-violet radiation and the other near ultra-violet and visible radiations. The rate of fading is considerably faster for exposures made to the former light source and, in general, greater in ethyl acetate than in ethanol irrespective of the type of radiation. The changes in spectra of the solutions on fading involve the formation of new absorbing systems which for compounds with a β -amino group strongly resemble the spectra of the corresponding anthrones, and for 1,4-substituted compounds the leuco-forms of the dyes. The addition of 10% of water to an ethanol solution of 1,4-diaminoanthraquinone greatly increases the rate of fading caused by short-wave ultra-violet radiation, while the addition of 10% of benzene reduces the rate. The presence of benzene also causes the production of additional photoproducts which may be the result of a complex interaction between the benzene and ethanol. The spectra of the photoproducts of 1-mono-, 2-mono- and 1,5-di-aminoanthraquinone in ethanol are very similar to the spectra of the fading products of these dyes on N-methoxymethyl nylon after exposure to near ultra-violet and visible radiation in an atmosphere of nitrogen.

INTRODUCTION

The art of the dyeing of textile materials has been practised for several thousand years. The impermanence of the colour of dyed fabrics to light has, therefore, long been a matter of concern and it is not surprising that there are references to this problem in early writings. Pliny writing at the beginning of the first century castigated the people for placing a value on cloth dyed with Tyrian purple equal to that of pearls. The cloth he commented faded hourly but pearls were of permanent value and beauty. It is recorded that the success of Perkin's synthetic dye Mauve was due in great part to the work of the silk dyer, Keith, who demonstrated its good light fastness compared with contemporary dyes. By current standards it is of low fastness but its success led to an extensive study of synthetic dyes and their stability to light.

Fading by light.

Since the action of light on a coloured substance may involve an on tone or off tone change in colour the fading of a dyeing by light should strictly be defined as a change in depth of shade or hue. The fading may take place rapidly at first and subsequently tail off, or vice versa. It may also proceed at a uniform rate. Some changes in shade are not permanent. A dye may exhibit phototropy, that is undergo a change in hue on exposure to light which may be reversed on storage in the dark; prolonged exposure may, however, lead to permanent fading. It is also possible that fading products are themselves unstable and can be further changed by light action or by an internal molecular rearrangement.

Factors affecting the light fading of dyed textiles.

(i) Radiation.

The nature and rate of the colour change involved in the light fading of dyes is determined by the intensity and quality of the light. The energy associated with a quantum of light depends on the wavelength and is considerably greater for short wavelength than long wavelength radiation. The greater the amount of energy absorbed by the molecule the greater the chance of bond rupture and decomposition.

In practice the majority of fading occurs with natural light. The fading of dyes with light sources of dissimilar spectral character, for example mercury - vapour lamps and sunlight, may be quite different.

On absorption of light a molecule gains energy and its electrons are rearranged. Normally in the ground state all the electrons in a molecule are paired with opposite spins. The absorption of light raises an electron to a higher energy state without change of spin direction to give the singlet excited state. It is possible, however, for a transition to take place, directly or indirectly, to a triplet state in which the electron spins are not coupled. Absorption of light by this state results in the formation of a triplet excited state. The life-time of the triplet level is considerably longer than that of the singlet excited state. Return to the ground state of an excited electron may take place by the emission of radiation in the form of fluorescence or phosphorescence, by thermal reactions involving collisions with other molecules, or by participation in a chemical reaction. It has been suggested that the triplet state by virtue of its longer life-time will exhibit a higher

photochemical reactivity than the singlet excited state.

(ii) Atmosphere.

There is considerable evidence that in many cases fading in vacuo is negligible, although some results to the contrary have been obtained.[1] Bolis[2] and Gebhard[3] considered that the fading that did occur in a vacuum was due to incomplete removal of air.

Fading has also been found in many instances to be negligible in nitrogen but Ackerman[4] found that aqueous solutions of acid and basic dyes faded as quickly in nitrogen as in air. More recently Egerton and Roach[5,6] have shown that the fading of simple aminoanthraquinone compounds on polymer films was not prevented in nitrogen, some dyes being found to fade equally fast in nitrogen and oxygen.

The presence of air or oxygen generally increases the rate of fading and as a result a mechanism involving oxidation is generally considered to be involved. The influence of moisture in air on the fading rate is considerable and to account for this Gebhard[7] proposed a mechanism involving the formation of perhydroxyl ions by direct combination of water and oxygen. The presence of volatile peroxides on exposure of vat dyed materials has been demonstrated by Egerton[8-10] but there is, however, no definite relationship between the formation of peroxides and fading.[11,12]

(iii) Substrate.

It was soon realised after the introduction of the first synthetic dyes that the substrate can seriously influence the light fastness of a dye. Certain basic dyes are more stable on cellulose acetate than

on mordanted cotton and indigo is less fast on cotton than on wool. The anthraquinonoid vat dyes generally show a very high light fastness on cotton but only a poor fastness on nylon. It has been suggested that the low fastness of the vat dyes on the synthetic fibres may be due to the state of the dye in the fibre. The highly crystalline nature of the synthetic fibres often results in a low degree of dye aggregation. The energy absorbed by the dye is thus not able to dissipate itself so easily by thermal means.

(iv) Added agents.

In view of the apparent oxidative nature of light fading Gillet and Giot[13] studied the influence of anti-oxidants incorporated in the material. It was found that some dyes were protected, but only in the presence of large amounts of the agent. It was suggested that those dyes which were not protected, such as the nitro and triphenylmethane colours, faded by a different reaction mechanism.

The pre- or after-treatment of many dyes with metal salts to produce metal chelates frequently increases the light fastness. But the presence of a delustring agent such as titanium dioxide can lower the fastness[14]. In addition the application of a crease-resisting finish to dyed cloth frequently reduces the stability of the dye. The final pH of the fabric is also important[15].

The presence of another dye on the fabric can sometimes alter the fastness properties. Anthraflavone has a poor light fastness by itself but in conjunction with Caledon Blue GCP relatively fast shades may be obtained. The reverse is also possible. A combination dyeing of

Caledon Jade Green and Cibanone Orange R quickly fades with loss of the green, yet alone these dyes have quite high light fastness properties.

Nature of fading products.

The identification of the fading products and the subsequent differentiation between those resulting from primary and secondary processes is made difficult by the low yields obtained. In only a few cases has it been possible to isolate them and make a positive identification. Normally identification is by supposition only. With a few exceptions photoproducts may be divided into two classes, (i) those that arise from decomposition of the dye molecule and (ii) those that are the result of phototropic changes. In the first class they are normally the result of photo-oxidation but nitro dyes appear to fade by reduction.[16,17]

Haller and Ziersch[12] identified 1,2-naphthoquinone amongst the fading products found when cotton dyed with β-naphthol azo dyes was exposed to a carbon arc. Iwamato[18] found that crystals of the oxalates of Malachite Green and Crystal Violet were converted to p-dimethylaminobenzophenone and Michler's ketone respectively by the action of air and sunlight. Isatin was isolated by Hibbert[19] from cotton dyed with indigo which had been exposed to sunlight and later it was shown that derivatives of isatin resulted from the fading of indigoid dyes[20]. Couper[21] found that the exposure of cellulose acetate dyed with 1, 4 - bis(methylamino)anthraquinone to a carbon arc in air caused N - dealkylation, hydrolysis of amino and methylamino to hydroxy groups, oxidation of amino to imino groups and methylamino to methylimino groups, nuclear hydroxylation, nuclear deamination and possibly other

oxidative destruction of the dye.

The phototropic changes of many azo and stilbene dyes are apparently due to stereochemical changes. A dyeing of p - aminoazobenzene on cellulose acetate on exposure to light changes colour from yellow to orange. The original colour is restored by placing the fabric in the dark. It is thought that the change caused by light involves a partial conversion of the yellow trans isomer to the cis form. Support for this idea has been given by Hartley[22] who also found that for a solution of azobenzene the degree of isomerism was dependent on the solvent. The aminoazo dyes that are phototropic on cellulose acetate and ethylcellulose do not exhibit this property on cellulose or nitrocellulose[23]. Prevention of these changes may be effected by introducing substituents which restrict the free rotation about the central double bond.

Phototendering of textiles.

Undyed cellulosic textiles exposed to air and sunlight undergo slow oxidative destruction. The process, which is dependent on the susceptibility of the fabric to oxidative attack, is greatly accelerated by the presence of moisture. A further marked increase in the rate may be caused by the incorporation of certain dyes and inorganic pigments in the material. Such dyes exist in all the classes with perhaps the exception of the reactive dyes, there being no information on their behaviour as yet. The tendering activity of dyes in the vat dye range is more noticeable to the consumer by virtue of their high light fastness and subsequent end use.

Egerton[8-10][24-26], in a series of papers, has discussed the factors affecting tendering and has suggested that for dyed materials the action is due to an energy transfer from the excited dye to oxygen with the subsequent formation, in the presence of moisture, of hydrogen peroxide. Many of the factors influencing the light fastness properties of a dye on a textile substrate also influence its tendering activity but these do not necessarily act in unison. They do depend, however, on the ability of the dye to take part in or promote light initiated thermal and chemical reactions. The ability to promote such reactions will be modified by the environment of the dye but will depend on its chemical structure. While tentative generalisations may be made covering particular structures and substituents in any one class of dyes they may not apply to all cases. For example, halogenation of indigoid and anthraquinonoid vat dyes frequently increases the light fastness but in some cases halogenation may be ineffective or even decrease the light fastness. The sulphonic acid group normally favours light fastness but azoic dyes have, in general, a much greater light fastness than direct dyes. Many of the yellow and orange benzamidoanthraquinone dyes have been found to be photo-tenderers but the benzamido group is not necessarily responsible for their reactivity[27].

The suggestion has been made that the yellow and orange vat dyes owe their activity to their high absorption of blue and ultra-violet light. It has been shown, however, that an active and an inactive dye may have almost identical absorption spectra[28]. Furthermore, the tendering dyes in other classes are not confined to the yellows and oranges.

Photoprocesses in idealised systems.

The complexities of the processes of fading and tendering have caused many workers to study the action of light on model systems. In these systems commercial dyes are frequently replaced by simple colouring matters, textile materials by organic solvents and the source of illumination is normally a mercury-vapour lamp, the emission of which may or may not be filtered. The results from such idealised systems while being an accurate record of the photoprocesses for those systems may in fact bear little resemblance to the action of sunlight and air on a dyed fabric. The state of the dye in solution is entirely different both in terms of its degree of aggregation and its contact with the surrounding medium. In addition the mobility of any active species formed is likely to be quite different in the two systems.

Couper[21] has shown from a study of the action of light and air on 1,4 - bis(methylamino)anthraquinone dyed on cellulose acetate and of light on a solution of the same dye in ethyl acetate through which was bubbled air or nitrogen that the photoproducts produced on the cloth differed from those in solution. In the experiments on dyed cloth the changes involving the formation of some thirteen photoproducts were brought about by a carbon arc and have already been mentioned. A mercury arc was used for the irradiation of solution. The only fading products identified when air was bubbled through the solution were 1 - imino - 4 - methylimino and 1 - amino - 4 - methylaminoanthraquinone. When nitrogen was passed through the solution the yield of these two products was much less but there were other products, one of

which appeared to be a leuco-compound.

The photochemistry of azobenzene and a substituted azobenzene in propan-2-ol and iso-octane in the presence of varying amounts of oxygen has been studied by Blaisdell[29]. The fading promoted by a mercury-vapour lamp emitting no wavelengths lower than 290 mμ was shown to be dependent on the pressure of oxygen and due to the reduction of the azo linkage to give initially a substituted hydrazine and later substituted anilines. It was postulated that a hydrogen atom was abstracted from the solvent.

Bamford and Dewar[30] compared the tendering activity of a number of vat dyes on viscose rayon with their autoxidation of tetralin, their polymerisation of styrene and the deactivation of their excited state by oxygen. They were unable to find any correlation between tendering activity on viscose rayon and either the ability to promote polymerisation of styrene or the deactivation of the excited dye by oxygen. There was, however, a very limited correlation with the autoxidation of tetralin. These results led them to conclude that the tendering of cellulose by vat dyes, in the presence of moisture, involved a preliminary oxidation of the hydroxyl ion by the excited dye:

$$D^* + OH^- \longrightarrow D^- + OH^\cdot$$

followed by the formation of hydrogen peroxide.

Either one of these entities could then attack the cellulose. In the absence of oxygen it was found that a number of the dyes in tetralin solution were faded irreversibly on irradiation. It was

suggested that this was due to the eventual formation of an acid-leuco compound which tautomerised to a colourless anthrone and which could not easily be oxidised.

The suggested formation of an acid-leuco compound is in agreement with the work of Ciamician and Silber[31] who found that in the relative absence of air, benzoquinone in alcoholic media was reduced by the action of sunlight to hydroquinone. Meyer and Eckert[32] later postulated that anthrahydroquinone could be obtained by the action of sunlight on an ethanolic solution of anthraquinone. The presence of air caused the reoxidation of the photoproduct. Primary and secondary alcohols in these cases were found to be oxidised to the corresponding carbonyl compounds in the absence of air.

Bolland and Cooper[33] have studied the photosensitised autoxidation of aqueous ethanol in the presence of oxygen using anthraquinone 2,6 - disodiumsulphonate as sensitiser. The light source of a mercury-vapour lamp was filtered to give only wavelengths between 350 mμ and 420 mμ. The reaction was considered to proceed bya non-chain radical mechanism in which hydrogen was abstracted from the ethanol by the activated sensitiser. The sensitiser thus formed a semi-quinone radical which rapidly reacted with oxygen and was thereby converted back to the original quinone. They confirmed the view of Bamford and Dewar[30] that there was no reaction of the excited quinone with oxygen. The primary photoproducts were found to be acetaldehyde, acetic acid and hydrogen peroxide and it was stated that in the absence of oxygen the sensitiser was converted to the corresponding anthrahydroquinone.

Wells[34,35] has given details of the reactivity of alcohols to photo-initiated hydrogen atom transfer reactions and has shown that it is dependent on the ease of attack by the activated sensitiser on the carbon atom in the α position to the hydroxyl group. The rate of reaction is also dependent on the acidity of the solution, the oxygen pressure and water concentration.

In order to ascertain the primary nature and initial behaviour of the photo-excited state of a dye molecule in such systems the technique of flash photolysis has been employed. Bridge and Porter[36] have confirmed the existence of a semi-quinone radical of the type postulated by Cooper and have observed the presence of the longer lived triplet state. They showed that for a poor sensitiser of hydrogen atom abstraction, such as duroquinone, the singlet state alone and not the triplet state reacted with the solvent to produce a semi-quinone radical. They confirmed that the photosensitised oxidation of ethanol proceeds by hydrogen abstraction rather than electron transfer. Bridge and Maclean[37] have studied the "flashing" of anaerobic ethanolic solutions of commercial vat dyes and found the mechanism to be similar. It was observed that the so-called active vat dyes gave radicals in greater number and of longer life-time than the inactive dyes. The degree of permanent fading was also found to be greater for the "tendering" dyes. The effect of pH was to alter the concentration of the semi-quinone radical ion whose life-time in alkali was greatly prolonged.

In a recent paper Bridge and Reed[38] have shown that for duroquinone the excited state is in fact quenched by oxygen but the semi-quinone

radical is not. The unidentified excited state of the more efficient sensitiser anthraquinone 2 - sodium sulphonate is not quenched by oxygen (as Wells[35] has shown) but the semi-quinone radical is. The deactivation of the excited state by oxygen is ascribed to the life-time of that state. They point out that Schenk and Koltzenberg[39] found that inefficient sensitisers, such as aminoanthraquinones, promote an alternative and presumably less efficient oxidation of a substrate in which oxygen is transmitted to the reaction site combined with the triplet state implying, as has been observed, that these dyes readily pass into the triplet state.

The general conclusion to be drawn from the results of studies on the photoprocesses in solution is that the problems of fading and tendering are closley related. To test the applicability of the theories suggested it would seem necessary to examine closely the action of light on solutions of selected dyes in suitable organic solvents and on fabrics dyed with these dyes and to see how far the two systems are related, and where they differ to attempt to account for such differences.

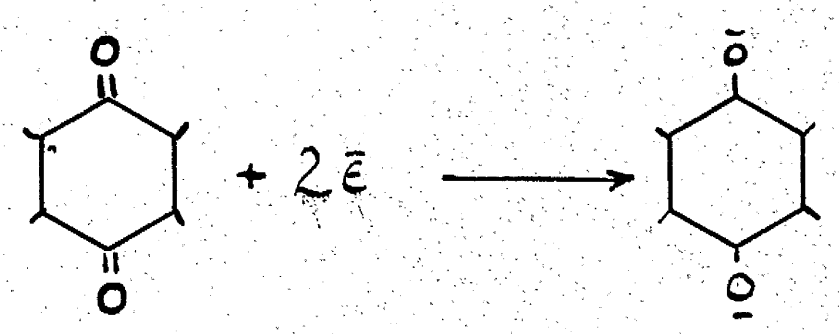
Reduced forms of anthraquinone and its derivatives.

Scholefield and Turner[40] have suggested that on irradiation the active vat dyes are photoreduced to the acid - leuco form. The work carried out on the effect of light on dyes in solution of organic solvents, already referred to above, gives support to this theory. It has also been suggested that anthrone formation can result from the exposure of vat dyes to light.[30] Moran and Stonehill[41] have suggested a mechanism whereby this could occur and comment that in the absence

of oxygen a dye in the excited state may abstract hydrogen from an aqueous ethanolic solution to give an intermediate which would be spectroscopically indistinguishable from the acid-leuco form.

It is, therefore, important to consider the preparation and nature of the reduced forms of anthraquinone and its derivatives.

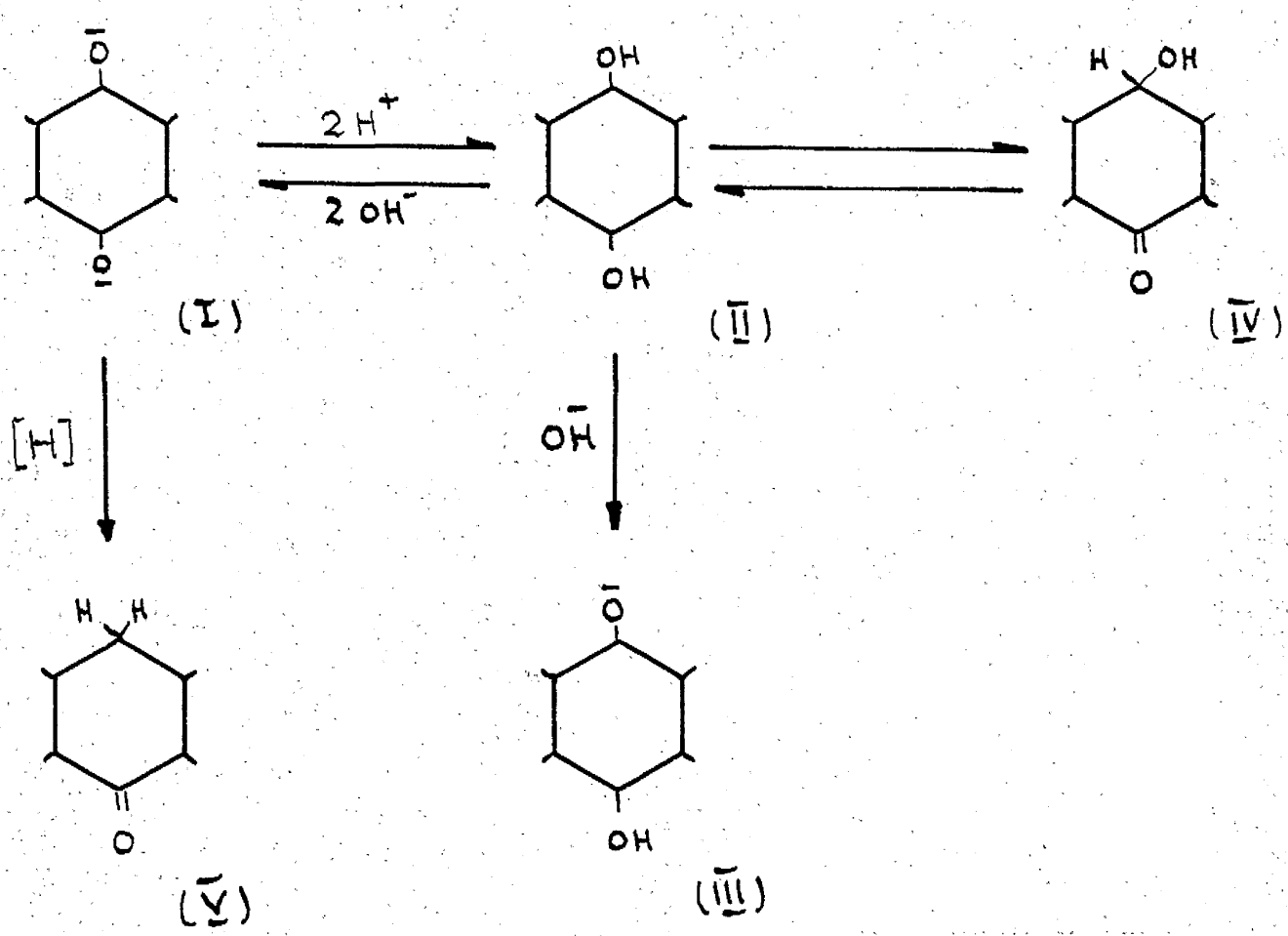
The reduction of anthraquinone vat dyes to give readily oxidisable, alkali soluble compounds may be effected by the action of sodium dithionite and sodium hydroxide in water. Ionically this process may be represented as follows:



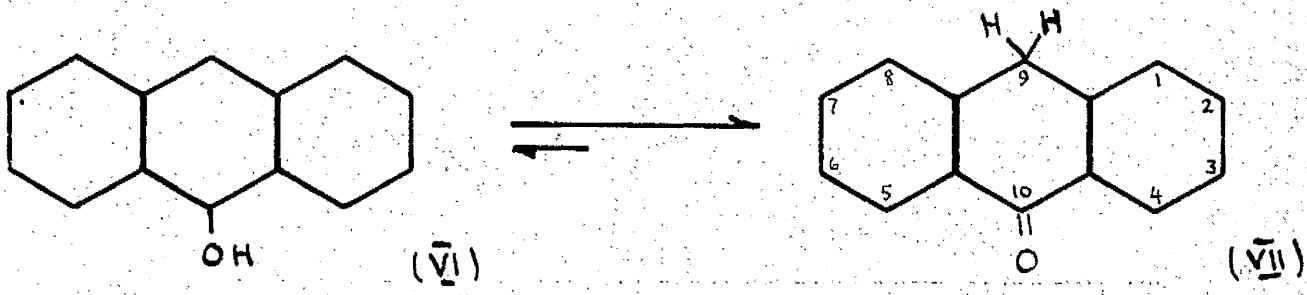
(I)

The ionic form (I) is usually quite stable at normal and slightly elevated temperatures provided that there is sufficient alkali and reducing agent to maintain it in the ionised state. It is easily reoxidised to the parent quinone. When, however, the alkaline vat (I) is acidified the unstable acid-leuco compound (II), or anthrahydroquinone, is precipitated. The anthrahydroquinone recombines with alkali to form either the ionised form (I) or an intermediate ionic form (III), depending on the concentration of alkali. In solution it undergoes trans-annular tautomerism to give the oxanthrone (IV). The initial reduction process can proceed further to give an anthrone (V)

or for very severe reducing conditions to a derivative of anthracene.



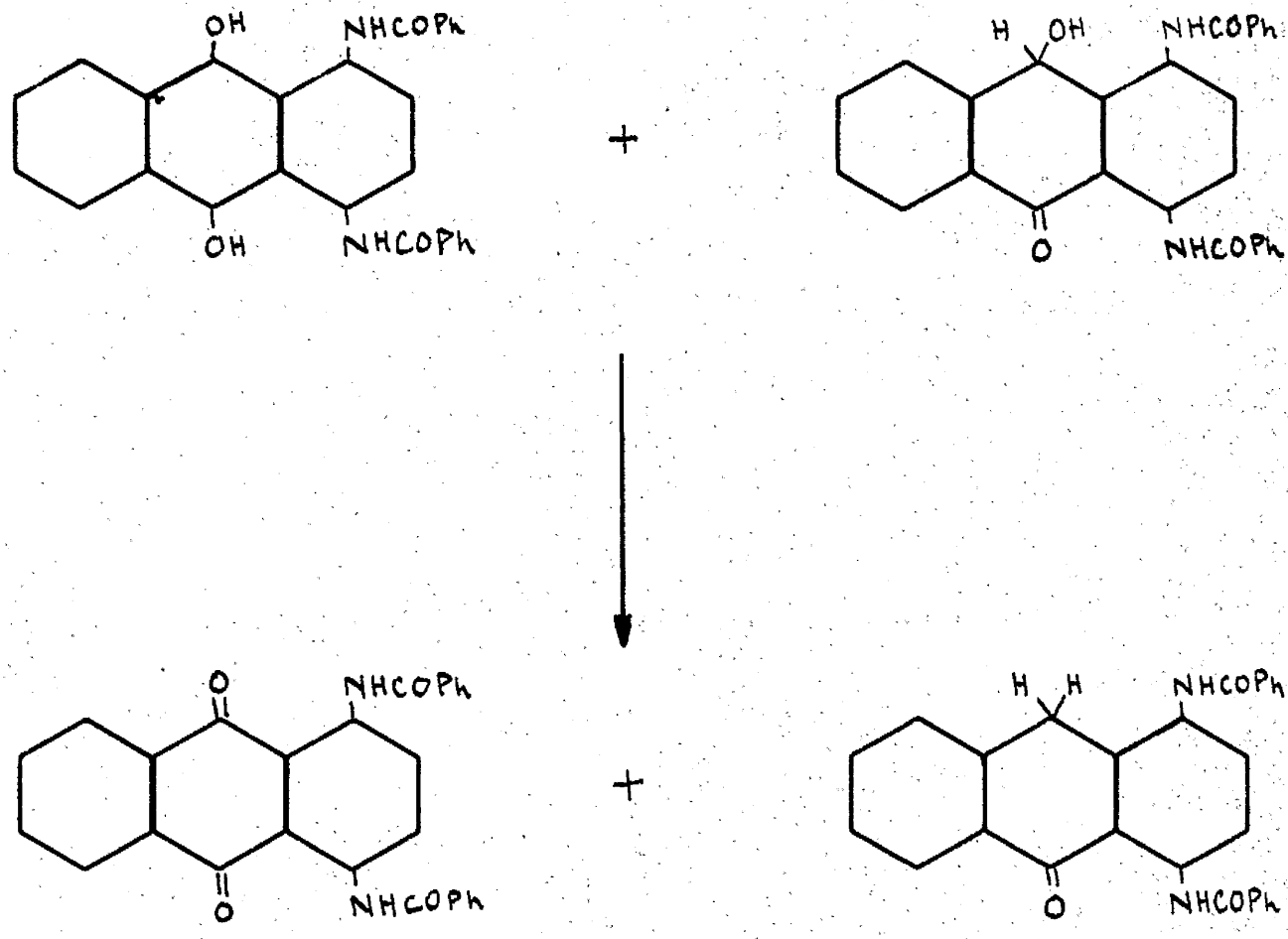
Thus for anthraquinone normal reduction with dithionite and caustic soda leads to the formation of the red alkaline vat, acidification of the vat to the pale yellow anthrahydroquinone which is tautomeric with the colourless, non fluorescent oxanthrone. Over reduction leads to the formation of anthr-10-ol (VI) which rapidly tautomerises to anthr-10-one (VII)



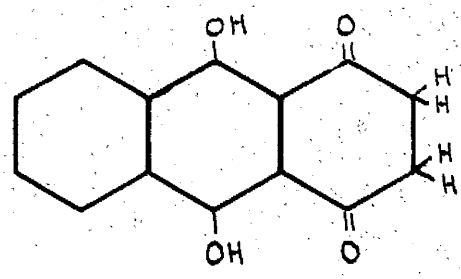
(VI) (VII)

Anthr-10-one, which is pale yellow, may be more easily obtained by direct reduction of anthraquinone in boiling glacial acetic acid with tin and hydrochloric acid.[42]

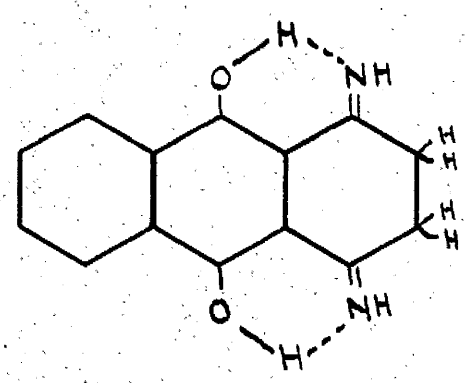
Oxanthrone may be prepared by hydrolysis of 9-bromoanthr-10-one with water, or by the careful oxidation of anthracene[43]. In alcoholic hydrochloric acid it is in equilibrium with anthrahydroquinone in the ratio of 3:97 but this ratio does not necessarily hold for anthraquinone derivatives. Coffey[44] reports that the acidification of the alkaline vat of 1,4-dibenzamido-anthraquinone initially gives the anthrahydroquinone which rapidly tautomerises to the corresponding oxanthrone. The latter compound is stable to mild oxidising agents and is only slowly converted, for example by strong alkali, to the normal leuco form. It is easily reduced further to the anthrone. Whereas the anthrahydroquinone is a reducing agent the oxanthrone is in fact an oxidising agent for the anthrahydroquinone and when warmed in pyridine it partially isomerises to the acid-leuco compound. This in turn reacts with a further molecule of the oxanthrone giving, by disproportionation, the original dyestuff and the anthrone.



The stable reduced forms of quinizarin (1,4-dihydroxyanthraquinone) and 1,4-diaminoanthraquinone differ from anthrahydroquinones and resemble oxanthrones. An oxanthrone structure for leuco-quinizarin is not consistent with its chemical properties and a 1,4-diquinone form has been suggested.[45]



Similarly a 1,4-diketoimine structure has been assigned to leuco-1,4-diaminoanthraquinone. Coffey[44] points out that the transfer of hydrogen to the 2,3-positions may be responsible for the frequent elimination of substituents in these positions for compounds such as 1,4-diaminoanthraquinone-2-sulphonic acid during reduction. The stability of compounds such as leuco-1,4 diaminoanthraquinone may be due to hydrogen bonding as follows.



Bradley and Maisey[46] have prepared the anthrones of a number of anthraquinone derivatives by vatting with sodium dithionite and alkali at elevated temperatures. They showed that 1-dimethylamino- and 1-piperidinoanthraquinone gave anthrahydroquinones unaffected by prolonged heating and excess of reducing agent. 1-amino-, 1-hydroxy-, 2-ethylamino-, 2-dimethylamino- and 1,5-diamino-anthraquinone gave relatively stable anthrones. The anthrones of 1-methylamino- and 2-amino-anthraquinone were found to be much less stable. 1,4-diamino-anthraquinone behaved differently in that ammonia was liberated and after aeration quinizarin remained.

It is possible to obtain two anthrones from a mono-substituted derivative of anthraquinone. Coffey[44] records the percentage yields of the forms produced by the reduction in the presence of low quantities of alkali of a number of anthraquinone compounds. Where chelation between the carbonyl group and substituent was possible it was suggested that the carbonyl group removed in the formation of the anthrone was that remote from the substituent. Thus 1-hydroxyanthraquinone gave 70% of the 4-10-isomer and 30% of the 1-10-isomer, whereas 1-chloro-anthraquinone gave only 1-chloroanthr-10-one. However, it would have been expected that as there is little intra-molecular hydrogen bonding in 1-aminoanthraquinone[47] the predominating anthrone from the reduction of this compound would have a 1-10 structure. This in fact was not found to be so and Coffey[44] reported that 85% of the yield was in the form of the 4-10-isomer.

Anthrones cannot normally be oxidised back to the parent quinone but usually produce a derivative of bianthrone . However, Bradley and Maisey[46] have succeeded in regenerating the normal oxidised form for a number of anthrones.

Scope of work.

A spectrophotometric study has been made of the light fading of anaerobic solutions of a number of simple aminoanthraquinone compounds in ethanol and ethyl acetate and in addition for 1-aminoanthraquinone in carbon tetrachloride and n-hexane. The effect of the addition of a small quantity of benzene or water to an ethanolic solution of 1,4-diaminoanthraquinone has been examined.

Two light sources have been used, one a low-pressure mercury-vapour lamp, emitting most of its radiation at a wavelength of 253.7 mu and the other, a high-pressure mercury-vapour lamp, radiating wavelengths in the near ultra-violet and visible region.

The absorption spectra of the solutions have been measured during the fading process and the results compared with those obtained by Egerton and Roach[5,6] in a study of the fading of some of the dyes on polymer films.

Anthrones of the aminoanthraquinone compounds have, where possible, been prepared and their spectra measured in the solvents used in the photochemical work. These spectra have been compared with thoseof the irradiated solutions and also with the faded dyed polymer films of Egerton and Roach[5,6].

EXPERIMENTAL

(A) Dyes.

The following dyes were available: 1-amino-; 2-amino-, 1,4-diamino-, 1,5-diamino-, 1,4,5-triamino, 1,4,5,8-tetramino-anthraquinone. These compounds had been purified by several recrystallisations from ethanol and had been used in a study of the action of light on dyed polymer films by Egerton and Roach[5,6]. Details of the physical properties of these compounds are given in reference 5. A commercial sample (supplied by I.C.I.Ltd.) of 2,7-diaminoanthrquinone was also recrystallised five times from ethanol, and the purified sample had a melting point of 336-7°C. The value recorded in the literature is given as above 330°C.[48]

When the purified dye samples were chromatographed by spotting paper with solutions of the dyes in acetone, drying and developing with petroleum ether saturated with methanol[49] no band separations were observed.

(B) Preparation of anthrones.

4-aminoanthr-10-one, 2-aminoanthr-10-one and 1,5-diaminoanthr-10-one were prepared and recrystallised by the methods of Bradley and Maisey[46]. It was found that these compounds could also be made by warming 1 part of quinone with 25 parts of ethanol and adding a boiling solution of 4 parts of sodium dithionite and 1 part of sodium hydroxide in 75 parts of water. It was then necessary to boil the mixture for several minutes and to precipitate the reduced product with cold water or by cooling. A reduced form of 2,7-diaminoanthraquinone was made in this

manner. By analogy with Bradley and Maisey[46] this should be 2,7-diaminoanthr-10-one. The original deep red solution became a deep yellow orange on boiling for three minutes and a yellow crystalline precipitate was formed. It was moderately soluble in water and gave a yellow-green fluorescent solution. It was freely soluble in ethanol in which it exhibited a marked blue fluorescence, it was also freely soluble in ethyl acetate but not fluorescent. It melted at 198-200°C.

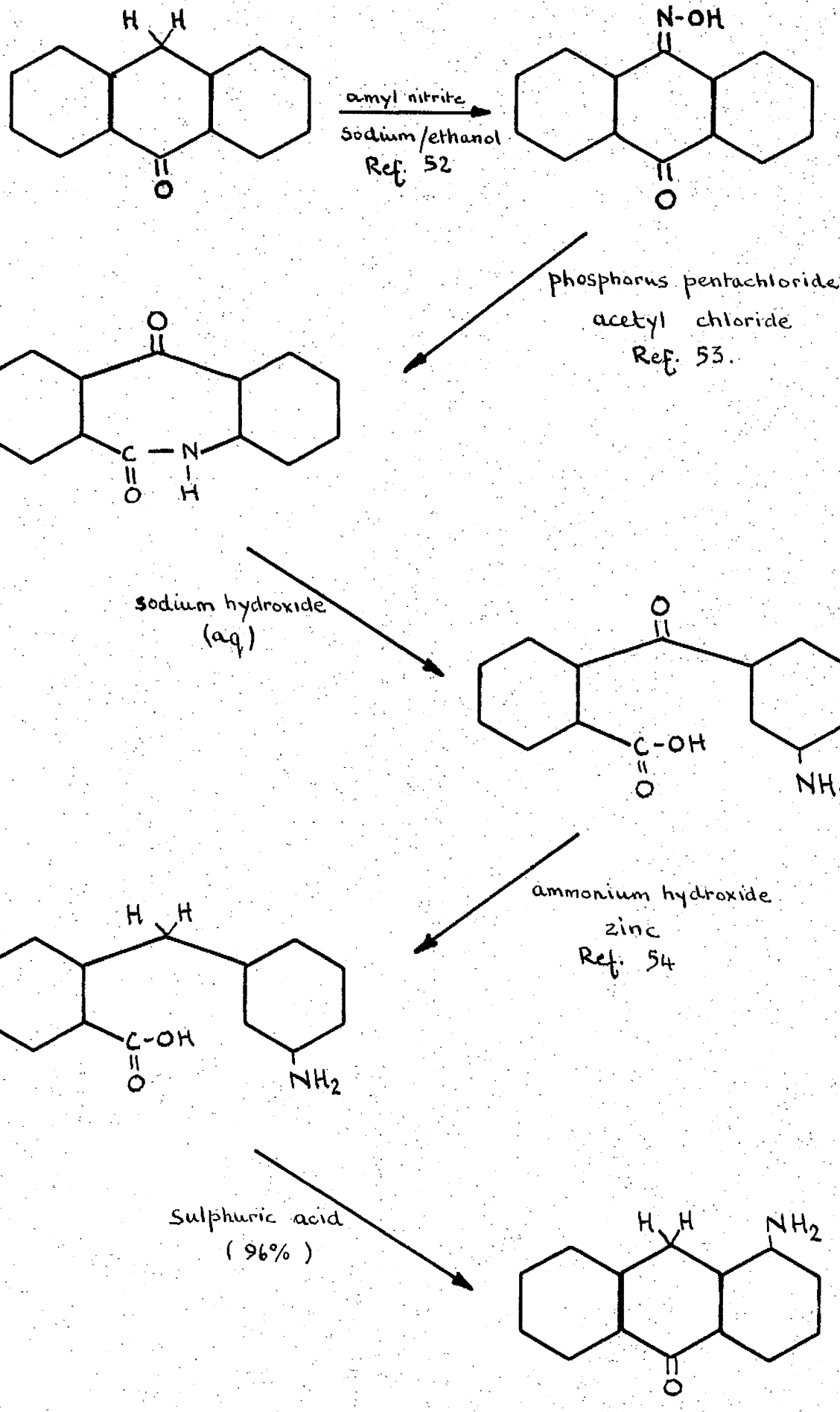
Bradley and Maisey[46] recorded that 2-aminoanthr-10-one was too unstable for satisfactory analysis. The product obtained in the present work was found to be fairly stable in air, no change being detected either visually or spectrophotometrically after storing a sample in an open Petri dish for a fortnight. It was difficult to determine the melting point since at about 190°C the colour of the sample changed. The compound seemed to be affected so that melting did not take place till about 300°C depending on the rate of heating. If, however, the melting point tube was placed in a preheated block at a temperature of greater than 210-212°C rapid melting took place. Maki[50] recorded that this compound melts with decomposition at 295°C which is comparable with the first value obtained. During trial preparations of this compound a buff precipitate was obtained on one occasion that was stable and melted at 179-181°C. Recrystallisation from 50% aqueous acetone did not alter this value. Later attempts to reproduce the conditions under which this compound was obtained were unsuccessful. It was thought that it might be 3-aminoanthr-1o-one.

Both this substance and 2-aminoanthr-10-one exhibited a marked blue fluorescence in ethanol and none in ethyl acetate. Both were extremely soluble in these solvents and slightly soluble in water.

Several unsuccessful attempts were made to prepare leuco-1,4-diaminoanthraquinone. The general method of reduction with sodium dithionite and low quantities of alkali resulted only in the elimination of the amino groups and the formation of leuco-quinizarin. The same end product was obtained by reduction with tin and hydrochloric acid in boiling glacial acetic acid. A mixture of leuco-quinizarin and what was presumed to be leuco-1,4-diaminoanthraquinone was obtained by heating 20g quinizarin, 185 ml 18% ammonium hydroxide and 21.5g sodium dithionite for five hours at 90°C in an autoclave under 4 atmospheres pressure[51].

It was possible to follow the course of the reduction of 1,4-diaminoanthraquinone in ethanol by sodium dithionite spectrophotometrically. It was observed that two intermediate forms existed before leuco-quinizarin was formed. This was thought to be due to the formation of leuco-1,4-diaminoanthraquinone followed by the elimination of an amino group to give leuco-1-amino-4-hydroxy-anthraquinone.

Two methods were used to try and obtain a sample of 1-aminoanthr-10-one, neither of which was successful. The first method is detailed in the following reaction scheme.


amyl nitrite
Sodium/ethanol
Ref. 52
phosphorus pentachloride
acetyl chloride
Ref. 53.
Sodium hydroxide
(aq)
ammonium hydroxide
zinc
Ref. 54
Sulphuric acid
(96%)

Flett[68] reports that 4-aminoanthr-10-one may be isolated from the filtrates of the preparation of 4-aminoanthr-10-one by the method of Bradley and Maisey[46]. "It originally passes the filter in solution as the aminoanthranol, but separated on cooling and aerating as the anthrone. After crystallisation from chlorobenzene with charcoal it gave creamy white needles of melting point 172°C." Attempts to produce this isomer by this method met with no success.

It was also not found possible to prepare a stable sample of the oxanthrone form of either 1-amino- or 1,5-diamino-anthraquinone. An alkaline leuco was prepared in the normal way for each and then acidified with either hydrochloric acid or acetic acid. The resulting precipitates were rapidly converted to the original oxidised form of the compounds. Attempts to prepare the oxanthrone form of 1,4-dibenzamidoanthraquinone described by Coffey[44] also failed. In all cases acidification of the alkaline leuco resulted in rapid formation of the original oxidised form of the quinone.

(C) Solvents.

(i) Ethanol.

All ethanol used was refluxed over caustic soda (25g/litre) for at least six hours and then fractionally distilled through an all glass Dufton column of effective length 30cm, bore 2cm, lagged with two layers of $\frac{1}{8}$ in diameter asbestos rope. The first and last quarters of the distillate were rejected. The middle fraction was further distilled using an all glass Hempel column of effective length 50cm, bore 2.5cm, lagged with two layers of asbestos rope and packed with

¼in glass Raschig rings. The fraction having an optical density of less than 0.1 at 261 mμ for a 1 cm light path, measured against water, was collected. Prior to purification the ethanol contained, in addition to oxidation products, benzene which was detected by observing the characteristic absorption bands at 255 mμ and 261 mμ using 4 cm quartz cells. After the above treatment the residual benzene concentration was of the order of 1 in 20,000 at the most, which, while low enough for most purposes, was not suitable for photochemical work.

For spectroscopic and photochemical work the distilled ethanol was treated as follows - water was removed by treatment with freshly prepared aluminium amalgam[55] over a period of one week, the amalgam being changed every two days. The ethanol was decanted off and distilled via the 50 cm Hempel column, the rate of distillation being adjusted to give a flow of approximately 60 ml per hour. Due to the large amount of distillate required the distillation was permitted to run overnight and collection commenced early in the morning after some 500 ml had distilled over, the initial charge being in the order of 1500 ml. In this way it was possible to collect about 400 ml of spectroscopically pure solvent. During the distillation a constant check was made on the optical density at 261 mμ. When the value had fallen to less than 0.11 for a 4 cm light path - that is, a maximum benzene impurity of 1 in 70,000 it was considered that the ethanol was sufficiently pure and the distillate was collected in the manner to be later described.

Ground glass apparatus was used with electric heating.

(ii) Ethyl acetate.

Hopkin and Williams "Spectrosol" brand ethyl acetate was used. It was distilled fractionally through a Hempel column of effective length 60 cm, bore 2.5 cm, lagged with two layers of asbestos rope and packed with $\frac{1}{4}$ in glass Raschig rings. The first and last quarters of the distillate were rejected. It was found that by doing so it was possible to obtain solvent of slightly greater ultra-violet transparency than the original material. The distillate was allowed to stand over 8 mesh Drierite (freshly baked at a temperature of 160°C) for 24 hours, decanted and allowed to stand over a fresh charge of Drierite for a further 24 hours. It was again decanted off before a final fractional distillation at a rate of 60 ml per hour. It was possible to collect about 750 ml of pure solvent from 1500 ml of the first distillate. Again a constant check was kept on the ultra-violet absorption during distillation.

(iii) Carbon tetrachloride.

Hopkin and Williams "Spectrosol" grade carbon tetrachloride was treated as for ethyl acetate. Since this solvent boiled unevenly an asbestos jacket was constructed for that part of the distillation flask not surrounded by the heating mantle and this improved the rate of distillation. Again the optical density in the region 265 mu to 340 mu was continually measured during distillation.

(iv) n-Hexane.

"Spectrosol" grade n-hexane (Hopkin and Williams) was treated in

the same manner as ethyl acetate and carbon tetrachloride. During distillation a constant check was made of the infra-red absorption in the region 2.5μ to 25μ (sodium chloride cell, 0.1 mm light path) as well as the ultra-violet absorption in the region 200 mμ to 300 mμ (4 cm fused silica cell).

The absorption spectra of the four solvents are shown in Fig. 1

(v) Storage of solvents.

It was found more convenient, particularly in the case of ethanol, to produce a number of batches of pure solvent which could be stored until required. To this end pyrex glass ampoules were constructed Fig. 2 . After thorough cleaning in the manner to be described B14 ground glass sockets were sealed on to the lead-in tube and side-arm such that there was a length of about 15 cm of tubing between the T piece, or junction, and each ground glass joint. The side-arm was constricted at a point 7 to 8 cm from the junction. Since moisture was liable to condense in the ampoule during the sealing on of the joints the ampoule, before use, was fitted to a vacuum line consisting of a high vacuum pump which could be isolated from a liquid nitrogen trap by a single way vacuum tap and which in turn could be isolated from the ampoule by a two way vacuum tap (one side open to the atmosphere). High pressure rubber tubing, fitted with ground glass joints, connected the three sections together. The vacuum that could be obtained was of the order of 10^{-3} mm of mercury. The ampoule was connected to the vacuum line by way of the side-arm while the lead-in tube was kept closed by means of a B14 ground glass stopper. The vacuum was applied for a period of

Absorption spectra of solvents

Fig. 1

4cm light path measured against distilled water

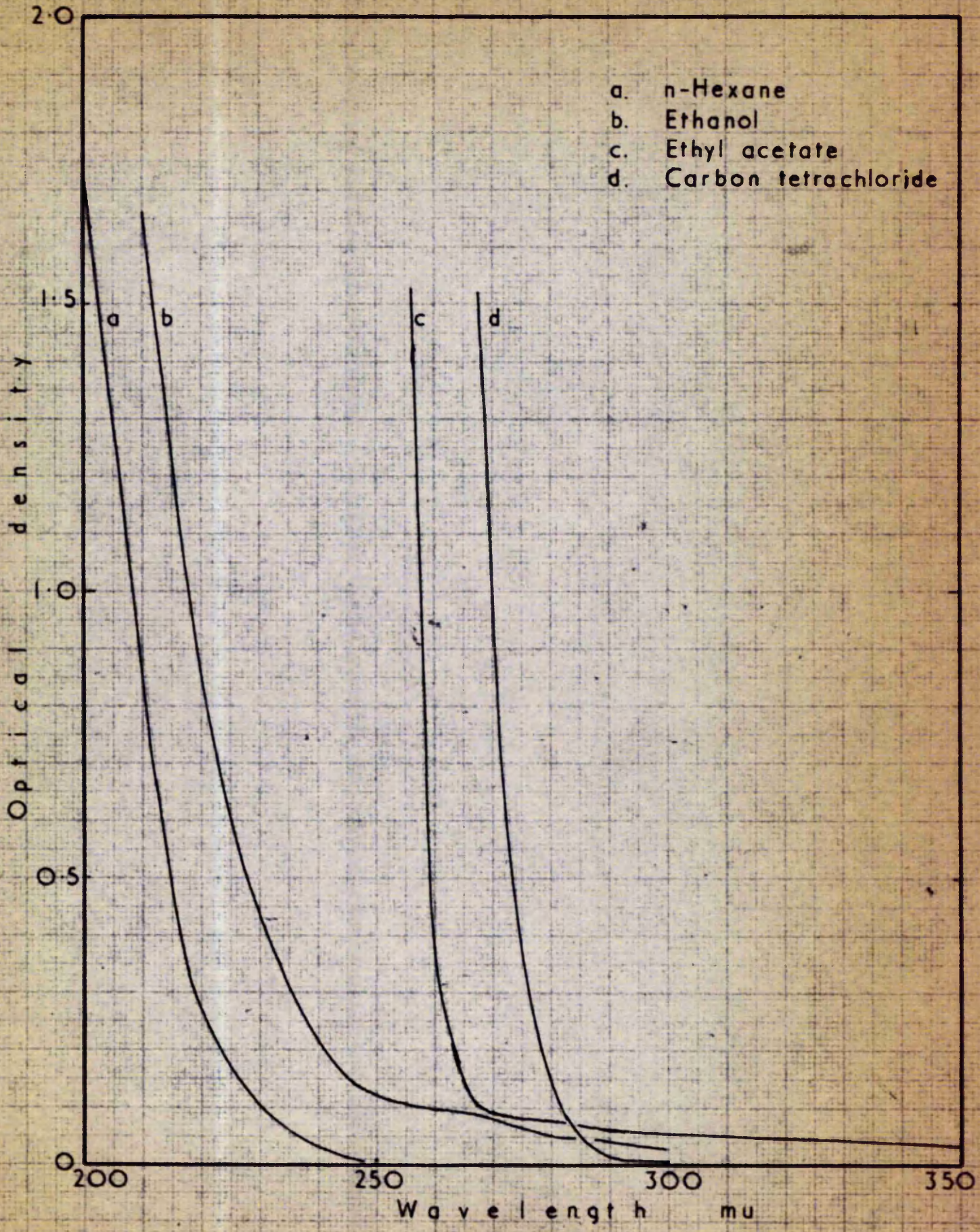
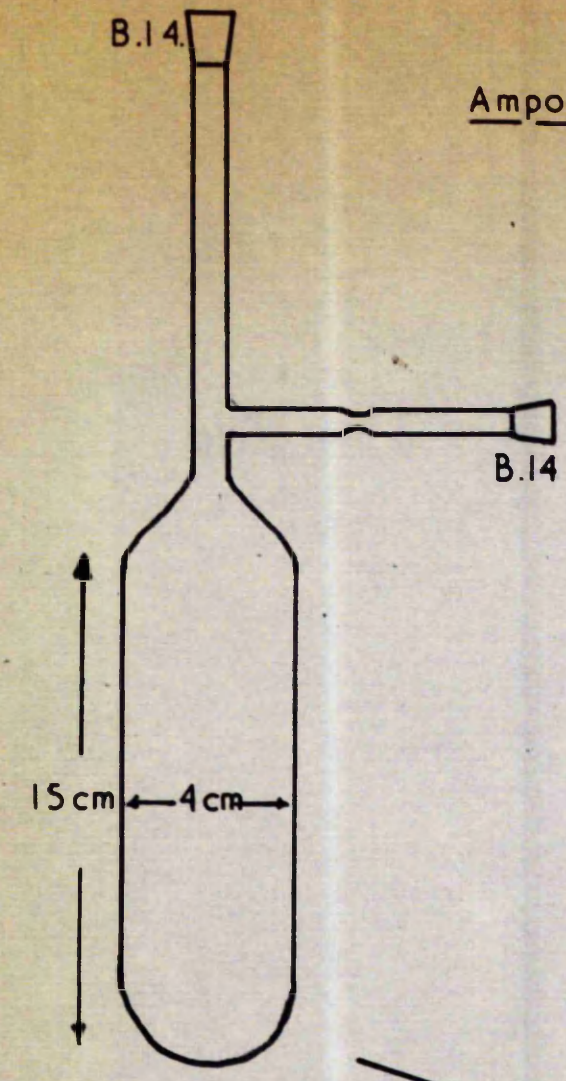


Fig 2

Ampoule for solvents



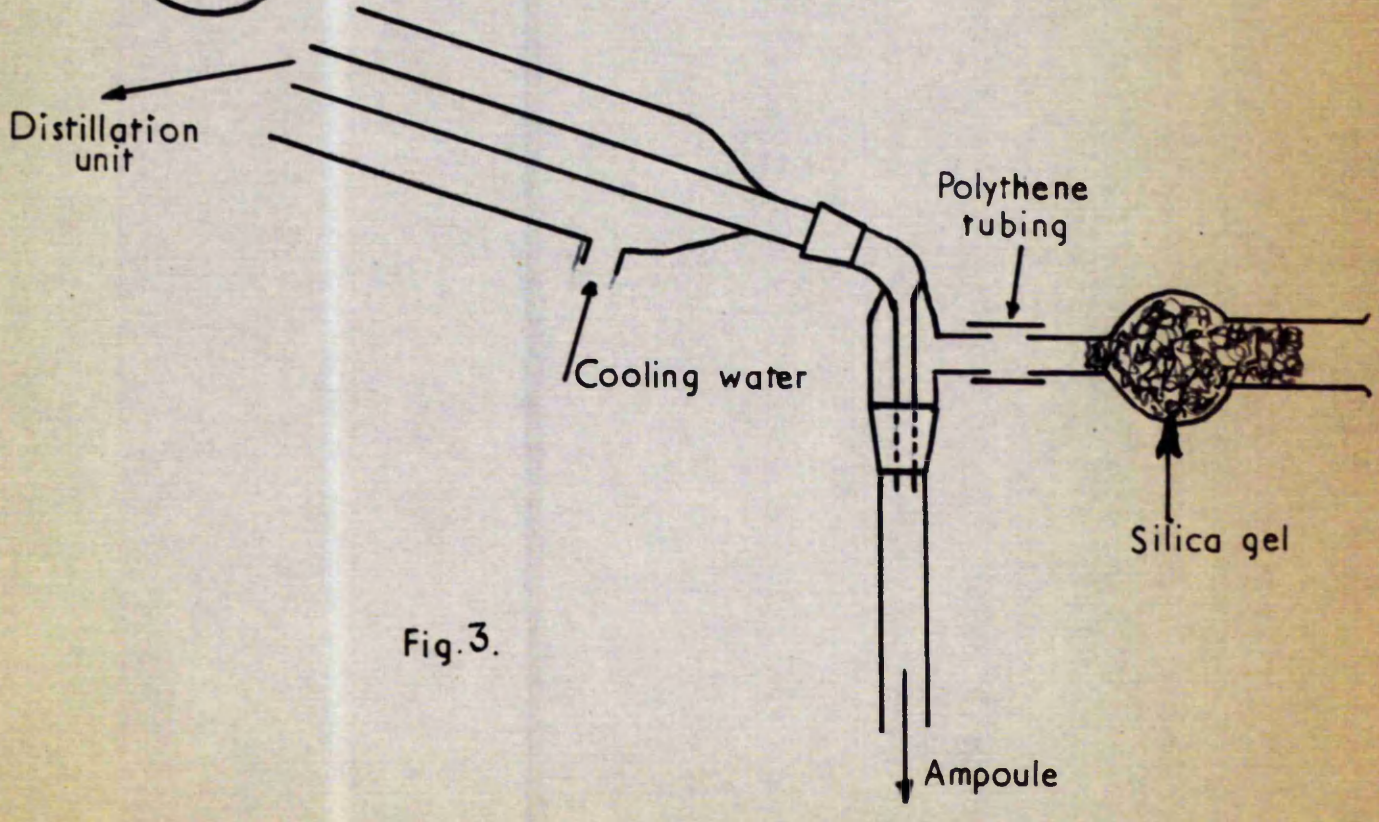


Fig. 3.

30 minutes during which time the ampoule was twice warmed up to a temperature of about 500°C by a gas flame after which it was allowed to cool slowly. The vacuum was broken at the two way tap and the ampoule removed. It shouldbe noted that no grease was allowed to comein contact with the ground glass joints of the ampoule although all other joints were greased with high vacuum silicone grease. When the ampoule was removed from the vacuum line a stopper was immediately placed in the side-arm socket.

When required the ampoule could be fitted directly to the distillation unit by means of the B14 socket on the lead-in tube. Water vapour was prevented from entering the distillation apparatus by a silica gel drying tube, Fig. 3. Sufficient solvent, estimated visually, was allowed to distil over into the ampoule as would be required for each later single experiment. The quantity required was of the order of 75 to 100 ml and the time taken to distil this amount between 1½ and 2 hours.

The ampoule was removed when charged and immediately stoppered. A clean 10 ml measuring cylinder was put in its place to collect the solvent distilling over in order to measure its absorption spectrum. The ampoule was fitted to the vacuum line described above but this time the cone fitting in to the side-arm socket was greased. The solvent and tube were cooled in an acetone and cardice slush bath to a temperature of less than -70°C. The stopper in the lead-in tube was removed and this section of the ampoule sealed off at a point 7 to 10 cm above the junction.

The vacuum was applied for 30 minutes after which time the two-way tap was closed, the ampoule removed from the cooling bath and allowed to warm up for 30 minutes. The cooling bath was replaced and the solvent cooled for 30 minutes. Finally the vacuum was reapplied for some 10 minutes after which the ampoule was sealed off at the constriction. In this way it was possible to obtain up to six ampoules of pure solvent which were stored in the dark in a special box. When the solvent was required for use the side-arm was broken and the solvent poured into the container to be used.

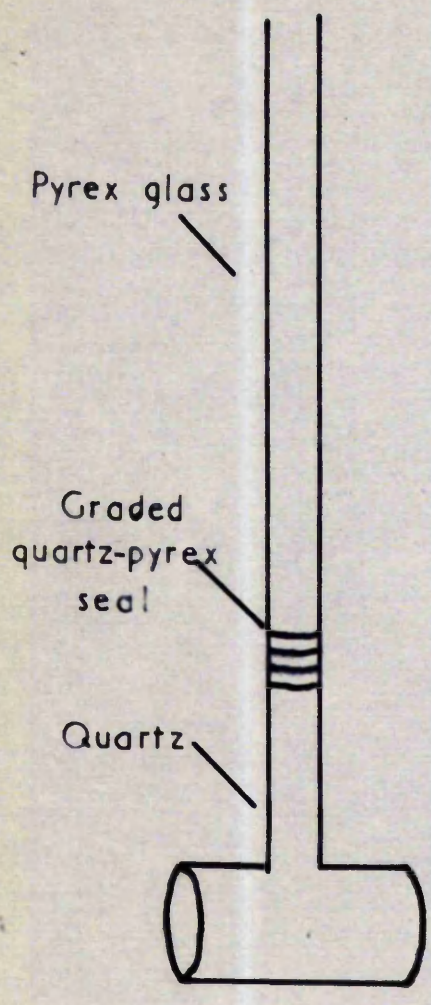
(D) Apparatus.

(i) Absorption and stirring cells.

The absorption cells in which the solutions to be irradiated were contained were made of fused silica and constructed by Thermal Syndicate Ltd., Fig. 4 . They consisted of a cylinder 3 cm long and 1.7 cm diameter (internal measurements) with a short tube of 6 to 8 mm internal diameter attached to the centre of the side of the cylinder. To this was sealed a tube of pyrex, of similar bore, by way of a graded seal. This enabled the cell to be sealed on to other pyrex glass apparatus.

The degassed solutions were prepared in pyrex glass vessels fitted with a vertical reciprocating magnetic stirrer which could be operated under vacuum (Fig. 5). The solutions could be transferred while still under vacuum to the silica absorption cells and sealed off. The stirrer consisted of a thin pyrex glass rod looped at the stirring end while at the upper end was sealed a piece of tubing of the same

Fig.4
Absorption cell



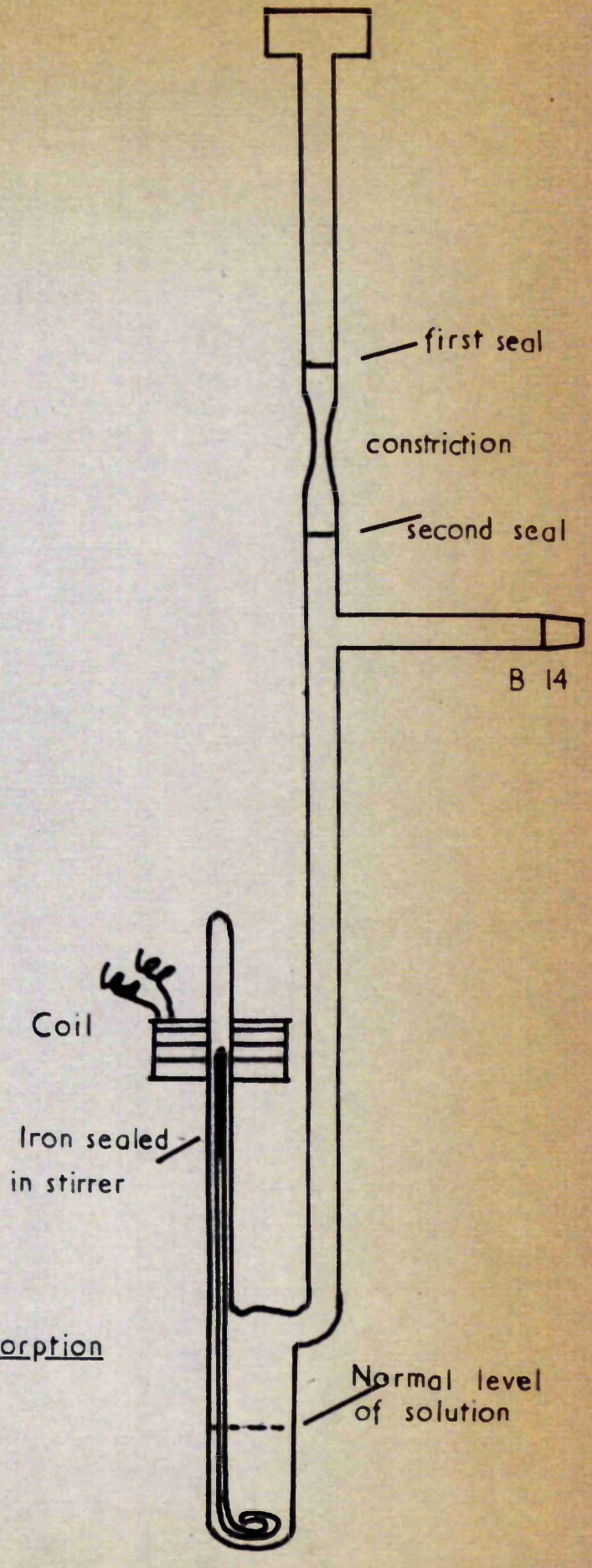


Fig.5

Srirring and absorption cells

diameter containing a rigidly held one inch long, iron rod. The stirring cell could be fitted to the vacuum line by means of a side arm terminating in a B14 ground glass cone. The silica absorption cell was sealed on to the upper end of the stirring cell. To facilitate sealing off under vacuum a short length of glass tubing which had a thick walled constriction in it was sealed on to the stirring cell between it and the absorption cell. The stirring cell and the absorption cell were thus joined by a straight piece of glass tubing in which there was a side arm enabling them to be attached to a vacuum line and also a constriction at a set distance from the absorption cell. It was important that the constriction was not more than 25 cm from the base of the absorption cell as this was the maximum length that the cell box cover fitted to the spectrophotometer could contain.

(ii) Vacuum line.

The vacuum line consisted of an Edwards Speedivac rotary oil pump, type 2S20, fitted with a phosphorus pentoxide trap and capable of giving a backing pressure of at least 10^{-3} mm of mercury, followed by a two stage mercury diffusion pump capable of producing vacua in the order of 10^{-5} mm of mercury. The pressure could be measured on a reduced McLeod gauge fitted into the line between a liquid nitrogen trap and the diffusion pump. The liquid nitrogen trap served a dual purpose by preventing back streaming from the two pumps and in condensing any organic vapours carried over from the cells. A block diagram of the set up is shown in Fig. 6 . The connection between the rotary pump and the diffusion pump was of rubber pressure tubing but thereafter

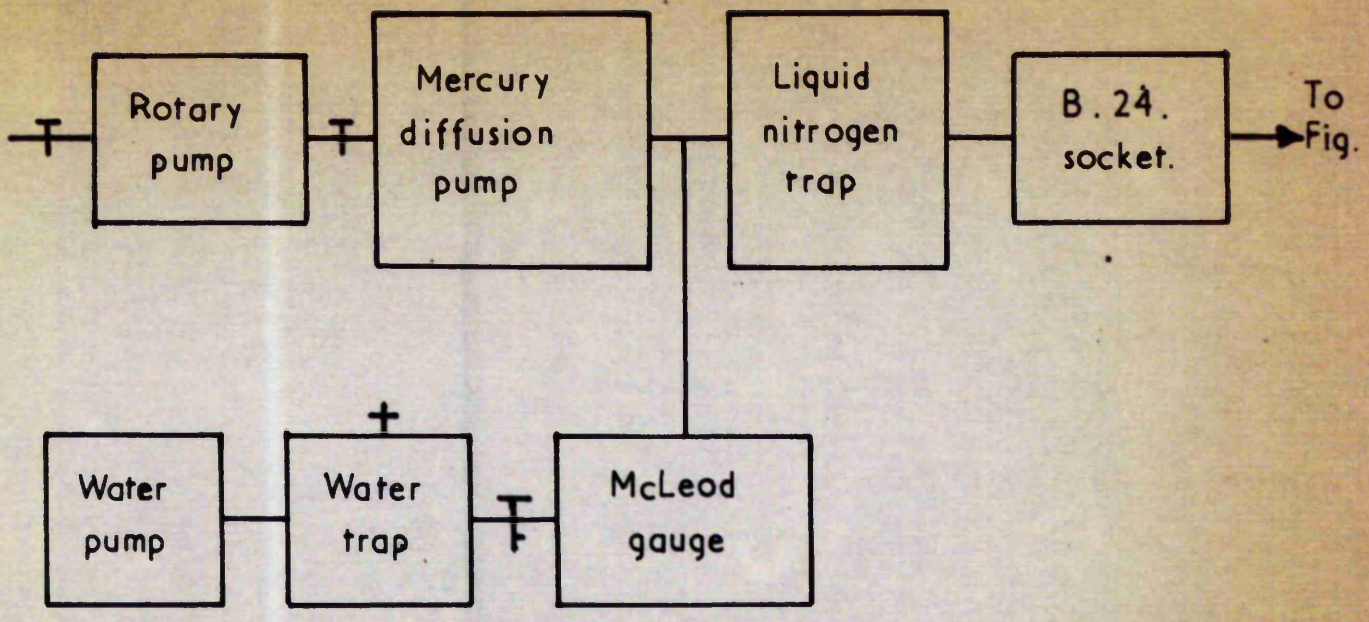


Fig. 6

Vacuum line

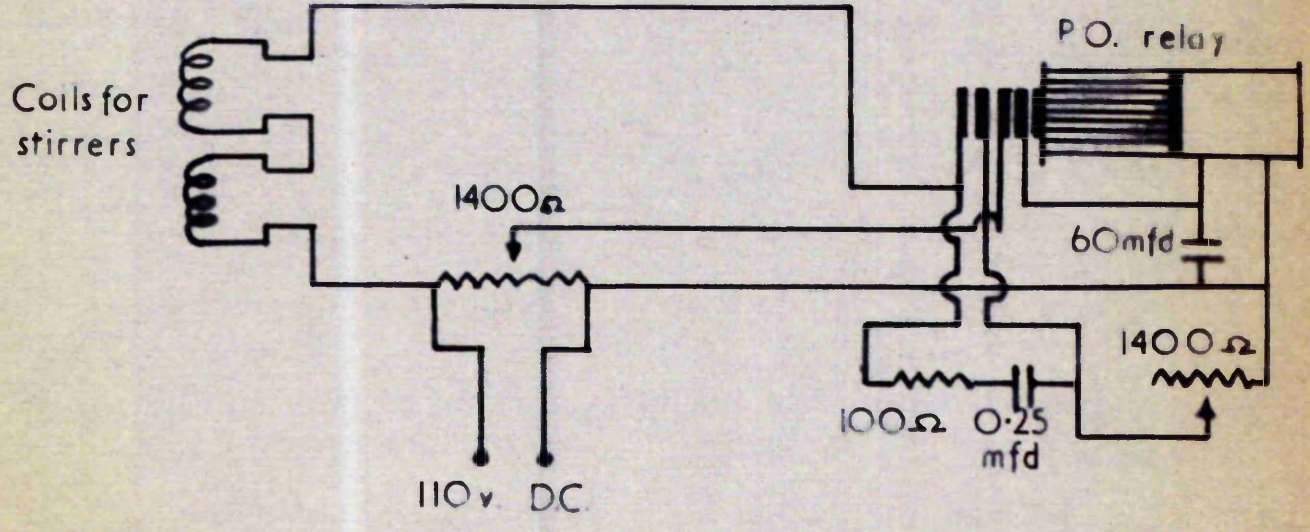


Fig. 7

Circuit diagram for magnetic stirrer

all connections were of glass tubing terminating in ground glass joints greased with Edwards' Silicone High Vacuum grease. After each run it was customary to strip down the apparatus, clean and regrease all joints.

The diffusion pump was heated by a 150 watt Electrothermal heating mantle which was found to give the correct rate of boiling without the need of a voltage regulator.

The reduced McLeod gauge was sealed into the vacuum line between the cold trap and diffusion pump. The mercury column was drawn down between readings by means of an Edwards' metal water pump. A water trap with a vacuum release valve was fitted between the pump and gauge; the connections being of rubber pressure tubing.

The arrangement for connecting the cells to the vacuum line is shown in Fig. 8 . It was possible to degas two solutions simultaneously, the cells being connected by B 14 cones and sockets to individual single way vacuum stopcocks. These in turn were connected by B 14 cones and sockets to the two branch lines which terminated at the common opening of a two way tap. Through this tap it was possible to connect the cells to any atmosphere or to the vacuum line. Again all connections were greased with Edwards' silicone grease.

The magnetic stirrers were operated by external coils through which passed an intermittent direct current. They had been constructed so as to fit closely on to the stirring cells and consisted of approximately 2,500 turns of 35 s.w.g. enamelled copper wire. The intermittent current was supplied by a Post Office relay which was comparatively slow in operation. The circuit diagram is given in Fig. 7 .

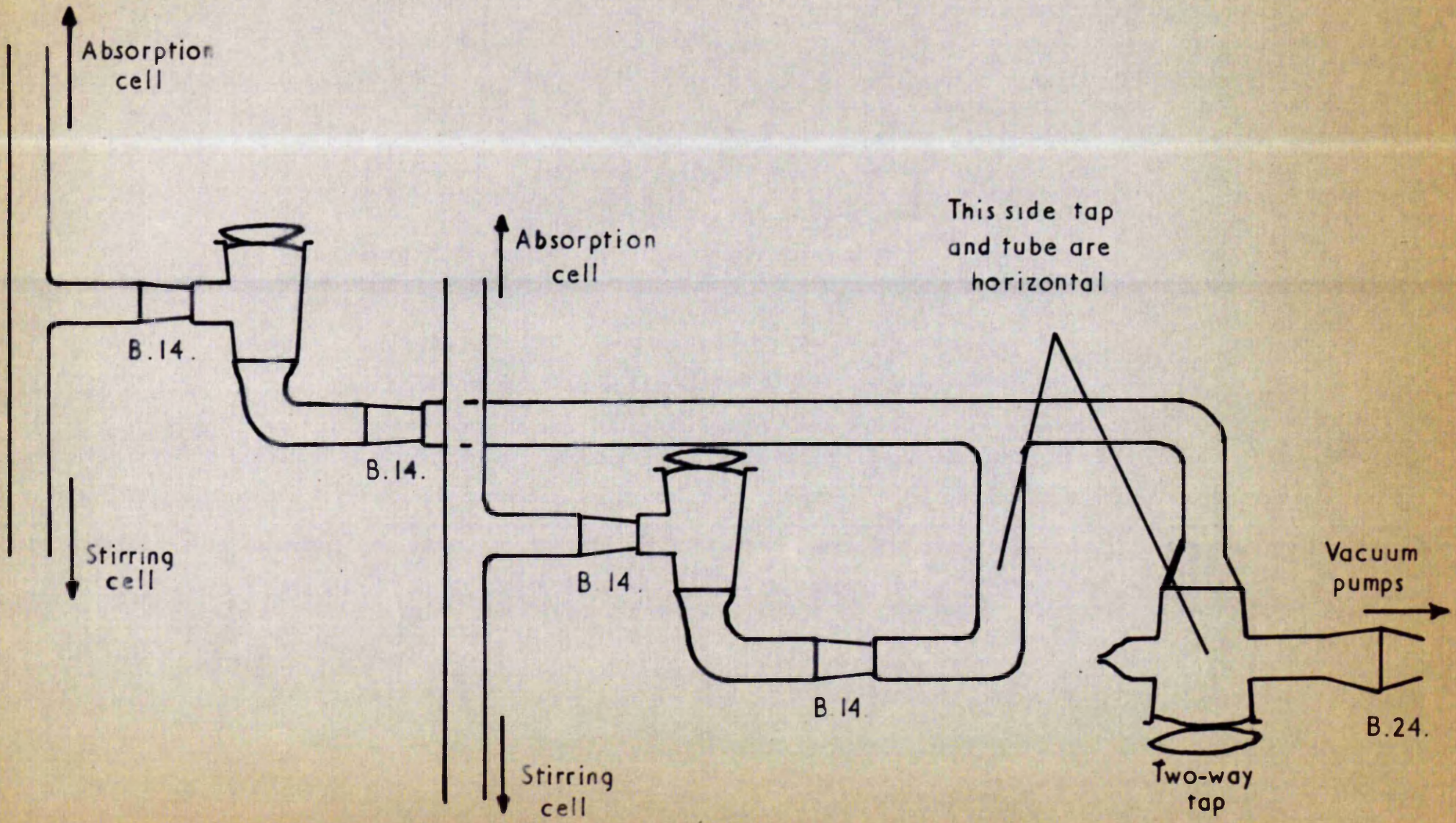

Absorption cell
B.14.
Absorption cell
This side tap and tube are horizontal
B.14.
Stirring cell
B.14.
Vacuum pumps
B.14.
B.24.
Stirring cell
Two-way tap

Fig. 8

The two variable resistors in the circuit enabled the rate of stirring and the amplitude to be partially regulated. The current passing through the coils was of the order of $\frac{1}{4}$ amp and this caused the stirrer to be drawn into the coil and when the circuit broke for it to fall under its own weight.

(iii) Cleaning of apparatus.

Apparatus that had come in contact with silicone grease was degreased in petroleum-ether (60-80°) and then scrubbed in hot water containing some Teepol. After this preliminary treatment all glassware and quartz cells were cleaned in the same manner. They were washed successively in hot distilled water, hot ethanol and in boiling distilled water, and then allowed to stand at room temperature in contact with freshly prepared chromic acid for at least four weeks. The acid was changed two weeks prior to the apparatus being required. Finally before use each piece of apparatus was washed in 500 ml of boiling distilled water, twice a day for six days. Between washing treatments apparatus such as stirring cells and quartz cells were filled with boiling water and allowed to stand. Short lengths of glass tubing, ground glass joints and stoppers were kept immersed in beakers of distilled water. It was considered that this procedure would ensure the complete removal of all absorbed dichromate ions. This was important since these ions are known to effect the photochemical oxidation of alcohols in a similar manner to quinones[56].

After the final washing the apparatus was placed in an electric oven on trays covered with chromatography paper. The oven had

previously been washed out with ethanol followed by water and dried out at a temperature of 100°C for 24 hours. Drying of the apparatus took place over two days at a temperature of at least 120°C.

(iv) Preparation of apparatus for use on the vacuum line.

As far as was possible absorption cells were matched in pairs so that any two for a particular "run" were the same. Matching was carried out at the cleaning stage immediately prior to immersion in chromic acid by determining the absorption at the following wavelengths: 200, 210, 220, 225, 230, 235, 240, 245, 250, 275, 300, 350, 400, 500 and 600 mu, measurements being made against an air path with the cells containing distilled water.

Normally all glass blowing was done the day before the apparatus was required. Each item was left in the oven until required. The constrictions were first constructed and sealed on to either the ampoule or stirring cell, followed by the glass joints or quartz cell. Immediately glass blowing was completed for one piece of apparatus the open ends were securely stoppered to prevent the entry of foreign particles. Moisture condensing during sealing on was removed at a later stage.

(v) Operation of vacuum line.

(1) All ground glass joints were greased.

(2) All taps were closed. The water pump turned on and also the cooling water for the diffusion pump.

(3) The two way tap on the McLeod gauge was gradually opened and the air in the line pumped out via the mercury reservoir.

(4) The rotary pump was switched on and when most of the air in the line had been drawn out by the water pump the tap between the rotary and diffusion pumps was slowly opened. The mercury in the McLeod gauge was pulled down as far as possible into the reservoir and vacuum shut off at the two way tap.

(5) Pumping was allowed to continue for a further five minutes at which time a reading was taken on the McLeod gauge of the pressure in the section as far as the main two way tap. Then the mercury was drawn back into the reservoir.

(6) Provided the indicated pressure showed that there were no leaks the main two way tap was opened and evacuation of the line as far as the single way taps was carried out for five minutes. The pressure was read again and, if satisfactory, the Dewar flask containing liquid nitrogen was placed in position.

If a leak in the system was suspected during one of the above sequences an Edwards' Speedivac high frequency tester, Model T2, was used to detect any holes in the glassware. If this failed to indicate anything the vacuum was released in the reverse manner to being applied. The apparatus was stripped down and all joints were regreased and at the same time the performance of the rotary pump was checked by means of and Edwards' Vacuastat. Pin-holes in glassware were temporarily stopped with Picien wax.

(7) With the cold trap in position the stirring cells were

fitted to the line (Fig. 8). The B 14 cones were only very lightly greased so as to avoid blocking the narrow opening. The solution to be degassed was poured into the cell through this opening at a later stage.

(8) The single way taps were opened and evacuation continued for five minutes before measuring the pressure. If unsatisfactory the cells were checked individually and appropriate steps taken to trace and prevent leaks. Removing a cell from the line could be carried out by letting air in at the two way tap.

(9) The cells were gently warmed with a flame to ensure that all traces of moisture were pumped off and the glass degassed as much as possible. This was done extremely carefully and at no time did the glass reach its softening point. The operation was repeated after an interval of 30 minutes.

(10) The solutions to be degassed were prepared next. An ampoule of the required solvent was opened and a few millilitres used to wash out two 25 ml graduated flasks. A 3 cm quartz cell was filled with solvent and the absorption spectrum determined against an air path. This indicated whether the solvent had become contaminated on storage. One of the flasks was half filled with solvent and a few dye crystals added. When a reasonably concentrated solution had been prepared part was transferred to the remaining flask which was then made up to the mark with fresh solvent. After shaking, some of this solution was removed, poured into a clean 3 cm cell and the optical density of the main ultra-violet band of the dye determined, using the first cell

as a solvent blank. Where possible the concentration of the solution was chosen so as to give an optical density of 1.5 to 1.8. For solvents which were opaque in the region of this band another band was selected and the optical density at this wavelength adjusted to give a figure that would normally have provided an ultra-violet band height of the required strength. Where the dye was particularly insoluble, the flask containing the solvent and dye crystals was placed in an electric oven at a temperature of about 50°C to facilitate dissolution of the dye.

(11) The two way tap was closed and air let into the end section of the line. The liquid nitrogen flask was removed and any condensed water pumped over.

(12) The required volume of dye solution was measured out into a measuring cylinder, a stirring cell removed from the line and the solution carefully poured in via the B 14 cone. The volume of solution required if no evaporation took place during evacuation was approximately 7 ml but, in practice, it was necessary to use more than this. For ethanol and ethyl acetate the volume measured out was 8.5 ml and for carbon tetrachloride and n-hexane 10 ml. It was more convenient to over estimate losses as the excess could always be evaporated off before sealing.

(13) The cone was regreased, the cell reconnected to the single way tap and the coil of the magnetic stirrer clamped in position. This was repeated for the second cell and the single way taps closed. The two way tap was opened and the line evacuated as far as the single way taps.

(14) The liquid nitrogen flask was refitted and slush baths of acetone

and cardice positioned so as to cool the contents of the stirring cells. It was found that evaporation of the solvent from these cells could be more easily controlled if some liquid nitrogen was added to the slush bath to lower the temperature to about -90°C.

(15) The heater of the diffusion pump was switched on.

(16) A period of one hour was allowed to elapse before the single way taps to the cells were slowly opened to permit degassing of the solutions. The stirrers were switched on ten minutes later and the cells evacuated for one hour.

(17) The single way taps were closed, the slush baths removed and the cells and contents allowed to warm up to room temperature over a period of one hour during which time the cell contents were kept in the dark by means of cloth covers fitted over the cells.

(18) The cooling baths were replaced and after 45 minutes the single way taps were opened and pumping continued for 45 minutes.

(19) The previous two steps were repeated twice, the warm up time was, however, cut to 45 minutes.

(20) During evacuation a constant check was maintained on the pressure in the system, and stirring was continued.

(21) At this stage it was considered that the solutions were sufficiently degassed for all practical purposes and could be transferred to the quartz cells.

(22) With the two single way taps shut the two way tap was opened to let air into the line between it and the single way taps. The stirring coils were switched off and removed from the cells.

The stirring cell and its single way tap were removed from the line and the cell carefully inverted thus transferring the solution to the quartz cell. The B 14 cone on the single way tap was regreased and the complete unit reconnected to the vacuum line. The process was repeated for the other cell and from then on each cell was treated separately.

(23) The two way tap was opened to permit evacuation as far as the single way taps, the slush baths fitted round the quartz cells and the solutions allowed to cool for 45 minutes.

(24) One of the single way taps was opened and the cell evacuated for 15 minutes at the end of which time the pressure in the system was measured.

(25) The cell and its contents were sealed off at the constriction by means of an oxygen-gas burner.

(26) The process was repeated for the remaining cell.

The seal-off pressure as measured by the McLeod gauge was normally 1 to 3 x 10^{-4} mm of mercury.

The cells were stored in the dark until required.

(E) Measurement of absorption spectra.

Absorption spectra were measured on a Unicam SP 500 quartz spectrophotometer, usually at wavelengths between 200 and 800 mμ.

A specially constructed holder was used with the 3 cm quartz cells, two of which could be accommodated in the holder (Fig.9). The cells were always placed the same way round and in the same wooden rest. Since the external dimensions of the cells were not uniform a

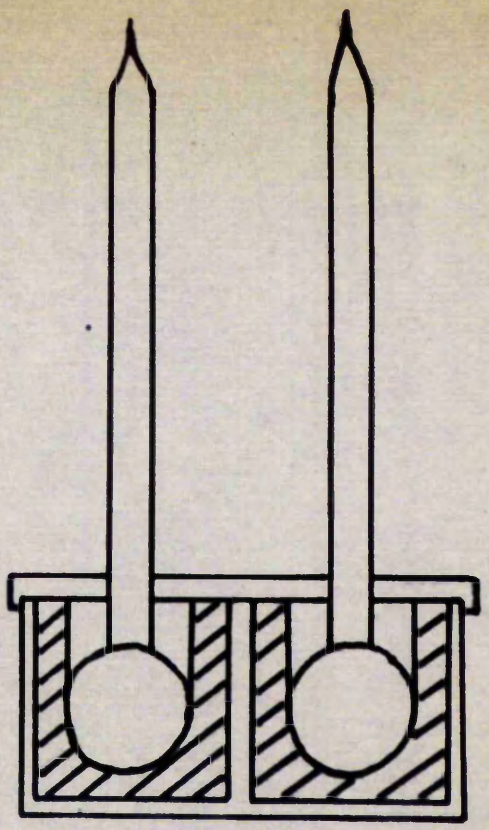


Fig. 9.

Cell holder for
spectrophotometer.

number of these wooden supports were constructed to enable the cells to be supported without undue strain.

To accommodate the long stems on the cells a special light proof lid to the cell box was used instead of the standard fitting.

In all experiments measurements were made against a standard cell containing solvent sealed off in the same manner as the dye solutions. A frequent check was made on the spectra of the solvent standards to see that they did not deteriorate with time.

The accuracy of the wavelength dial of the instrument was checked eadh week by the method recommended by the makers.

(F) Irradiation technique.

(i) Light sources.

A "Vitan" quartz mercury-vapour lamp manufactured by Thermal Syndicate Ltd. was used to provide ultra-violet radiation. This low pressure discharge lamp emits over 96% of the total radiation at a wavelength of 253.7 mμ. Other weak lines occur at 313.2 mμ, 365 mμ, 404.7 mμ, 435.8 mμ and 578 mμ. The arc tube is U shaped, at each end there being tubular electrodes. A small amount of mercury is contained in the tube and the lamp is filled with neon to a pressure sufficient to permit a luminous discharge. A specially designed transformer is required to operate the lamp. It supplies a sufficiently high voltage to ionise the neon which warms the tube enabling the mercury to vaporize. When sufficient mercury has vaporized it is preferantially ionised and the mercury discharge is thus maintained throughout the greater part of the arc. The neon discharge is visible only round the electrodes.

The lamp was set up in a vertical position with the electrodes at the base. It was held in a specially constructed stand which enabled the cells to be quickly set up in their exposure frame at a definite distance from the lamp. The lamp was switched on 30 minutes before solutions were irradiated.

A 400 watt Osram high-pressure mercury-vapour lamp manufactured by G.E.C.Ltd. (type MA/v soft) was used to provide visible radiation. The spectral distribution of this lamp has been determined by Barnes and Forsythe[57]. The most intense wavelengths emitted are at 577 to 579.1 mu , 546.1 mu , 435.8 mu , 404.7 mu and 365 to 366.3 mu . It consists of two concentric glass tubes with the space between evacuated, thus maintaining operational conditions by minimising heat losses from the discharge and variations in temperature. The inner envelope is of special refractory glass which absorbs almost all radiations below 330 mu . It contains the electrodes and the mercury and is gas filled to give a pressure of one atmosphere at 600°C after five minutes' operation. The outer envelope is of lime-soda glass. This lamp was operated in a vertical position with cap uppermost. In circuit with it was a series connected choke to limit the current and a capacitor to increase the power factor.

The surfaces of both lamps were kept scrupulously clean. The Osram lamp, which ran almost continuously throughout the research work, was cleaned once every three weeks. The Vitan lamp, being used only intermittently, was cleaned before use and once a week if used for any length of time.

The Osram lamp was discarded after 6000 operational hours and a new one was given a 500 hour running-in period. Before dye solutions were exposed to this lamp a warm-up period of at least 30 minutes was allowed when starting from the cold. The cleaning process used involved washing the particular lamp in hot soapy water followed by a thorough wash in hot water and a rinse in acetone. Lamps were dried in an electric oven at a temperature of 90°C. Care was taken to see that, after cleaning, the lamps were not touched with a bare hand but held only in a cloth.

(ii) Exposure apparatus.

The arrangement of the cells for exposure to the Osram lamp is shown in Fig. 10 and for the Vitan lamp in Fig. 11 . The cells were supported in a wooden frame (the type depending on the lamp, Figs. 12 & 13) which could be placed near the lamp so that each cell received a similar quantity of light radiation. The cell holders were rigidly fixed in place and the position of the cell in the holder noted so that the cell was always returned to its original position after absorption measurements.

The heat generated by the Osram lamp caused some of the dyes to come out of the solution and to adhere to the quartz stem. To minimise this effect the cells were removed from the holder and shaken twice a day and, on replacing in the holder, the reverse face was exposed to the lamp.

The lamps and cells were surrounded by cabinets consisting of a wooden frame with harboard walls. In the Osram lamp housing two

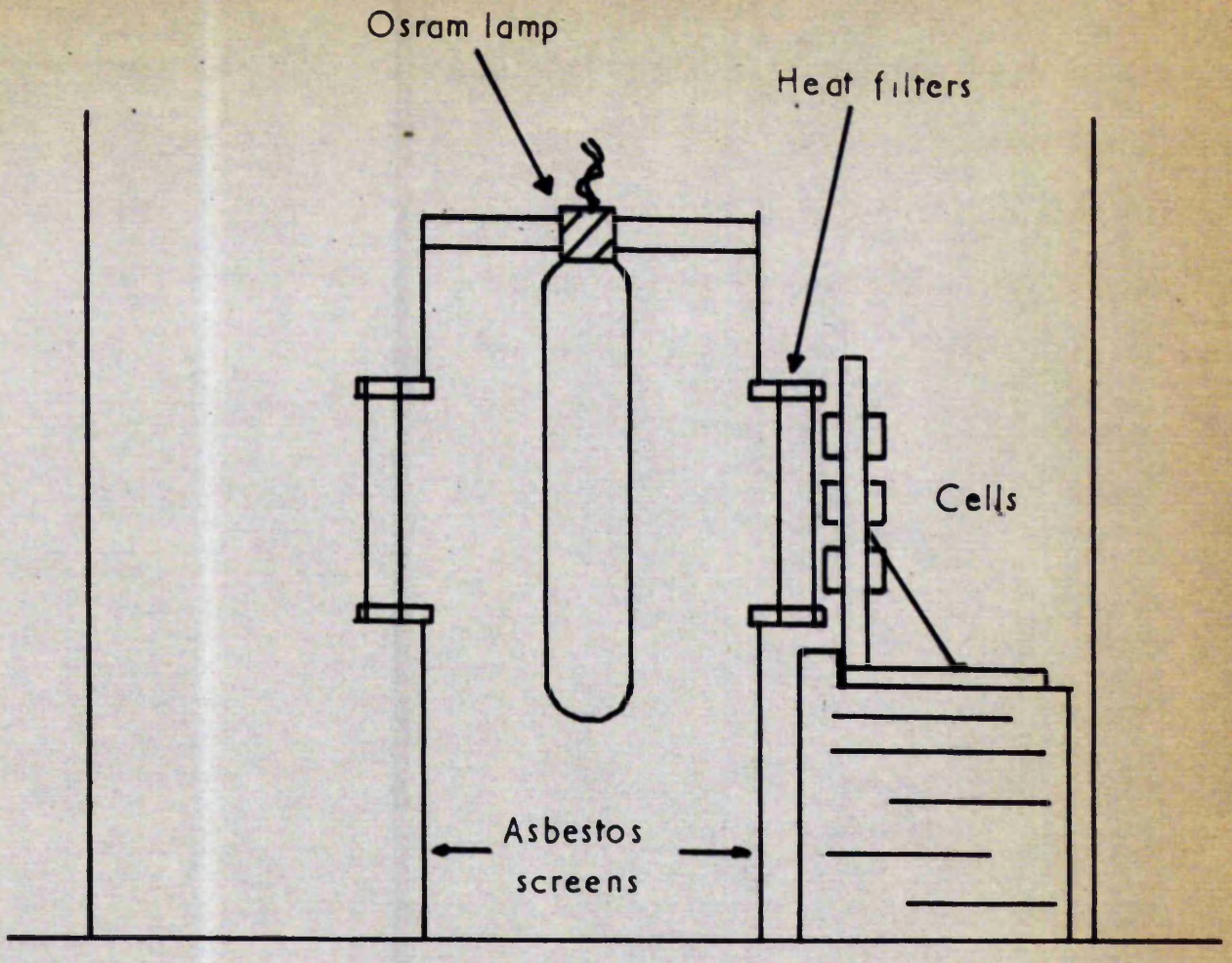


Fig.10

Side view of Osram lamp housing.

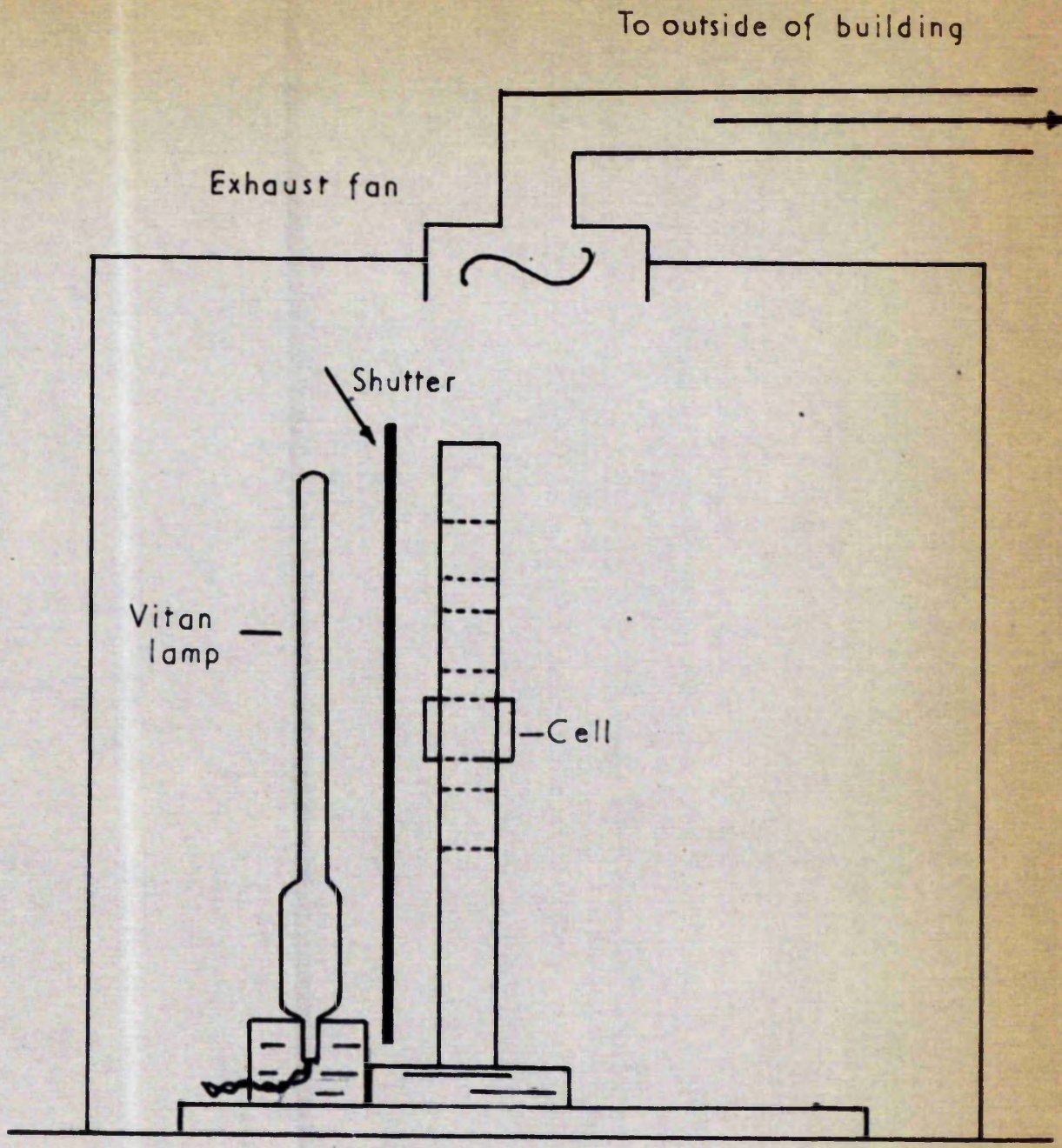


Fig. 11

Side view of Vitan lamp housing.

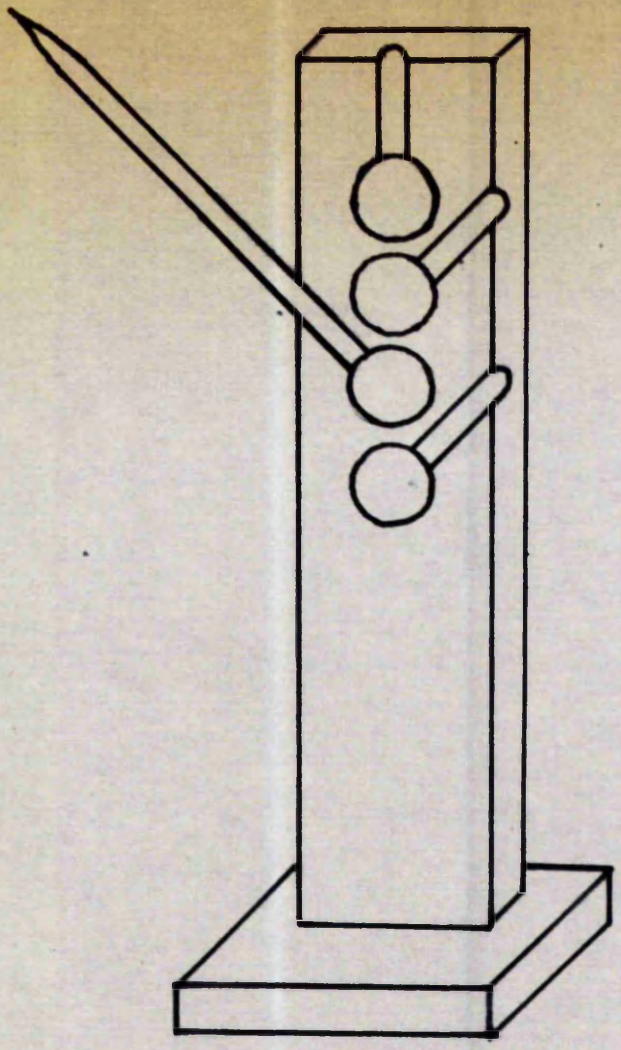


Fig. 12

Cell support for exposures to a Vitan lamp.

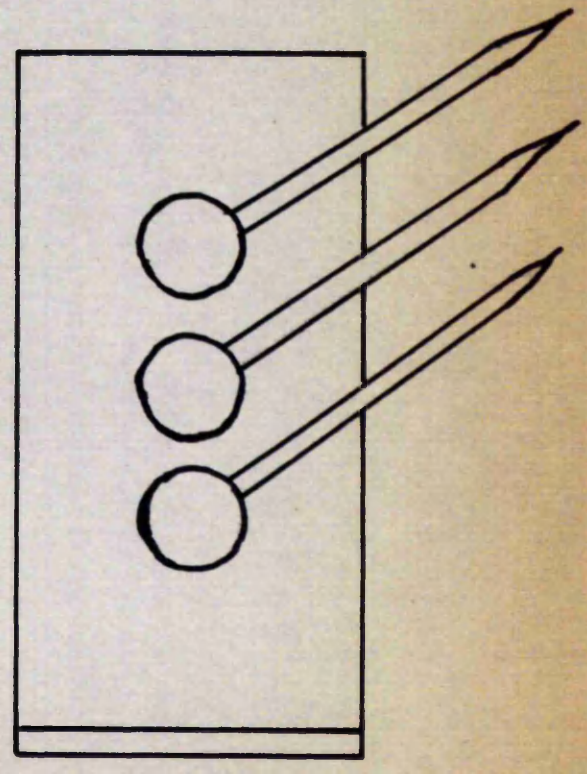


Fig. 13.

Cell support for exposures to an Osram lamp.

asbestos screens were placed, one on either side of the lamp and each having a window cut to the shape of the lamp. Two Chance ON 20 filters were fitted over each opening to cut down the amount of heat reaching the cells. The distance from the centre of the lamp arc to the cell centre was 8 inches and the operating temperature was 35 to 40°C. While it would have been possible to place cells on either side of the lamp, in practice only one side was used. It was possible to expose up to three cells at one time.

The Vitan lamp is of the cold discharge type and heat filters were not used. Since exposure times to this lamp were short a hardboard shutter was constructed that could be quickly slid between the cell and lamp thus reducing the number of times the lamp needed to be switched on and off. The cabinet surrounding the lamp was fitted with a powerful fan which led any ozone produced during exposure to the outside of the building. It would have been possible to irradiate four cells at a time but in fact only one position in the cell holder was used for all the experiments. The distance between the centres of the lamp and the cell was 2 inches and the operating temperature 15 to 20° C.

(iii) Treatment of cells after exposure.

After exposing a cell to an Osram lamp and prior to determining the absorption spectrum the cell was allowed to stand inverted in the dark for up to one day. This ensured that the maximum amount of dye that had come out of solution was redissolved.

The spectra of cells exposed to the Vitan lamp were normally measured within a few hours after irradiation. Before subsequent

exposures the cells were kept in the dark. Where continuous exposure times of greater than five minutes were necessary, the lamp was covered and the cell and contents shaken every five minutes to ensure complete mixing. Cells were also shaken at shorter intervals where the fading was extremely rapid.

Before determining an absorption spectrum all cells were stood in chromic acid for about ten minutes, washed with distilled water and dried with filter paper.

RESULTS AND DISCUSSION

The results have been set out as follows.

(I) Spectrophotometric study of the fading of anaerobic solutions of various aminoathraquinone compounds on exposure to

(a) a low-pressure mercury-vapour lamp (Vitan),

(b) a high-pressure mercury-vapour lamp (Osram).

The order of compounds is 1-mono-; 2-mono-; 1,4-di-; 1,5-di-; 2,7-di-; 1,4,5-tri-; and 1,4,5,8-tetra- aminoanthraquinone. Absorption spectra have been drawn to indicate the changes taking place after various periods of time. These changes have been compared with results obtained by Egerton and Roach[5-6] after exposure of some of these aminoanthraquinone compounds on polymer substrates and in the solid state.

(II) Absorption spectra of anthrones. The relation between the fading products of aminoanthraquinone compounds and the corresponding anthrones is discussed.

(III) General discussion.

PART I

Fading of anaerobic solutions of aminoanthraquinone compounds.

1 - Aminoanthraquinone.

A summary of the positions of the band maxima in the absorption spectra of 1-aminoanthraquinone in the solvents ethanol, ethyl acetate, carbon tetrachloride and n-hexane is given in Tables I and II. The spectra of the unexposed solutions are very similar except that in n-hexane there is an additional peak at 275 mu and also for this solvent and carbon tetrachloride there exists a slight inflection at 327.5 mu.

Included in Tables I and II and similar tables for compounds considered later in this thesis, are details of the positions of the band maxima of the solutions after exposure to the two light sources. The locations of the peaks were determined when the fading products were well defined and not after any definite length of exposure. Since the spectra of the fading products in some cases were found to resemble those of anthrones prepared from the unexposed dyes the wavelengths of the absorption bands for the corresponding anthrone are also recorded in the tables. 1 - Aminoanthraquinone is capable of giving two anthrones, 4 - aminoanthr-10-one and 1 - aminoanthr-10-one. The latter compound could not be prepared and only data for the former is given. Similarities in the positions of the ultra-violet absorption bands for 4 - aminoanthr-10-one in ethanol and the final fading products of 1 - aminoanthraquinone in the same solvent will be noted but it is thought that the complete spectrum of the 1 - 10 - isomer would correspond more closely to that of the fading products as the absorption

SOLUTION ETHANOL	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original	245	270	307.5			477.5	15/20
Exposed to Vitan		262.5			387.5	420	15
Exposed to Vitan stored	245	262.5			387.5		16
Exposed to Osram	245	262.5*			387.5	420	20
Exposed to Osram stored	245	262.5*			387.5	420	21
4-Aminoanthr-10-one	245	260			397.5		52
ETHYL ACETATE							
Original		267.5	305			467.5	17/22
Exposed to Vitan		259			400		17
Exposed to Osram		265			397.5		22
4-Aminoanthr-10-one		260			392.5		52

TABLE I

1-AMINOANTHRAQUINONE

SOLUTION CARBON TETRACHLORIDE	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original				304	327.5*	455	18/23
Exposed to Osram						375*	23
4-aminoanthr-10-one						387.5	52
n-HEXANE							
Original	240	265	275	300	327.5*	451	19/24
Exposed to Vitan	227.5*	262.5*				392.5	19
Exposed to Osram	232.5	260				390	24
4-aminoanthr-10-one	237.5	255				382.5	52
N-METHOXYMETHYLNYLON							
Original			275	312		482	Ref. 5,6
Exposed to Osram in N_2			272.5		392.5	430	

TABLE II

1-AMINOANTHRAQUINONE.

band in the region of 390 mu would most likely be at a shorter wavelength than for the 4-10-isomer.

The spectra of some exposed solutions have been found to undergo changes on prolonged storage of the solution in the dark. Where this has occurred the positions of the new maxima are also given in the tables.

In all cases a reference is given to the figure number of the solution concerned.

Observations on the changes in spectra during the light fading of aminoanthraquinone compounds on films of N-methoxymethyl nylon have been made by Egerton and Roach[5,6]. In some instances the changes in solution have followed similar courses. Where this has occurred the positions of the absorption maxima of the dyed polymer film before and after exposure have been given in the tables.

Fading by Vitan lamp.

Considerable changes were observed for each of the four solutions after irradiation. With the exception of the carbon tetrachloride solution (Fig.18) a new, well defined absorbing system was produced. With all four solutions (Figs.15,17, 18, 19) the absorption in the originally non-absorbing region of approximately 300 to 400 mu was increased while that at the initial visible band wavelength decreased.

The rate at which the initial visible band was degraded depended on the solvent. The estimation of the fading rate of all the compounds considered has been based on the percentage change in optical

density of their original visible absorption bands with time, on the assumption that Beer's law was obeyed at all times, and that the photoproducts were non-absorbing at the wavelength considered. The amount of fading has been calculated as :

$$\frac{\text{optical density of the original visible absorption band after exposure}}{\text{optical density of the same band before exposure}} \times 100\%$$

and this has been plotted against time of exposure. The time taken to produce a 50% loss in intensity of the initial visible absorption band for solutions of 1 - aminoanthraquinone of similar concentration exposed to the Vitan lamp was about 2.25 minutes for the ethyl acetate solution, 2.75 minutes for the carbon tetrachloride solution, 7.5 minutes for the ethanol solution and 25 minutes for the n-hexane solution (Fig. 14).

It is of interest to note that the fading occurs faster in solvents that absorb strongly the main radiation emitted by this lamp, viz 253.7 mu. In a hydrogen atom transfer reaction initiated by light involving dyes and organic solvents the dye is said to act as a sensitiser of the oxidation of the solvent. Where the solvent is the primary absorber of the radiation, as in the case of solutions of ethyl acetate and carbon tetrachloride, a photosensitised reaction can only occur by excitation of the dye molecules at the front face of the cell and the rate at which all the dye can enter into the reaction will depend on the rate of diffusion of excited dye molecules through the solvent. Such a reaction is likely to be slower than one where the

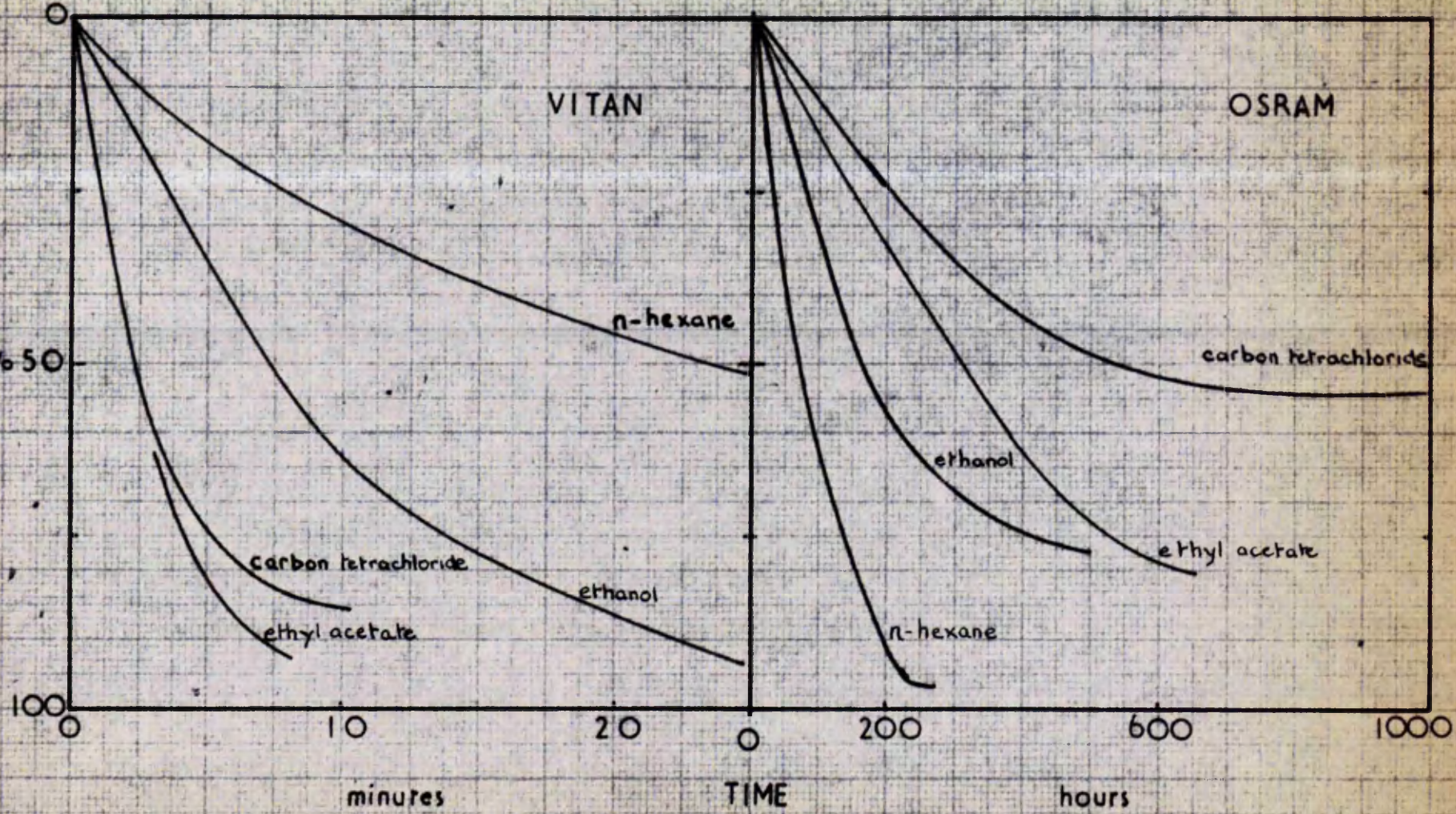
solvent is completely transparent to the radiation and excited dye molecules are formed throughout. The other possible reactions causing fading of the dye may involve photolysis of the solvent or an energy transfer from the solvent to the dye which then can react with the solvent. The latter reaction is again likely to be relatively slow. The fading of the dye in carbon tetrachloride cannot take place by hydrogen atom abstraction from the solvent and it seems likely that with far ultra-violet radiation fading may occur by reaction of the dye with radicals formed by photolysis of the solvent. The similarity of the fading rate of an ethyl acetate solution to a carbon tetrachloride solution may mean that the mechanism is similar and the different photoproducts are due only to the different nature of the radicals produced from the solvents.

The main spectral changes observed during the fading of the ethanol solution (Fig. 15) were a loss of absorption at 477.5 mu, and an increase in absorption resulting in the formation of a new band maximum at 387.5 mu. The peak at 307.5 mu was gradually eliminated but with little loss of absorbance in that region. The band at 270 mu increased in intensity and moved hypsochromically to 262.5 mu before finally merging with the band originally at 245 mu, which, on irradiation had decreased slightly in intensity but had moved bathochromically to a position at 262.5 mu. After irradiation for ten minutes most of the original spectral character had been destroyed and the new absorption band at 387.5 mu was of the same intensity as the peak formerly at 477.5 mu. An isobestic point existed at 440 mu.

A peculiar effect was noted after the solution had been exposed for a total time of 20 minutes followed by storage in the dark for two months. Although remeasurement of the spectrum revealed no changes, further irradiation for five minutes produced a complete change in the ultra-violet absorbing system with the formation of twin peaks at 245 and 262.5 mu (Fig. 16). The absorbance at 387.5 mu was slightly decreased but no other changes were detected. Further prolonged storage in the dark caused no more changes but another five minutes irradiation intensified slightly the peak at 245 mu and weakened that at 267.5 mu. The absorption spectrum in the ultra-violet at this stage resembled closely that after five minutes total irradiation (Fig. 15). Prolonged storage in the dark resulted in no further changes and it was concluded that the changes in the spectrum were light induced rather than the result of tautomerism of the photoproduct or a reaction between photoproducts.

In ethyl acetate solution absorption by the solvent precluded measurements below 260 mu, but above this value the results obtained after irradiation (Fig. 17) were generally similar to those obtained with ethanol solutions.

It was not possible to record the changes in spectra occurring in carbon tetrachloride below 265 mu (Fig. 18). The band at 304 mu lost all character but, unlike the previous two solutions, there was no corresponding decrease in absorption in that region. Absorption either side of 305 mu increased while that at wavelengths greater than 400 mu, where there was an isobestic point, decreased. No



I-AMINOANTHRAQUINONE

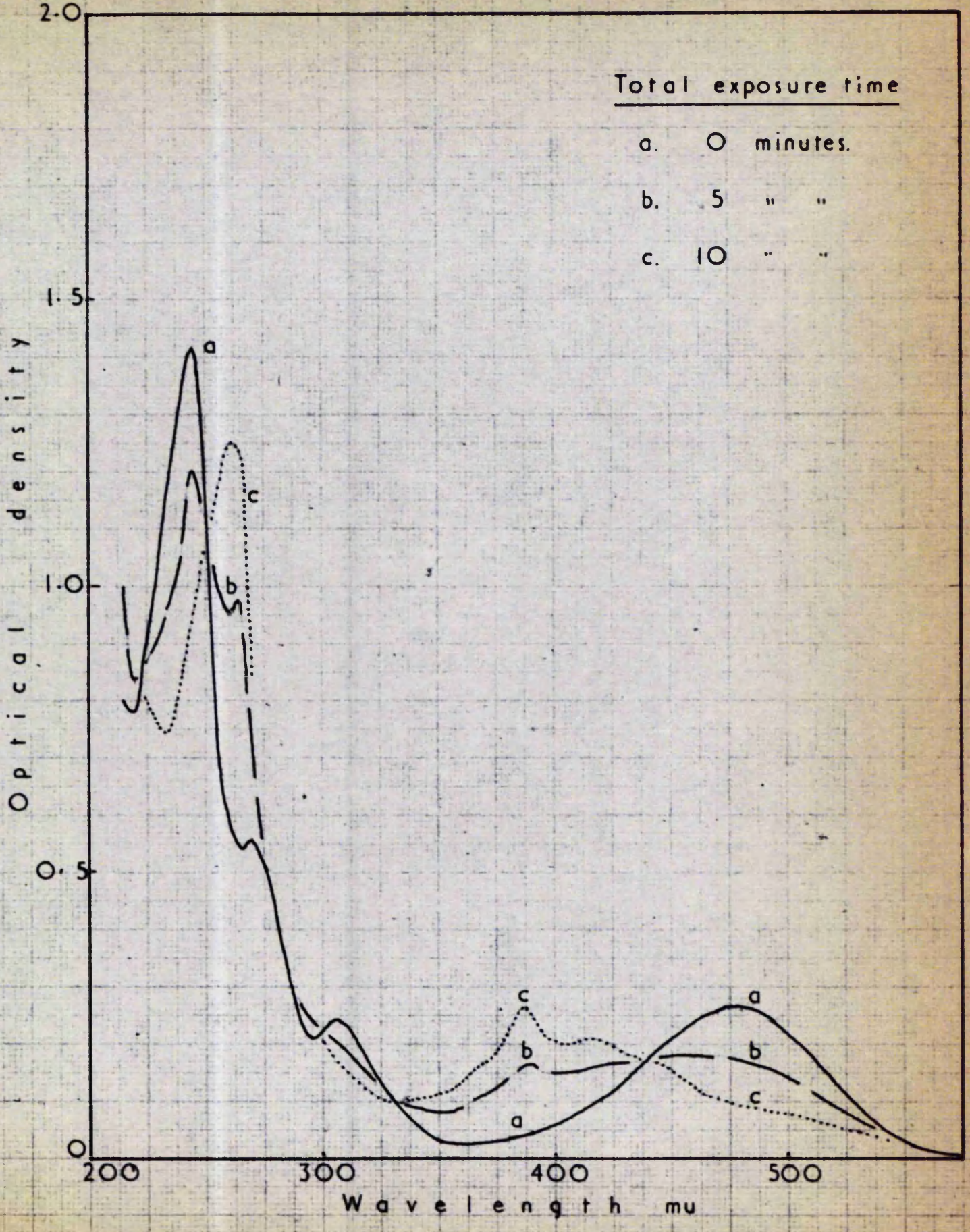
Percentage loss in optical density of the band in the visible region after exposure

Fig. 14

1-Aminoanthraquinone in ethanol

exposed to Vitan lamp

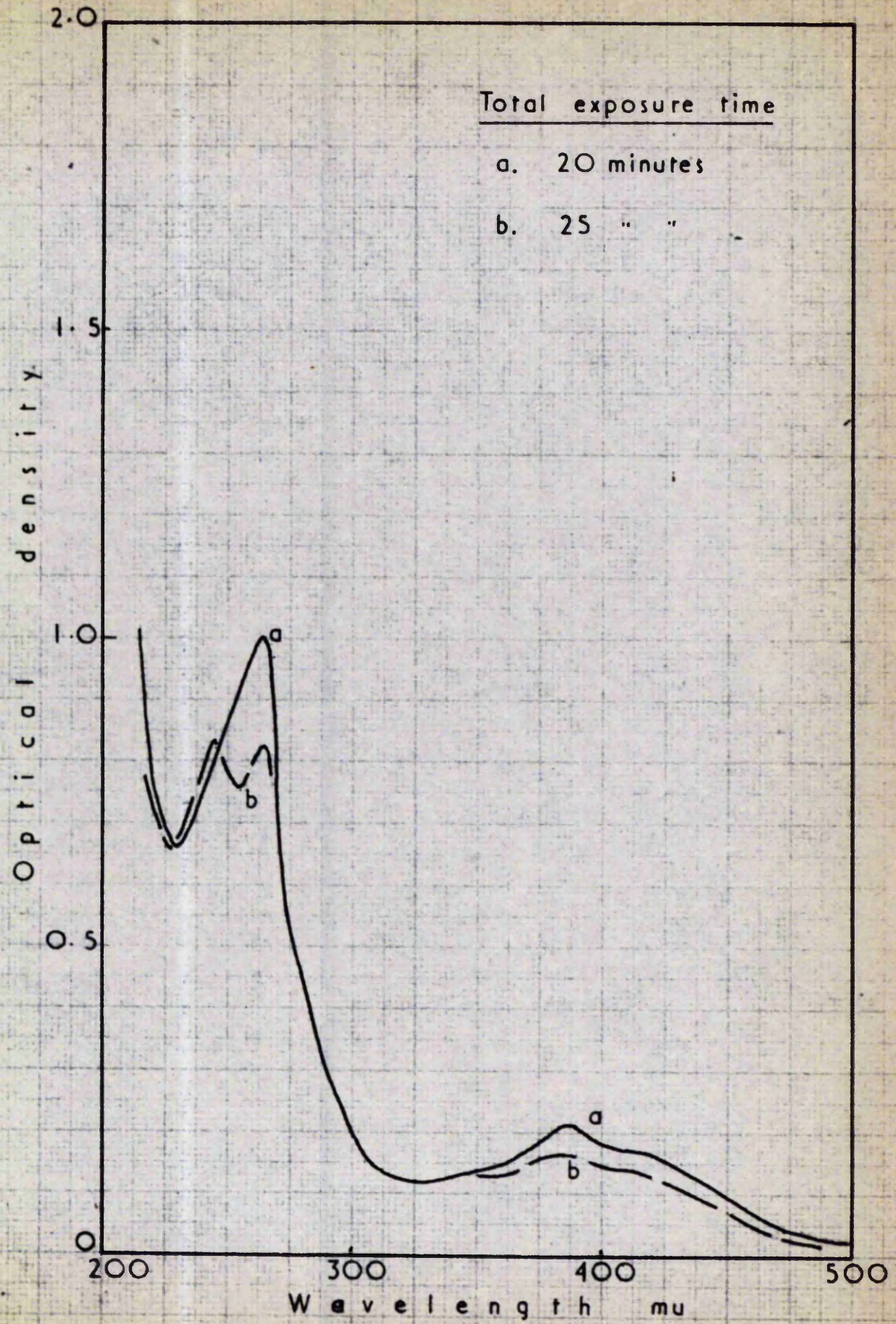
Fig. 15



1–Aminoanthraquinone in ethanol

exposed to Vitan lamp

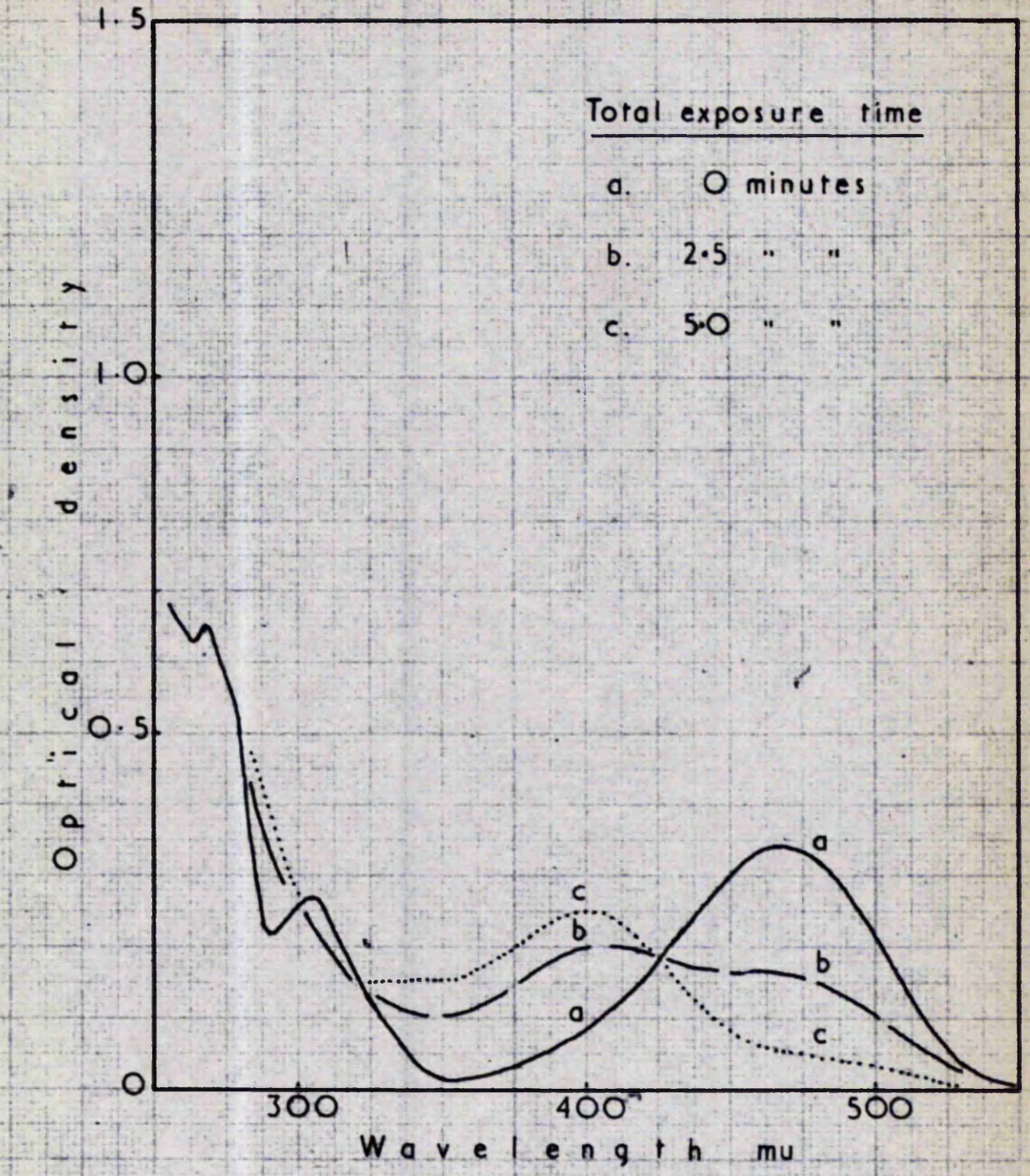
Fig. 16



1-Aminoanthraquinone in ethyl acetate

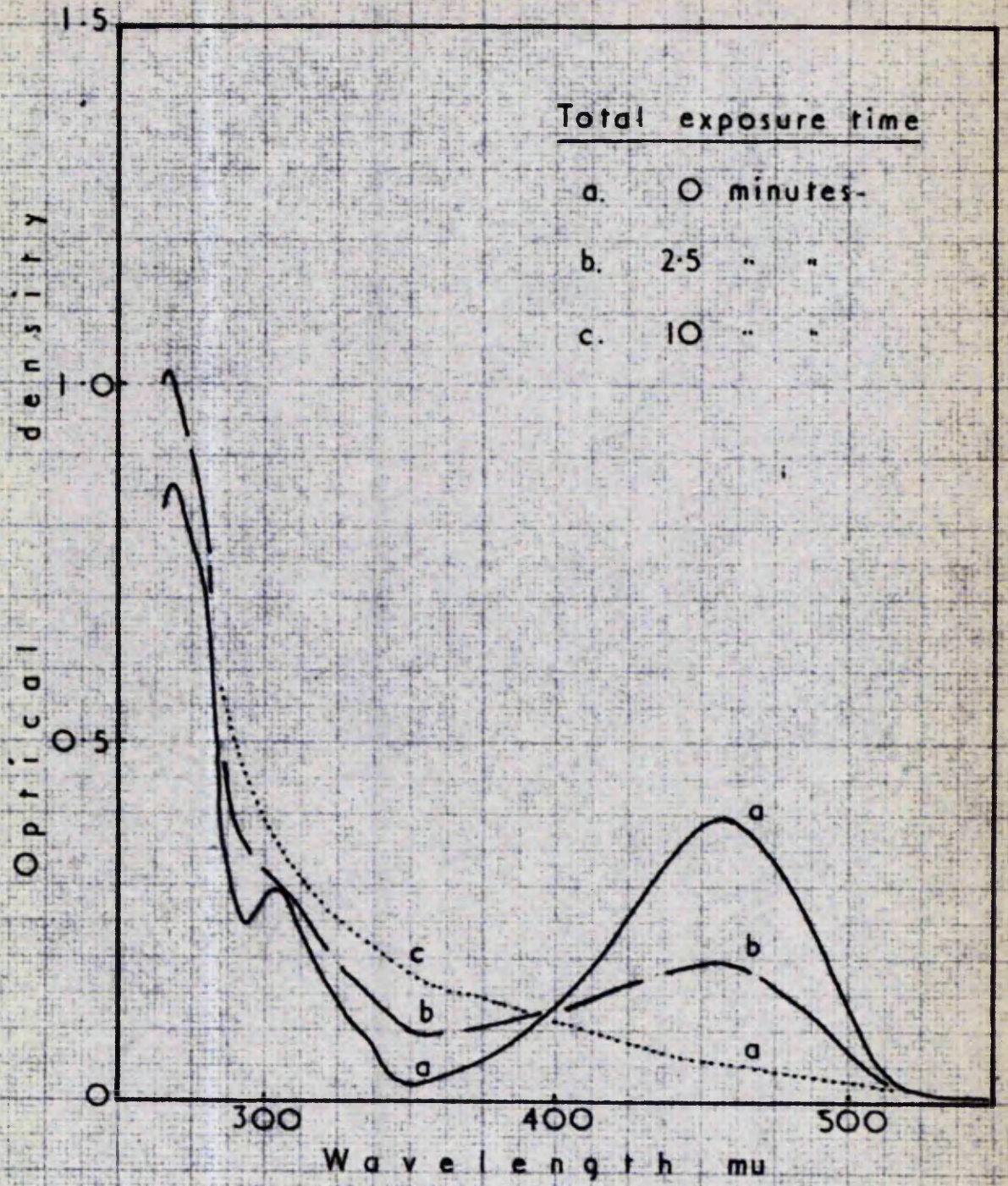
exposed to Vitan lamp

Fig 17



1-Aminoanthraquinone in carbon tetrachloride exposed to Vitan lamp

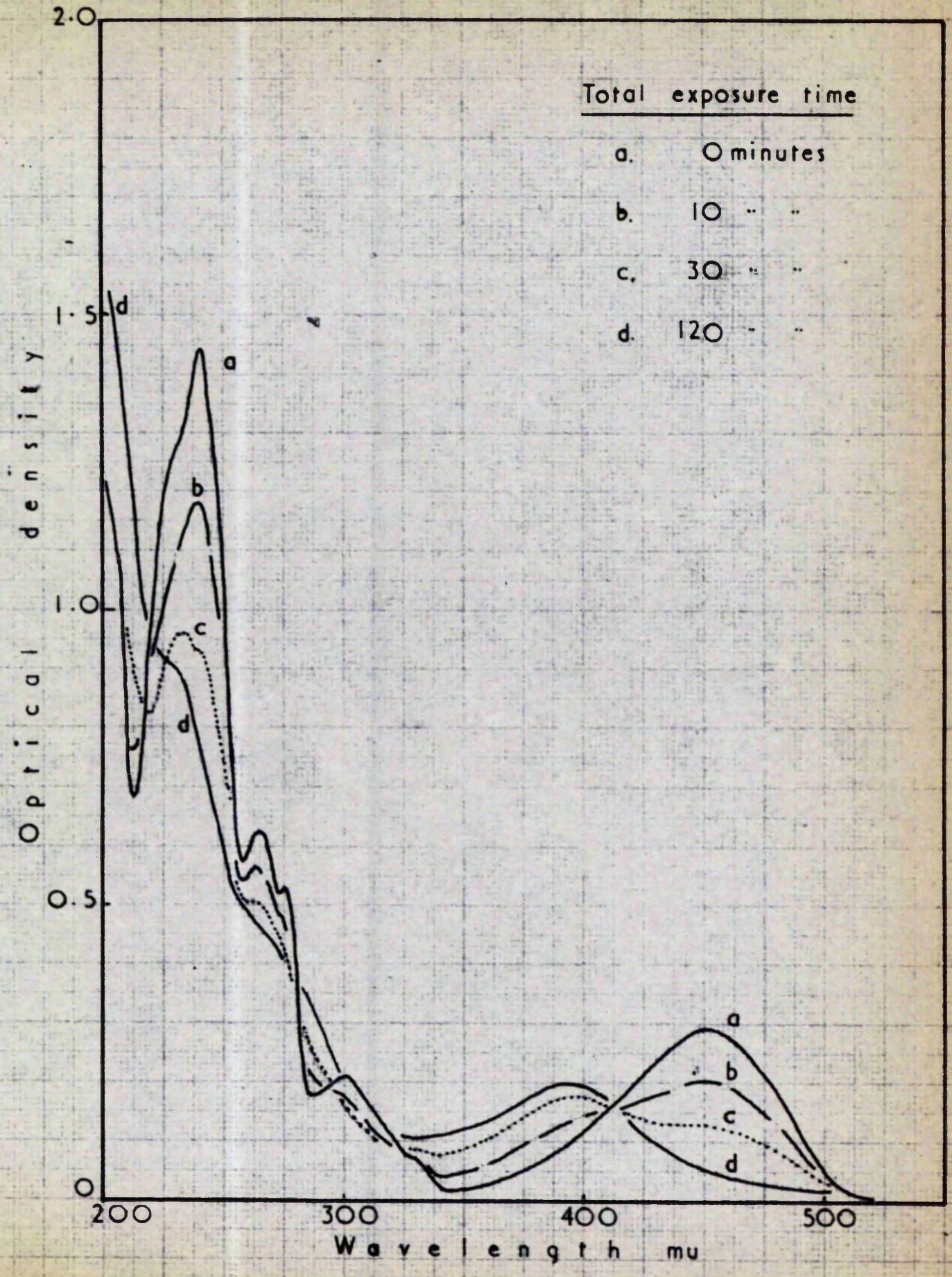
Fig 18



1–Aminoanthraquinone in n-hexane

exposed to Vitan lamp

Fig. 19



No observable new band was produced.

Irradiation of a solution of the dye in n-hexane caused a new band to be produced at about 392.5 mu while the original at 451 mu was degraded (Fig.19). An isobestic point was produced at about 415 mu. As for the ethanol and the ethyl acetate solutions the band at 300 mu lost its character but with only a slight loss in intensity in that region. This applied also to the bands at 265 and 275 mu and, to a lesser extent, at 240 mu. The last was degraded more slowly than the others and appeared to undergo a progressive hypsochromic shift unlike that in ethanol (Fig.15) which initially moved bathochromically.

Fading by Osram lamp.

The changes in the absorption spectra of solutions of 1-aminoanthraquinone exposed to this lamp were very similar to those produced by the Vitan lamp. The rate at which these changes took place was much slower and the speed at which the visible band decreased in intensity was this time greatest for the n-hexane solution followed by ethanol, ethyl acetate and finally carbon tetrachloride (Fig.14). This order was almost the reverse of the rate of fading to the Vitan lamp. Fading produced by the Osram lamp is unlikely to involve photolysis of the solvents and photosensitised reactions are more probable. If hydrogen atom transfer takes place the ease with which it does presumably depends on the ease of the attack by the excited dye molecule on the solvent and the availability of a hydrogen atom.

It would not seem impossible for ethyl acetate to be able to give up a hydrogen atom from the carbon atom alpha to the carbonyl group. Hydrogen atom abstraction from the solvent cannot take place in carbon tetrachloride and the fading must occur by a different mechanism. Bridge and Porter[36] have observed in flash photolysis studies that duroquinone in carbon tetrachloride solution may abstract a hydrogen atom from itself.

The changes in the spectrum of the ethanol solution of 1-amino-anthraquinone on exposure to the Osram lamp (Fig.20) were identical to those recorded initially for the Vitan lamp (Fig.15) although the rate of fading was much slower. The band at 270 mu first became an inflection during its hyperchromic and hypsochromic shift to a band at 262.5 mu while that at 245 mu decreased in intensity as it moved bathochromically to the same location. It seemed also that the visible band moved to shorter wavelengths as it lost its spectral character and there was evidence of a band at 420 mu in the results for a 300 hour exposure, at which time there was a maximum concentration of photoproduct. Prolonged storage in the dark of the solution after a total of 475 hours exposure caused a change in the ultraviolet spectrum that could not be reversed by a further 25 hours exposure (Fig.21). The change was similar to that recorded for the ethanol solution after 25 minutes exposure to the Vitan lamp (Fig.16). The band that had been formed at 262.5 mu moved hypsochromically to the position of the shortest wavelength band of the original solution, viz 242.5 mu, leaving only an inflection. There was, however,

approximately a 50% increase in absorption in the region of the position of the original visible band as well as a marked decrease in absorption for the corresponding band of the photoproduct. If this were due to reformation of the original compound it would account for the re-appearance of the peak at 242.5 mu.

Between 350 and 600 mu the changes observed for the ethyl acetate solution (Fig.22) were identical to those observed on exposure to the Vitan lamp (Fig.17). The photoproduct band again appeared at about 400 mu. Whereas previously the band at 305 mu was degraded and the absorption in the region 260 to 300 mu had remained almost constant, in this case it steadily increased on irradiation with the band at 267.5 mu becoming more pronounced and shifting apparently to 265 mu.

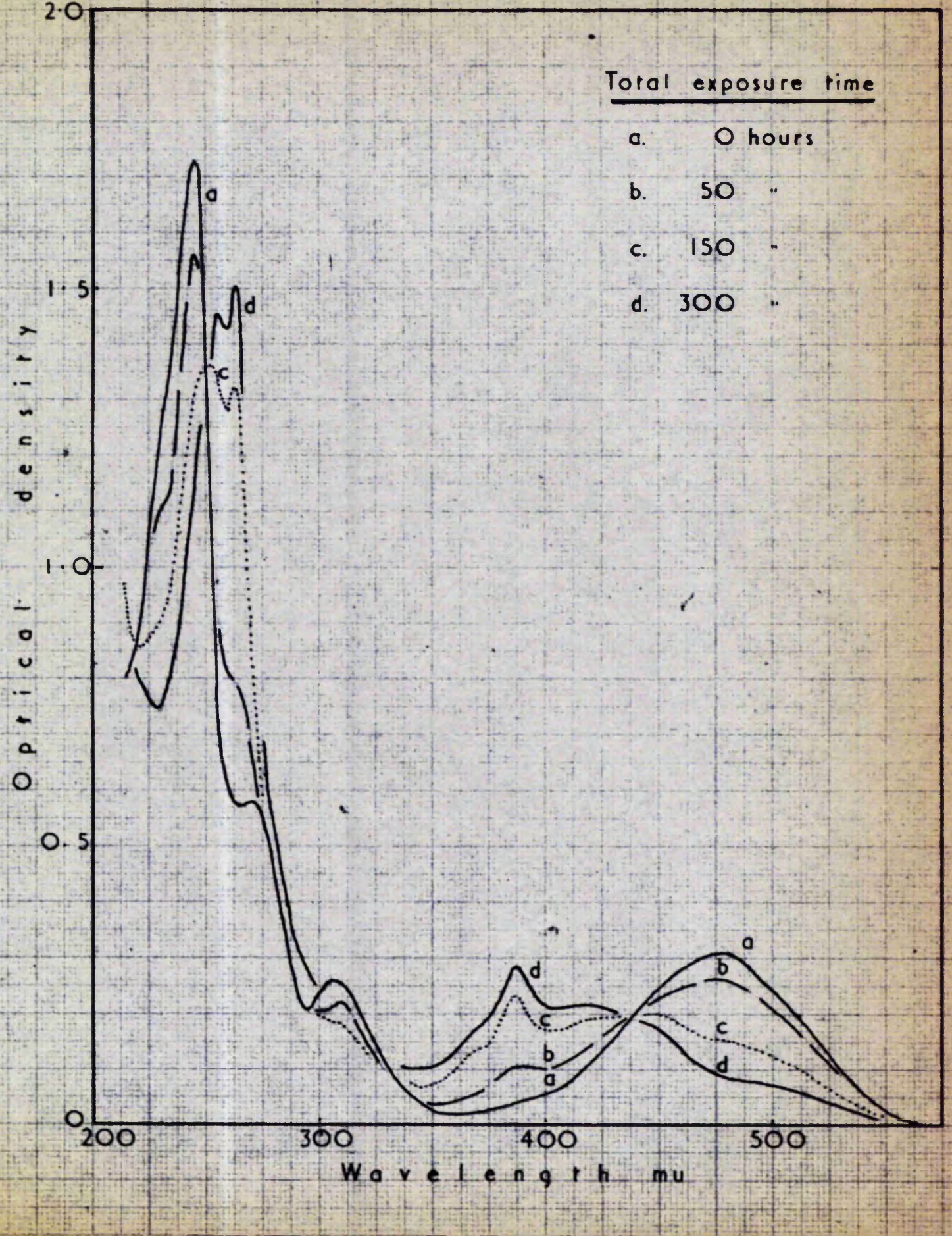
The above applies also to the changes observed on irradiating the carbon tetrachloride solution with the Osram lamp, (Fig.23). There was a greater increase in absorption from the cut off wavelength to the isobestic point at about 410 mu. After a 50% loss in intensity of the original visible band very little further loss in intensity resulted, yet the initial fading was quite rapid.

The spectrum of the fading product produced by irradiating the n-hexane solution, (Fig.24) was more well defined than that obtained when the same solution was exposed to the Vitan lamp, (Fig.19). The rate of fading to the Osram lamp was much greater than would have been expected from the Vitan lamp results. The new band maximum was at 390 mu and the isobestic point at 410 mu, both located only 2.5 mu to shorter wavelengths than those observed for the Vitan lamp. The

1-Aminoanthraquinone in ethanol

exposed to Osram lamp

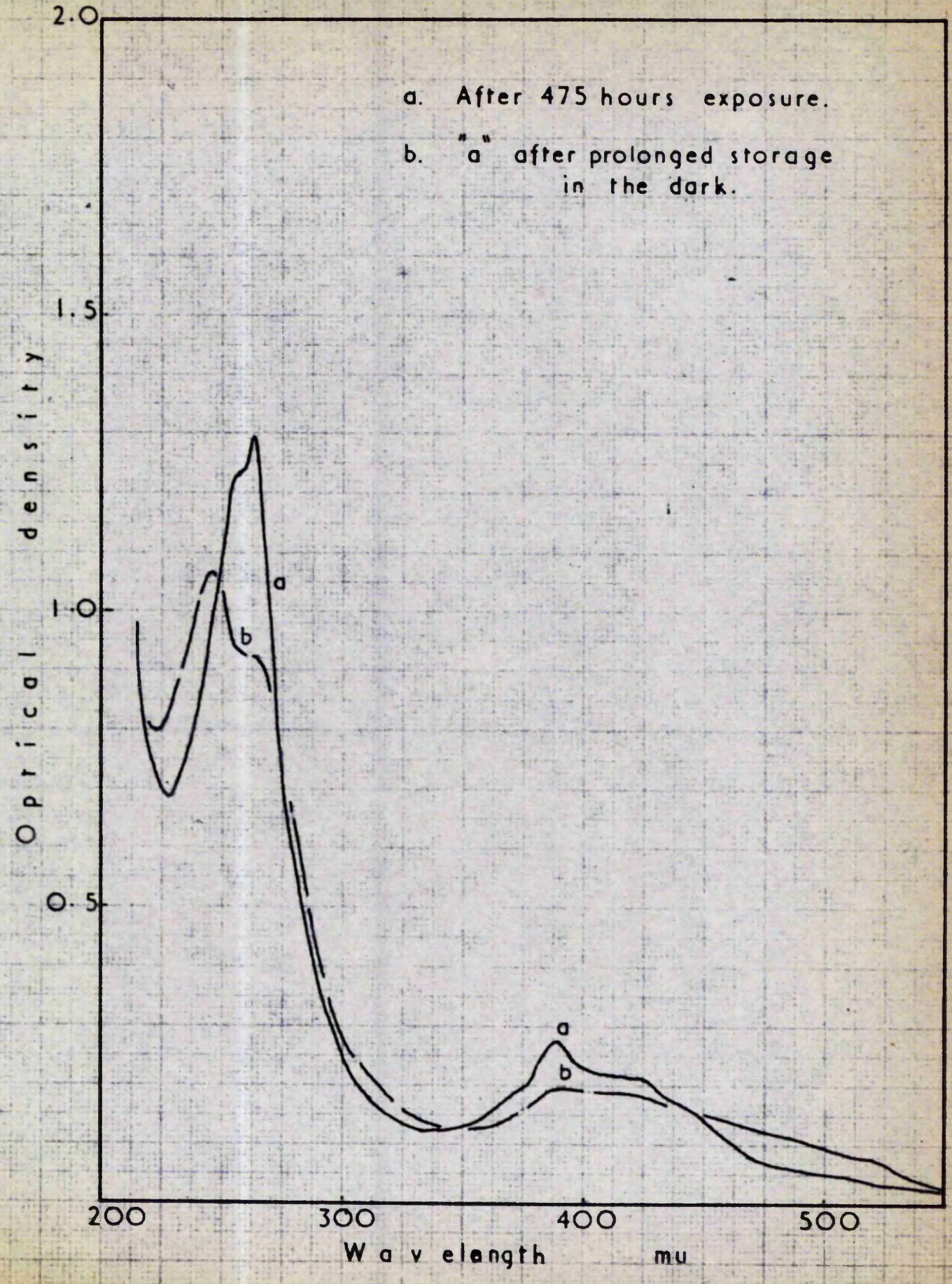
Fig. 20



1-Aminoanthraquinone in ethanol

exposed to Osram lamp

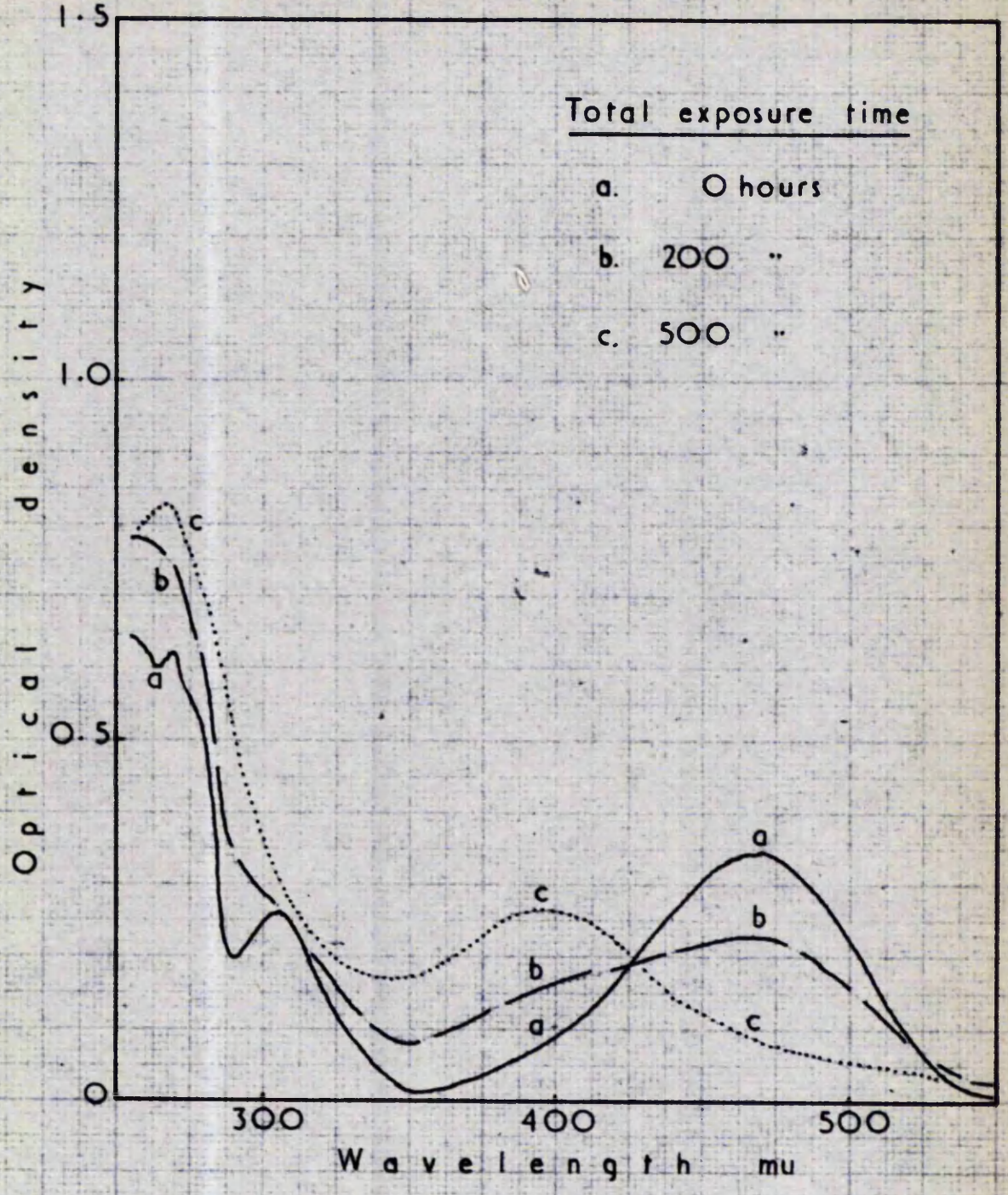
Fig. 21



1-Aminoanthraquinone in ethyl acetate

exposed to Osram lamp

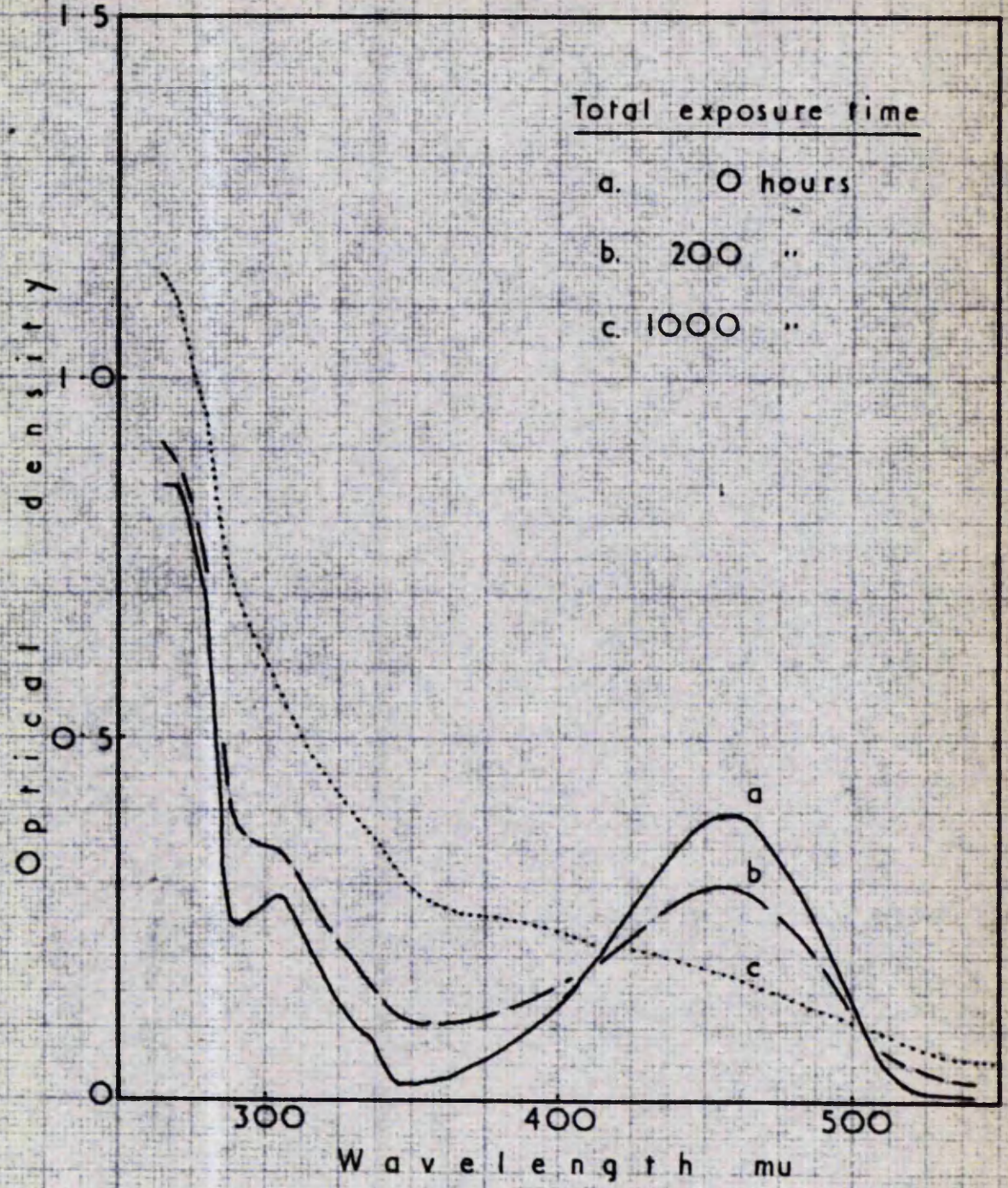
Fig. 22



1 Aminoanthraquinone in carbon tetrachloride

Fig 23

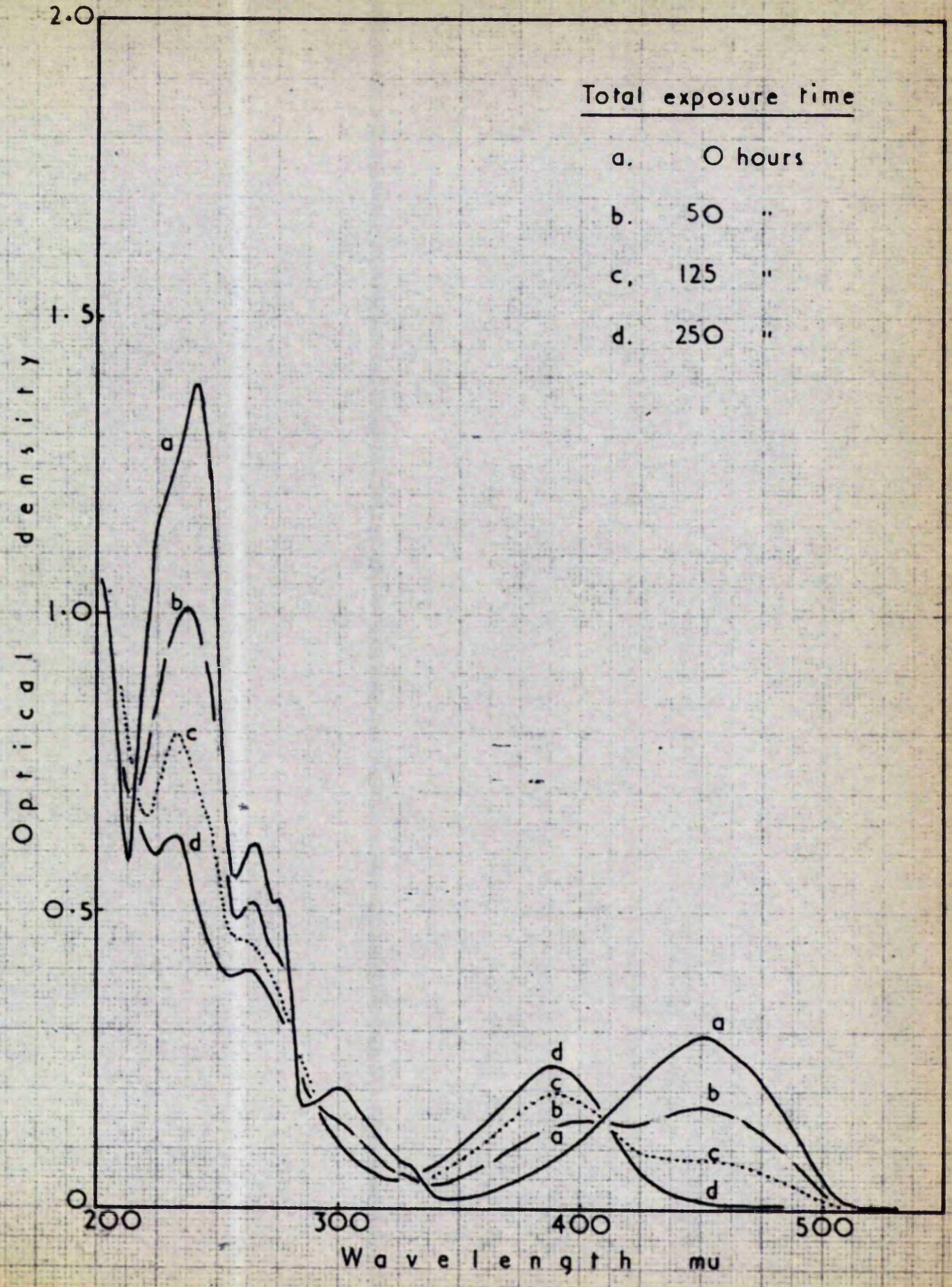
exposed to Osram lamp



1-Aminoanthraquinone in n-hexane

exposed to Osram lamp

Fig. 24



progressive loss in intensity of the bands at 265 and 240 mu was again observed, the latter undergoing a hypsochromic shift.

Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

Egerton and Roach[5,6] have studied the spectral changes produced by the exposure to an Osram lamp of films of cellulose acetate, nylon and N-methoxymethyl nylon dyed with 1-aminoanthraquinone. Only the changes occurring in the N-methoxymethyl nylon film in an atmosphere of nitrogen were strictly similar to those observed in the present work. The cut off wavelength of this dyed film prevented accurate measurements below 250 mu but there was a marked similarity in the absorption spectrum of the fading product to the spectrum of the fading product in the ethanol solutions after five minutes exposure to the Vitan lamp, (Fig. 15) and 150 hours to the Osram lamp, (Fig.20). Peaks were recorded for all three in the region 250, 270 and 390 mu with an inflection around 425 mu. The two short wavelength bands were not observed for the fading product in n-hexane solution, there apparently being degradation of these bands, (Figs. 19 , 24).

Unfortunately there is no record of the dyed films of cellulose acetate and nylon having been exposed in an atmosphere of nitrogen but in oxygen there was no evidence of a fading product of the type described. In fact fading was found to proceed on tone. The changes occurring in the N-methoxymethyl nylon film in an atmosphere of oxygen were not the same as in nitrogen althrough there were some similarities. They showed more resemblance to those occurring in

carbon tetrachloride solution on exposure to either lamp, (Figs. 18,23).

Because of changes in the polymer films themselves the only exposures made by Egerton and Roach[5,6] to the Vitan lamp were of solid dye films on quartz. An equal loss of absorbance at all wavelengths was recorded for exposures made in atmospheres of oxygen, nitrogen and moist air.

2 - Aminoanthraquinone.

The positions of the band maxima in the solvents ethanol and ethyl acetate, together with some ancillary data, are given in Table III. An inflection at 320 mu was more pronounced in ethyl acetate solution than in ethanol and there was evidence of an inflection located around 287.5 mu for this solvent.

Reference is made in the table to an unstable form of the anthrone. As stated earlier two forms of an anthrone of 2-aminoanthraquinone were prepared, one of which had been prepared by the method of Bradley and Maisey[46] and was thermally unstable. This is the form referred to in the table and according to Bradley is 2-aminoanthr-10-one. It is included as its spectra more closely resemble the fading products than those of the other form.

Fading by Vitan lamp.

Similar overall spectral changes to those recorded for the exposure of solutions of 1-aminoanthraquinone in ethanol and ethyl acetate to this lamp were observed for solutions of 2-aminoanthraquinone in the same two solvents, (Figs. 26,28). The observation of the progress of the fading was complicated by what appeared to be a post-irradiation effect which was noted only after several hundred hours storage in the dark of the irradiated solution. However this effect was minimised by carrying out the initial exposures in a short space of time.

Fading occurred most rapidly in ethyl acetate only 3.5 minutes

SOLUTION ETHANOL	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original	242.5		297.5	335*		447.5	26/30
Exposed to Vitan		265				377.5	26
Exposed to Vitan after storage	247.5	265				350	27
Exposed to Osram	245					351	30
Anthrone - Unstable form	250					355	53
ETHYL ACETATE							
Original		287.5	295	320*		427.5	28/31
Exposed to Vitan		255				327.5	28
Exposed to Osram			280	315		365	31
Anthrone - Unstable form						336	53

TABLE III

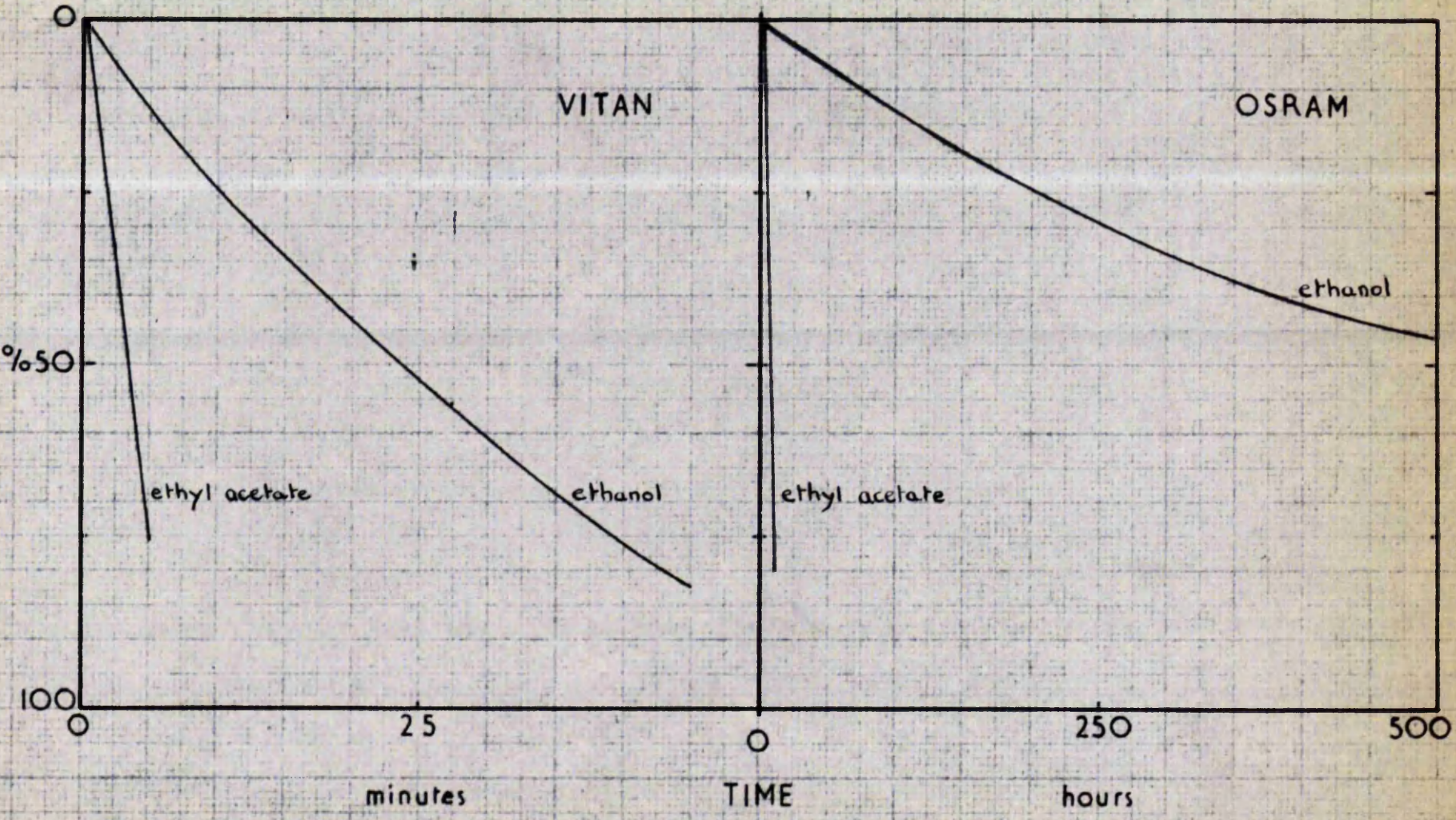
2-AMINOANTHRANQUINONE

exposure being required to produce 50% degradation of the main visible band, while 23.5 minutes were needed to produce the same loss in intensity for the ethanol solution, (Fig.25).

After five minutes irradiation of the ethanol solution, (Fig.26) the band at 242.5 mu was less intense and had undergone a bathochromic shift to produce a new band with a maximum at 265 mu. Coupled with this the band at 297.5 mu became an inflection and appeared to have moved hypsochromically to 280 mu. Isobestic points occurred at 350 and 405 mu, the absorption between these wavelengths having increased. There was evidence of a new band being formed at 377.5 mu. The original band in the visible part of the spectrum became less intense and underwent a hypsochromic shift. Further irradiation continued this shift and loss of intensity, coupled with the rise in intensity of the new band at 377.5 mu. The band at 242.5 mu continued to decrease in intensity while that formed at 265 mu increased. The former existed only as an inflection after 20 minutes total irradiation. The band formed after five minutes at 280 mu steadily increased in intensity, merging with the band at 265 mu to remain only as an infelction. There was evidence at this stage of a band being formed with a maximum at 350 mu. The absorption spectrum recorded after 45 minutes irradiation however showed a complete reversal of the trends previously observed in the ultra-violet, (Fig.27). A band maximum existed once again at about 245 mu, followed by an inflection at about 260 mu. The curve obtained did not pass through the isobestic points of the others and there was no evidence of a band at 377.5 mu but one did

however exist at 350 mu. The recording of this spectrum was unavoidably delayed for a period of three weeks and from the previous absorption spectrum, measured after a total of 40 minutes irradiation, it seemed that these changes could have occurred only as a result of storage. A further five minutes irradiation reversed the positions of the ultra-violet bands, (Fig.27), so that they resembled more closely those previously observed, the band at 350 mu remained unaffected. Storage for one week in the dark caused a partial rearrangement of the ultra-violet bands to give a spectrum similar to the 45 minutes absorption spectrum.

The irradiation induced spectral changes in the ethyl acetate solution, (Fig.28), involved destruction of the band at 295 mu to produce initially a new peak at 257.5 mu ; destruction of the band at 427.5 mu and the production of a new band at approximately 327.5 mu which subsequently disappeared. Isobestic points occurred at 265 and 385 mu. Storage in the dark after four minutes total irradiation produced slight differences (Fig. 29) which apparently could be nullified by further short irradiation. No intermediate band in the 325 to 400 mu region was produced unlike that observed for the ethanol solution.



2-AMINOANTHRAQUINONE

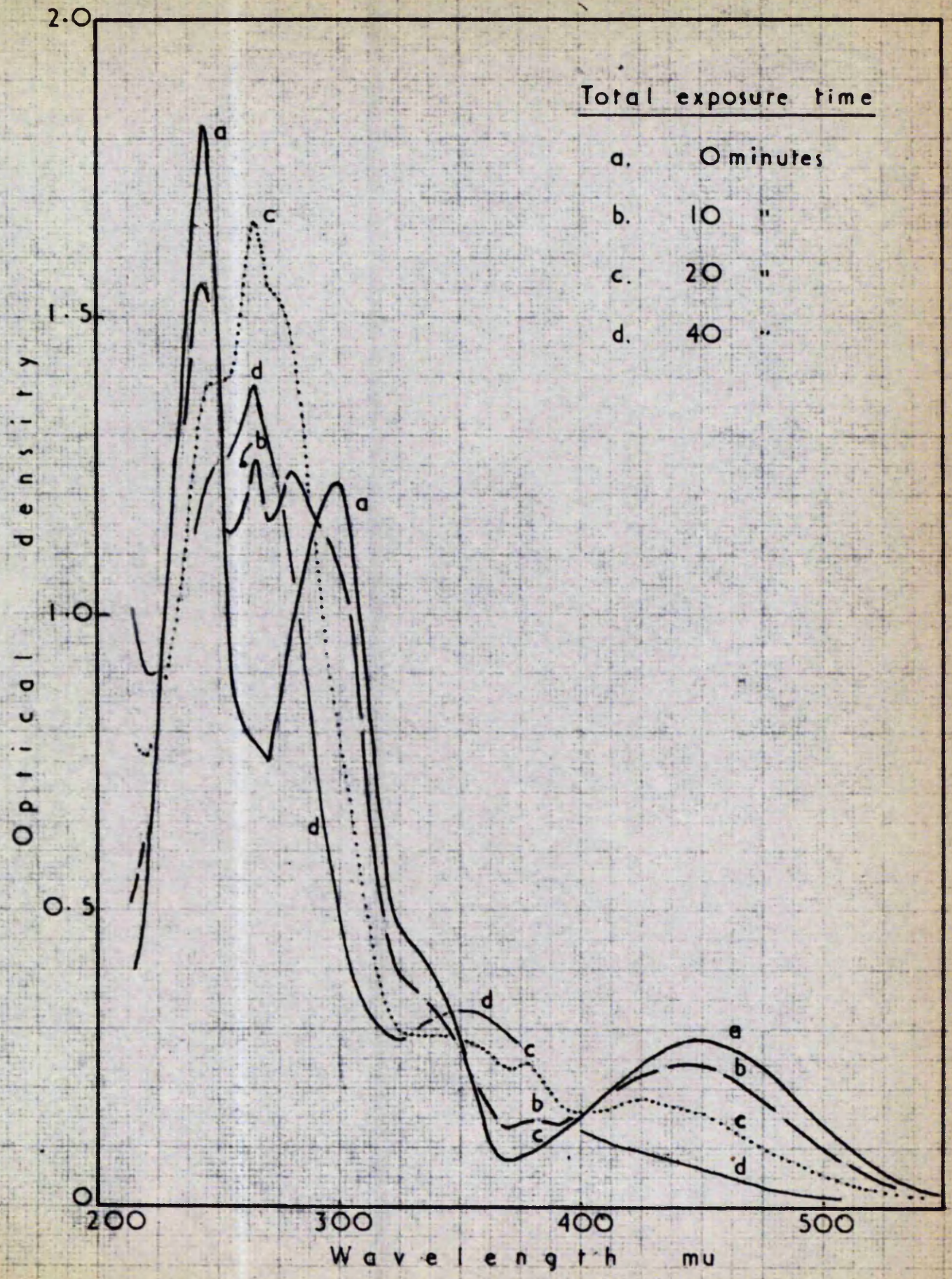
Percentage loss in optical density of the band in the visible region after exposure

Fig. 25

2-Aminoanthraquinone in ethanol

exposed to Vitan lamp

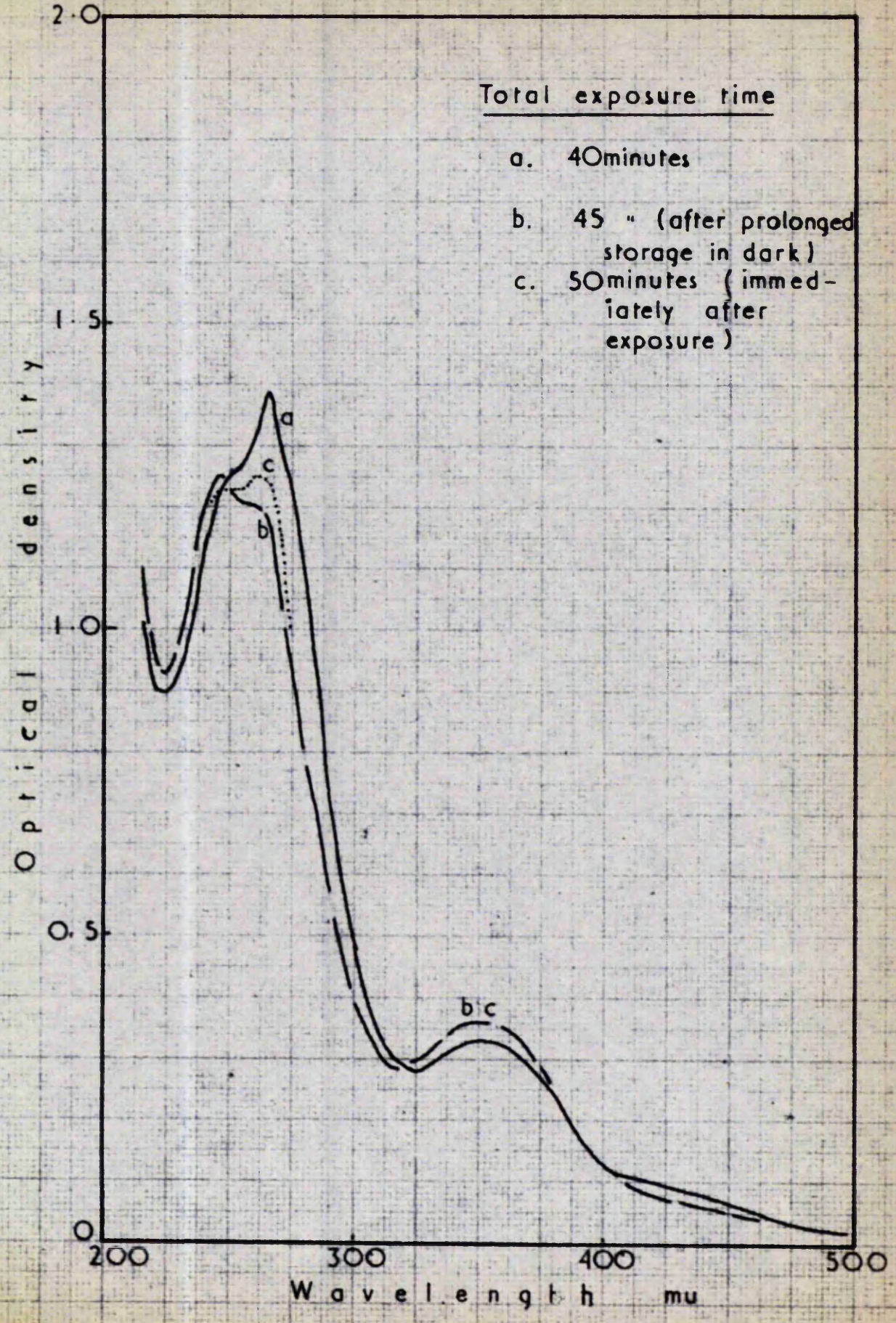
Fig.26



2-Aminoanthraquinone in ethanol

exposed to Vitan lamp

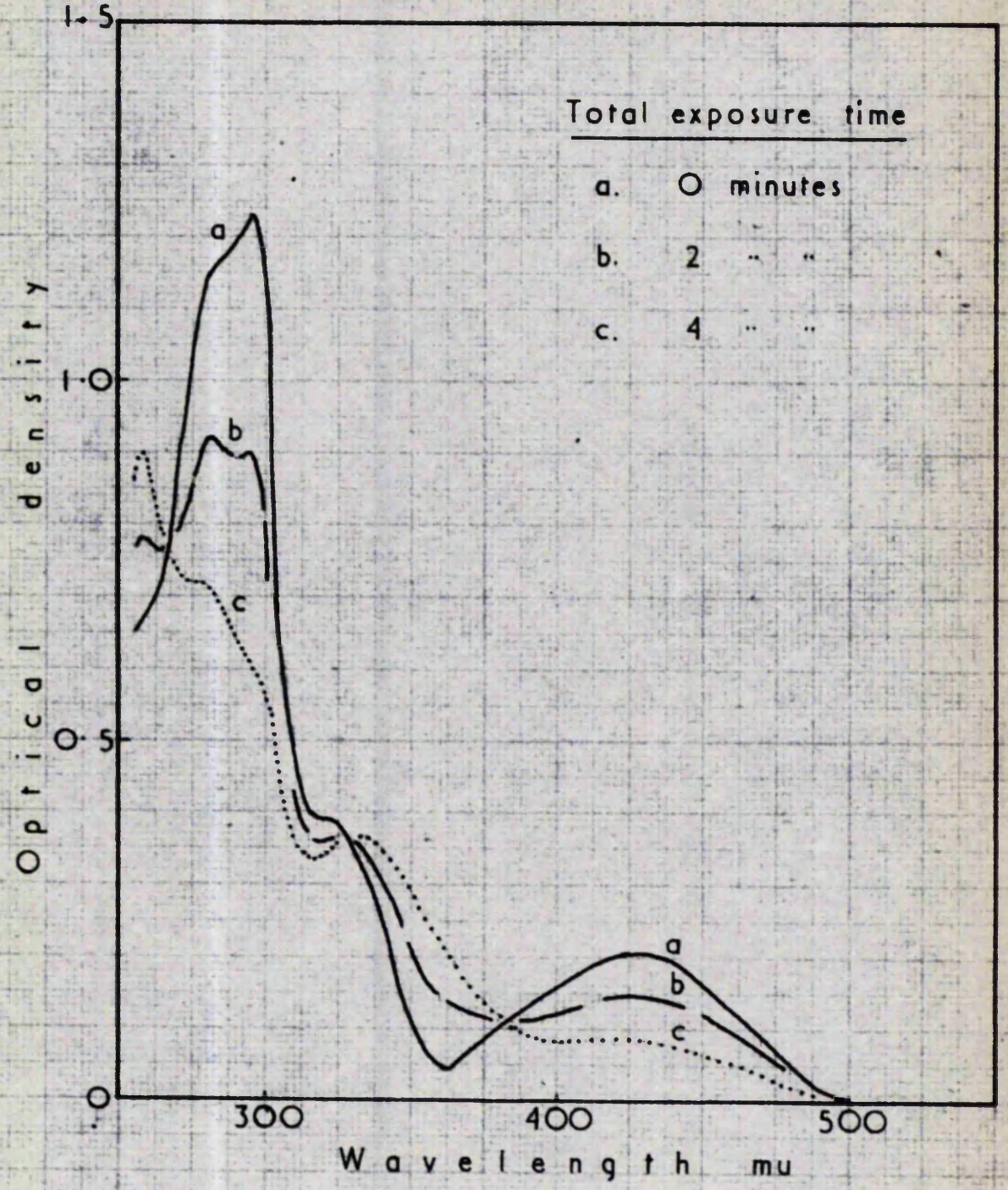
Fig. 27



2-Aminoanthraquinone in ethyl acetate

exposed to Vitàn lamp

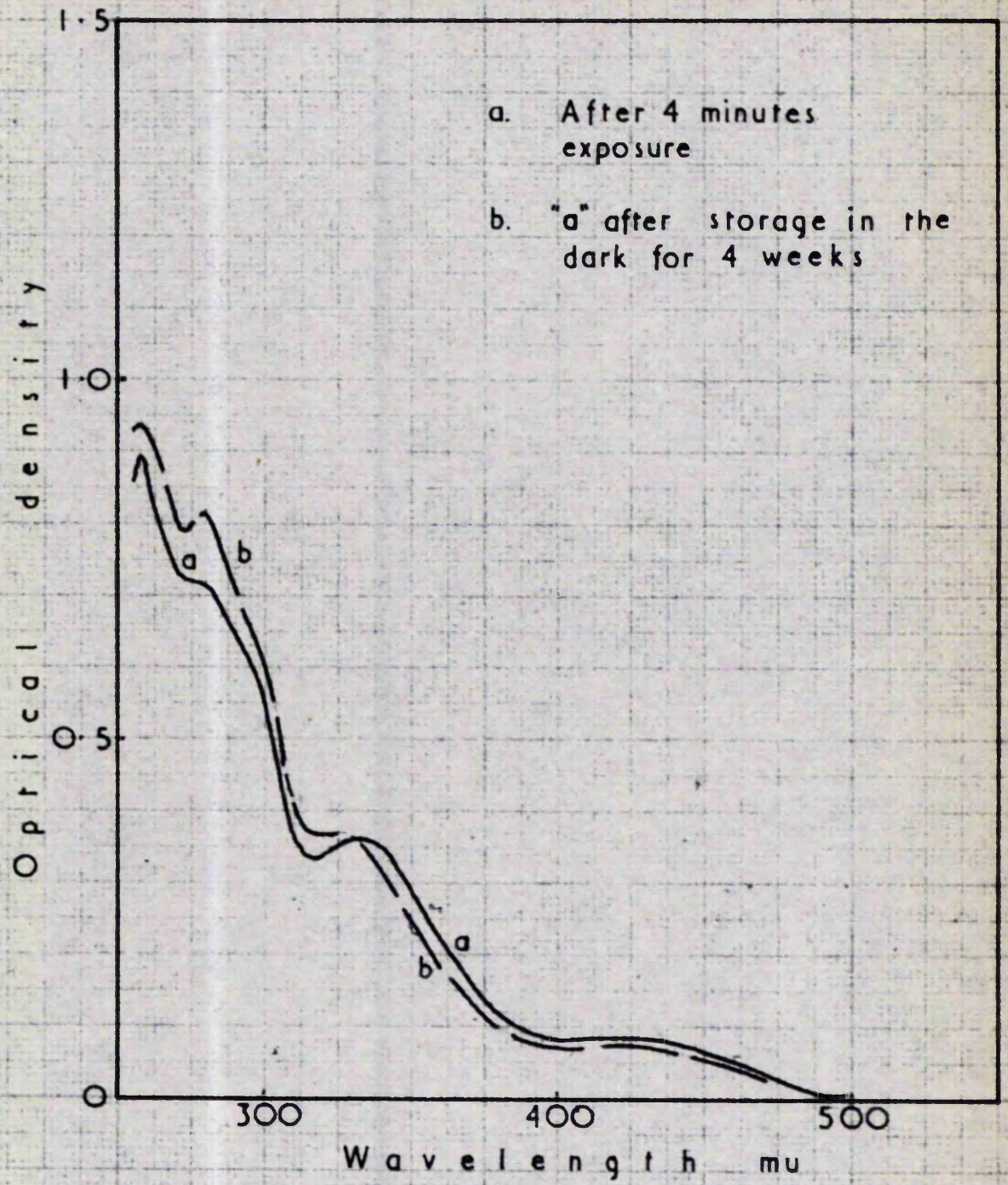
Fig. 28



2-Aminoanthraquinone in ethyl acetate

exposed to Vitan lamp

Fig 29



Fading by Osram lamp.

The most surprising feature of the results obtained on exposing the two solutions to this lamp was the extremely rapid fading of the ethyl acetate solution. The degradation of the band in the visible region after only five hours irradiation was equal to that after 1000 hours irradiation of the enthanol solution, (Fig.25).

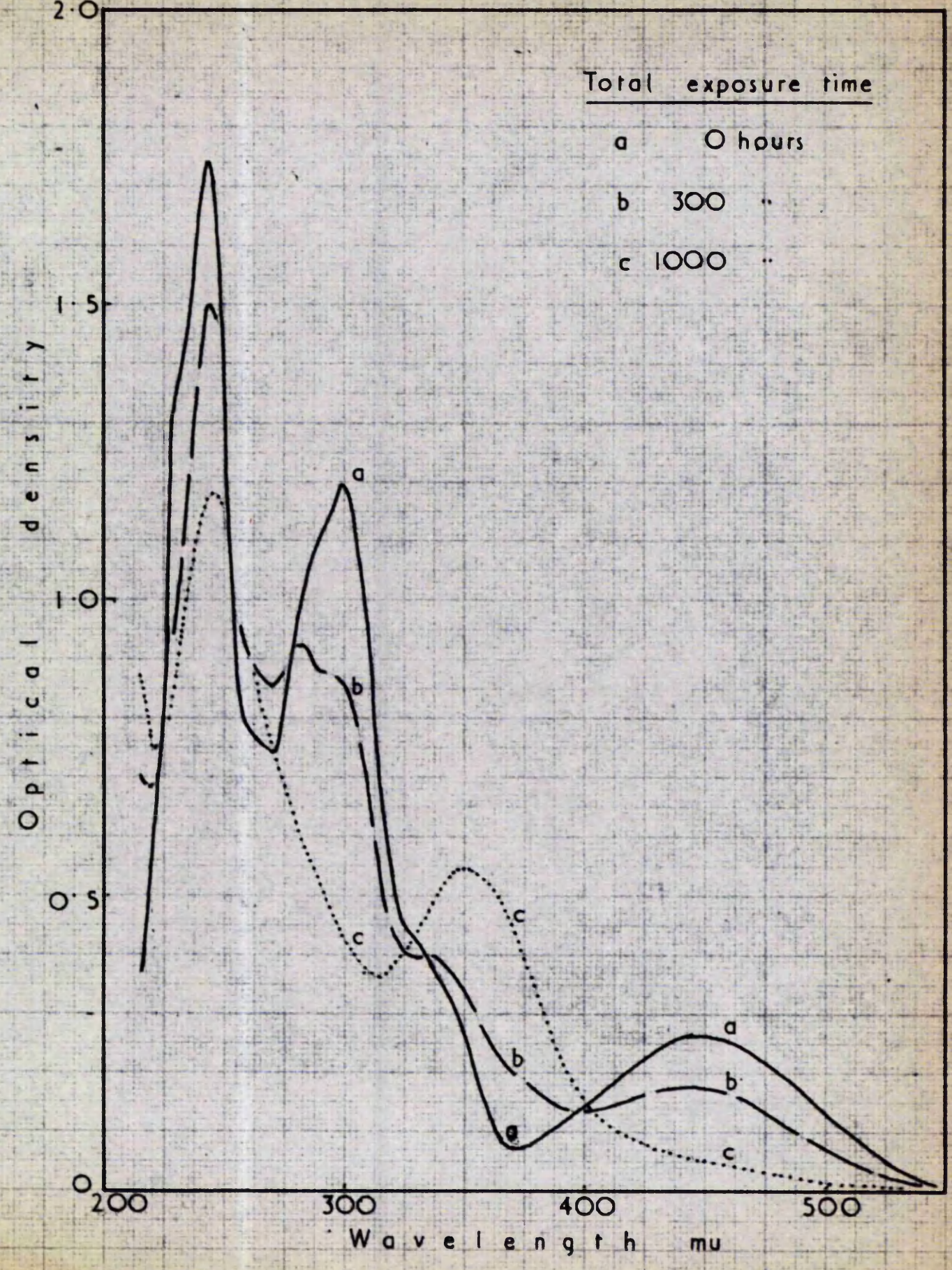
The shape of the spectrum of the ethanol solution after irradiation for 1000 hours (Fig.30) compared well with that obtained after storing the solution exposed to the Vitan lamp (Fig.27). Bands existed only at 245 and 351 mu. During the course of the irradiation the band in the visible region was slowly degraded and there was an increase in absorption between the wavelengths 335 to 400 mu. At one time it appeared as though a band might be forming at about 380 mu but instead one was formed at 351 mu which steadily increased in intensity to twice that of the original visible band. The two ultra-violet absorption bands were slowly degraded, that at 297.5 mu being completely destroyed after 1000 hours. During its destruction this band initially shifted to 280 mu leaving an inflection in its place. On storage in the dark midway through the experiment very slight changes in the absorption in this region were observed.

When the ethyl acetate solution was irradiated (Fig.31) the band at 295 mu, together with its inflection increased in intensity and moved hypsochromically to 280 mu. The weak band observed in the unexposed solution at 325 mu became an inflection located around 315 mu but was poorly defined. The absorption band at 427.5 mu

2-Aminoanthraquinone in ethanol

exposed to Osram lamp

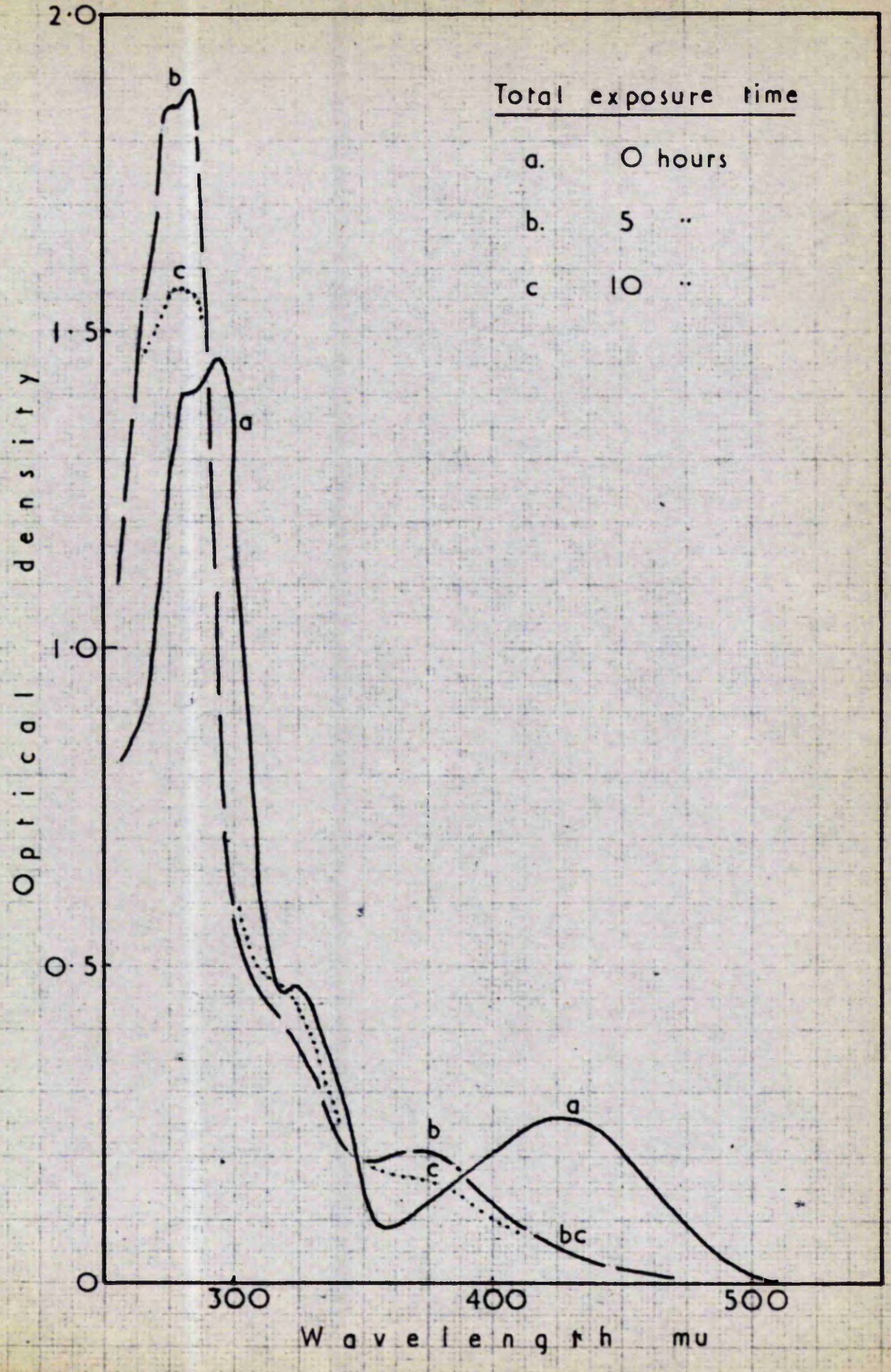
Fig. 30



2-Aminoanthraquinone in ethyl acetate

exposed to Osram lamp

Fig.31



was completely degraded after five hours exposure. Further irradiation lowered the intensity of the new absorbing system. The initial changes differed markedly from those observed for the solution exposed to the Vitan lamp (Fig. 28).

Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

The absorption spectra of films of cellulose acetate and nylon dyed with 2-aminoanthraquinone on exposure in oxygen to an Osram lamp were shown[5,6] to undergo, in general, a progressive loss of intensity at all wavelengths with exposure. There was a slight rise in absorbance in the region between the ultra-violet peaks similar to that recorded for an ethanol solution exposed to an Osram lamp (Fig.30). There was, however, no increase in absorption in the region 350 - 400 mu unlike that for the solution. The film of N-methoxymethyl nylon did exhibit some increased absorption in this region.

In nitrogen the changes were different. The cellulose acetate and nylon films showed a slight rise in absorption in the 350 - 400 mu region and again the changes in the ultra-violet region around 250 mu were similar to those occurring in the ethanol solution exposed to the Osram lamp. The cellulose acetate film eventually showed a single peak at 245 mu as did the ethanol solution. The N-methoxymethyl nylon film behaved differently but the changes were comparable with those which occurred initially for an ethanol solution exposed to the Vitam lamp (Fig. 26). A peak was formed at 270 mu and there was a slight inflection at about 390 mu.

The changes occurring on quartz did not indicate the formation of a new absorbing system.

1,4-Diaminoanthraquinone

Table IV summarises the positions of the band maxima of this compound in ethanol and ethyl acetate. It also includes data on an impure form of leuco-1,4-diaminoanthraquinone, the impurities being sodium dithionite and water. Attempts to make an anthrone from 1,4-diaminoanthraquinone, were unsuccessful as reduction by the general method which gave anthrones for other compounds, resulted only in the formation of leuco-quinizarin. The latter compound itself requires extremely vigorous reducing conditions to give an anthrone, presumably because of the chelation of the hydroxy groups with the carbonyl groups. However the values obtained for the positions of the bands of the sample of leuco-1,4-diaminoanthraquinone in ethanol corresponded very closely to those of the photoproduct and so no attempts to make an anthrone by other methods were made.

Fading by Vitan Lamp

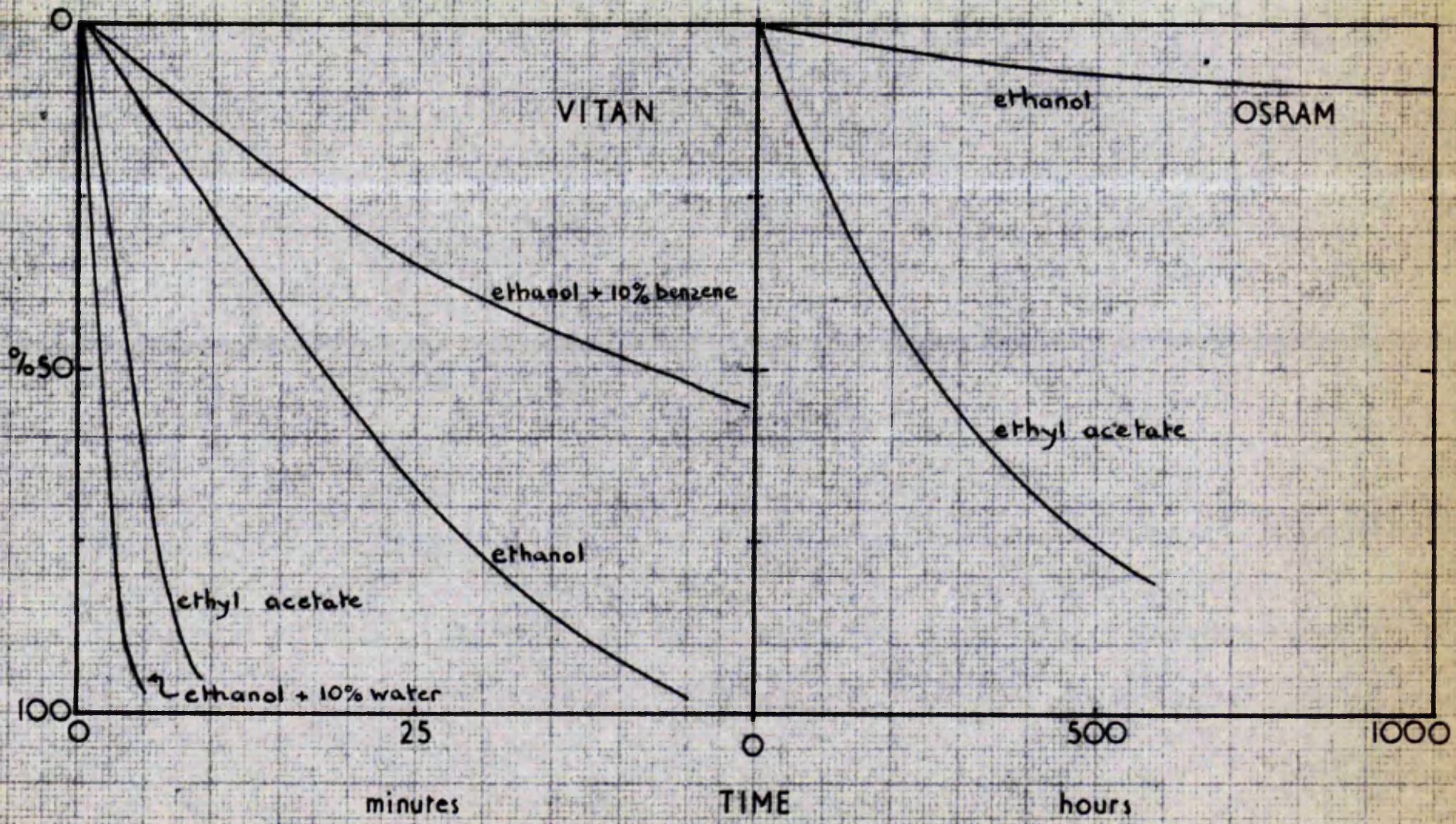
The striking feature of the results obtained when an ethanol solution of 1,4-diaminoanthraquinone was exposed to short-wave ultra-violet radiation, (Fig. 33), was the production of a new absorbing system in the visible spectrum. It was identical in structure to the original system which was simultaneously destroyed, but it was displaced by about 100 mu to shorter wavelengths. The intensity of the strong band at 251 mu was weakened only slightly and was not displaced. The inflection at 237.5 mu was displaced hypsochromically to 230 mu while that at 300 mu was smoothed out. The band maxima in the visible region moved from 552.5 and 593 mu to 457.5 and 487.5 mu, respectively while the inflection preceding the shorter wavelength band was displaced from 522.5 to 437.5 mu.

The spectrum of the fading product obtained on irradiation of the

SOLUTION ETHANOL	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original	237.5*	251	300*	522.5*	552.5	593	33/35
Exposed to Vitan	230 *	251		437.5*	457.5	487.5	33
Leuco (water present)				427.5*	450	480	54
ETHYL ACETATE							
Original			300*	520*	547.5	587.5	34/36
Exposed to Vitan					430	455*	34
Exposed to Osram					430	455	36
N-METHOXYMETHYL-NYLON							
Original			300*	530*	562	601	Ref. 5,6.
Exposed to Osram in O_2					535		

TABLE IV

1,4-DIAMINOANTHRAQUINONE



1,4-DIAMINOANTHRAQUINONE

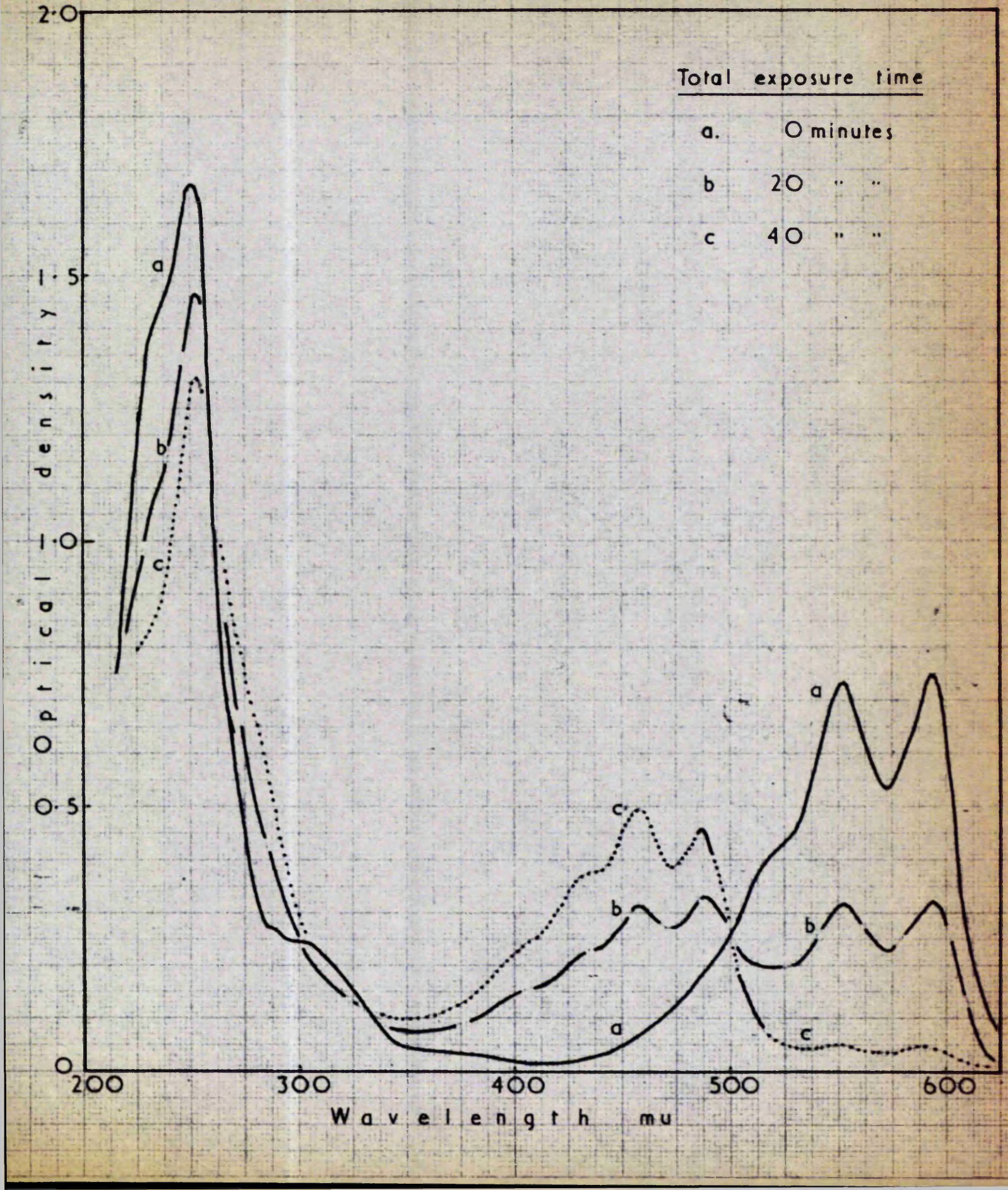
Percentage loss in optical density of the bands in the visible region after exposure

Fig. 32

1,4-Diaminoanthraquinone in ethanol

exposed to Vitan lamp

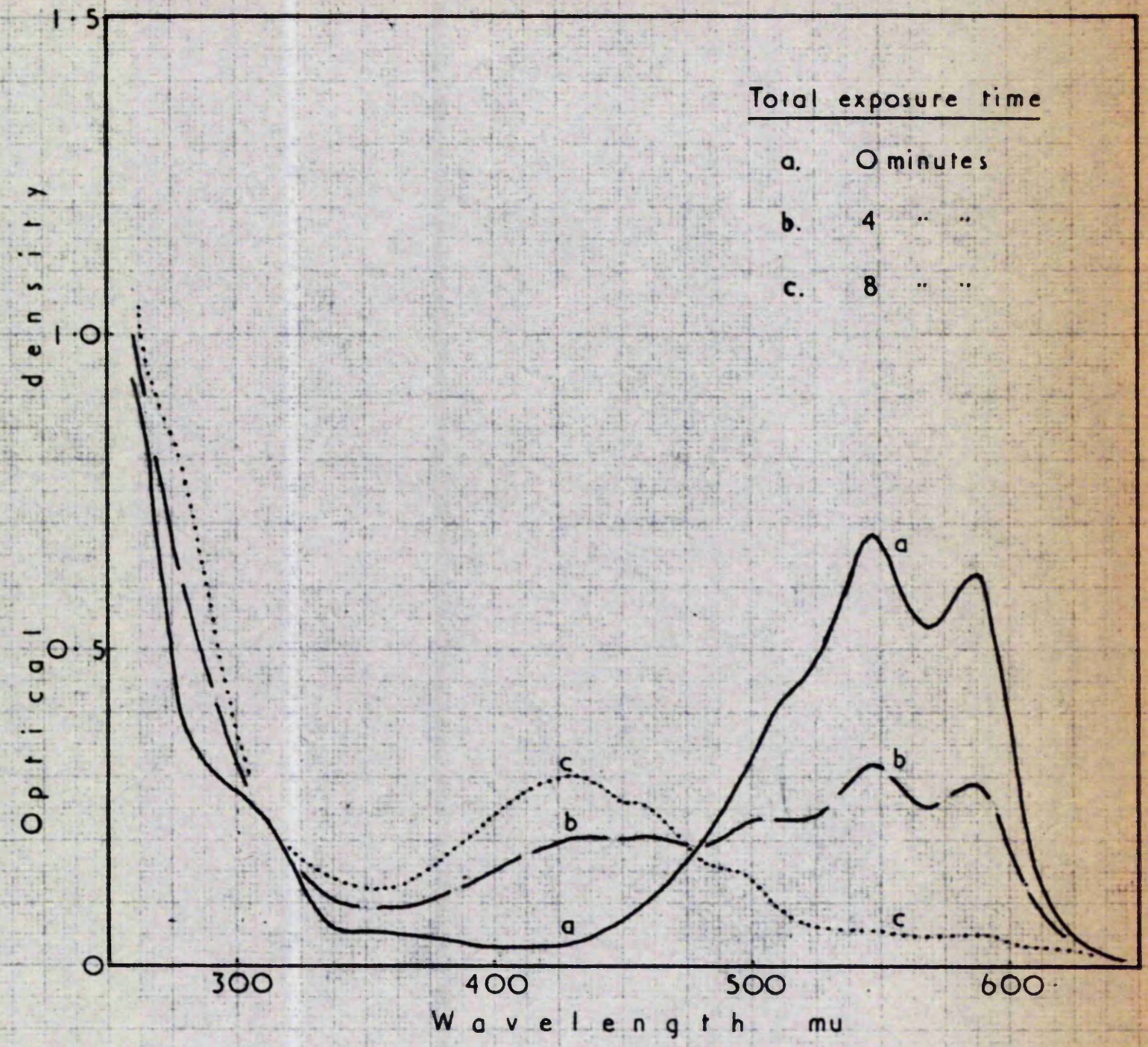
Fig. 33



1,4-Diaminoanthraquinone in ethyl acetate

exposed to Vitan lamp

Fig.34



ethyl acetate solution, (Fig.34), was much less well defined than that in ethanol. The rate of destruction of the original absorbing system in the visible region was some five times faster than that for the ethanol solution. The inflection at 300 mu was very quickly smoothed out and after four minutes exposure there was evidence of new twin peaks located around 430 and 457.5 mu. A further four minutes exposure consolidated the position of the band at 430 mu but there remained only an inflection at 455 mu. There appeared to be no evidence of an inflection preceding the 430 mu peak as had been observed in the ethanol solution.

Fading by Osram Lamp

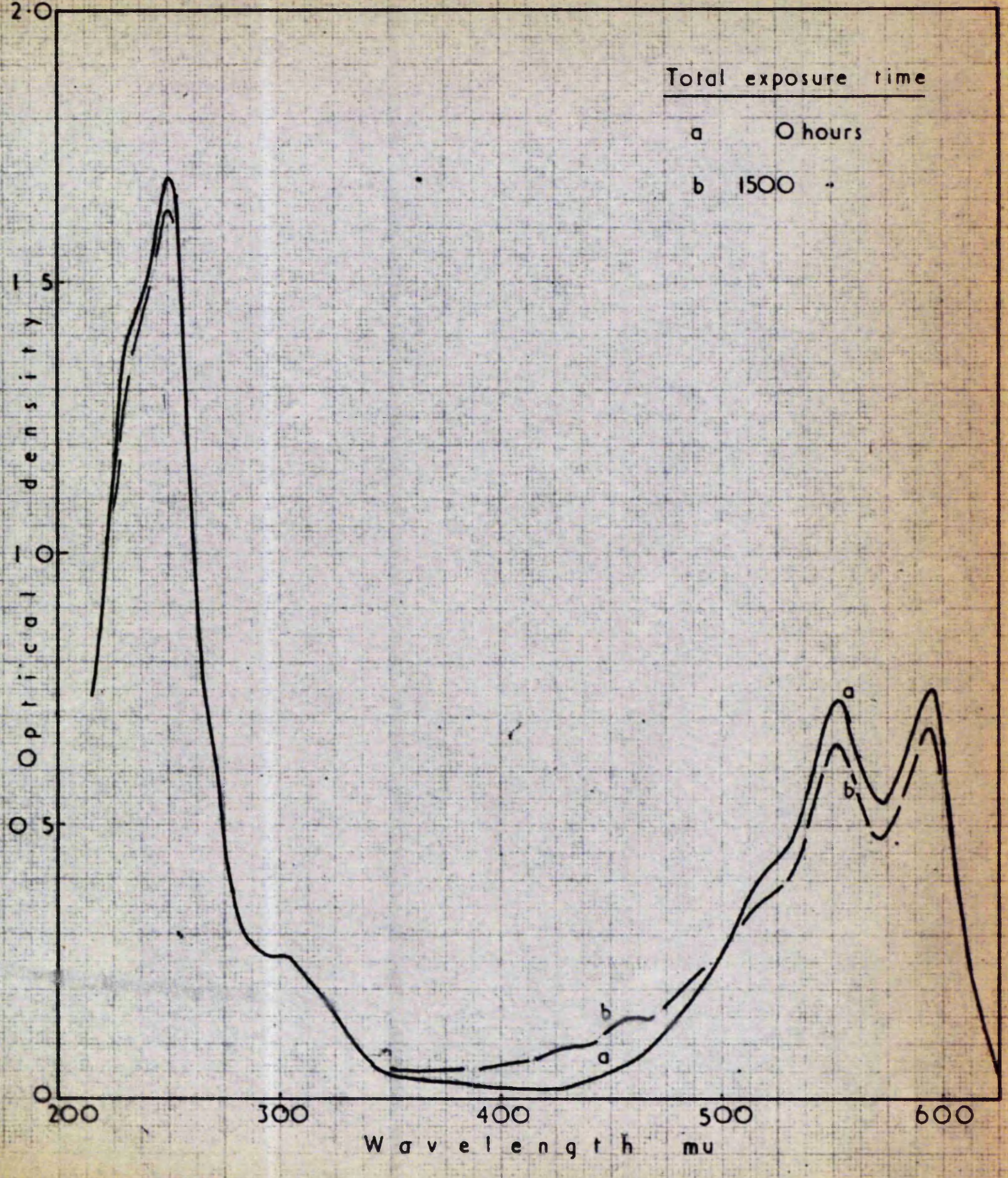
The ethanol solution, (Fig. 35) exhibited great stability on exposure to this lamp. After 1500 hours exposure only a 12% loss was recorded in the absorbance of the bands in the visible region. Coupled with this small loss in intensity there was a slight increase in absorption between 350 and 500 mu. There was also a plateau at 432.5 mu and a small peak at 460 mu together with an inflection at 495 mu. These were approximately the wavelengths of the inflection and two bands observed after exposure of an ethanol solution to short-wave ultra-violet radiation, (Fig.33).

The ethyl acetate solution, (Fig.36), was very much less stable but as with the exposure to the Vitan lamp, (Fig.34), the fading curve was poorly defined. Up to 500 hours exposure a twin band absorbing system was being formed with maxima at about 430 and 452.5 mu but on further irradiation this system lost its character. Progressive irradiation caused a hypsochromic shift in the area of maximum absorption; after 600 hours this was at 427.5 mu, after 800 hours at 400 mu and after 1000 hours at 387.5 mu.

1,4-Diaminoanthraquinone in ethanol

exposed to Osram lamp

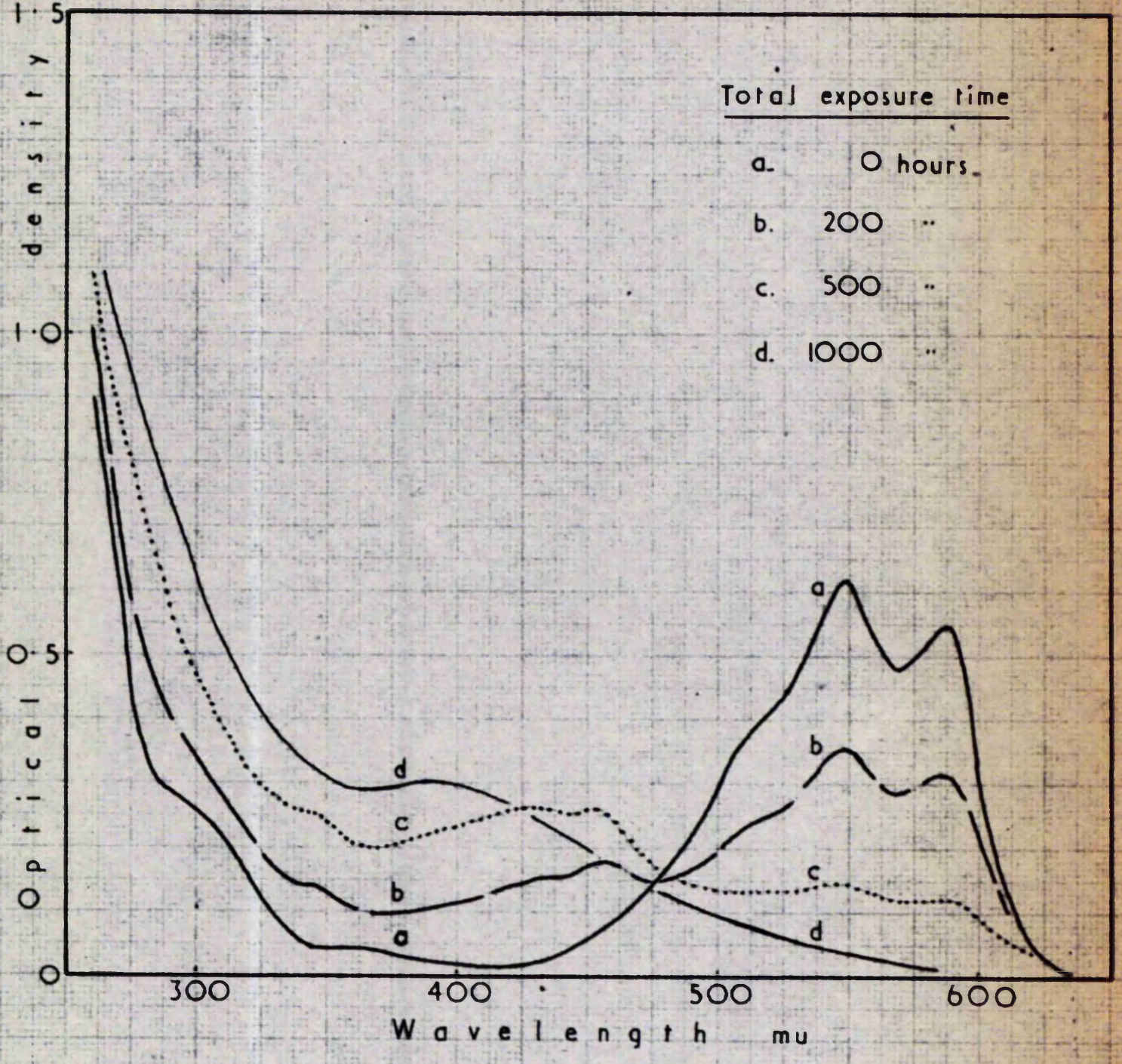
Fig. 35



1,4–Diaminoanthraquinone in ethyl acetate

exposed to Osram lamp

Fig. 36



Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

A lengthy exposure, in oxygen, to the Osram lamp of a dyed cellulose acetate film[5,6] resulted in a slight overall loss of intensity and, more important, in a merging of the twin peaks in the visible region of the spectrum to give a single band at about 550 mu. For nylon a small peak was formed at about 325 mu and there was a progressive loss of spectral character of the twin peak system in the visible which resulted in the formation of a single band with maximum at the shorter wavelength of the twin peaks. The changes in absorption spectrum of the dyed film of the N-methoxymethyl nylon were more profound in that absorption between 250 and 500 mu increased slightly as the twin peak system between 550 and 600 mu was degraded. A progressive hypsochromic shift was observed of the latter system after the longer wavelength band had almost completely been destroyed. The new band maximum was located at about 535 mu. The fading in solution was therefore markedly different from the fading of the dyed polymer films.

The effect of solvent impurities on the fading of 1,4-diaminoanthraquinone in ethanol by a Vitan lamp.

Rigorous efforts were made to ensure that the solvents used in all experiments were of the same quality and as pure as possible. The purification of ethanol is not easy as in an anhydrous condition it is extremely hygroscopic. It is difficult to see how the presence of water in ethanol, even in only fractions of a per cent, can be entirely eliminated where the making up of a dye solution to a required strength is involved. It was therefore considered important to observe the effect on the light fading of an ethanol solution of a dye in the presence of water.

The drying of ethanol is carried out commerically by azeotropic distillation with benzene. The presence of benzene to any extent can severely alter the ultra-violet transparency of ethanol and Gillam and Stern [58] recommend that benzene should be removed by stirring the ethanol with silica gel. In the present work it was found that in removing aldehydic impurities, also present in the ethanol, by refluxing for several hours in the presence of caustic soda and distilling through an efficient column much of the benzene was removed. Treatment with silica gel was not found to be really effective in removing the final traces of benzene and it was also thought that its use could introduce further impurities which might be less easy to remove and vary from batch to batch. It was for this reason that caustic soda was used in preference to 2,4-dinitrophenylhydrazine for the removal of aldehydic impurities. Multiple fractional distillations, while taking a considerable time, were found to remove completely all traces of the benzene absorption bands in the region of 255 mu for a 4 cm light path. In view of the lack of detailed

SOLUTION	WAVELENGTH OF ABSORPTION MAXIMA mu						Fig.
ETHANOL + 10% WATER	*Inflection						No.
Original				522.5 *	552.5	597.5	37
Exposed to Vitan		345	365	437.5 *	457.5	487.5	37
ETHANOL + 10% BENZENE							
Original				522.5*	552.5	592.5	38
Exposed to Vitan	335	350	370	437.5*	457.5	487.5	38

TABLE V

1,4-DIAMINOANTHRAQUINONE

information on the absorbance of ethanol in this wavelength region it was considered reasonable to assume that the absorbance giving an estimated maximum concentration of benzene of 1 in 70,000, referred to in the experimental section on solvents, was in fact due mainly to the ethanol and it was possible that benzene was completely absent. It was thought that photochemical studies of ethanol dye solutions where significant quantities of benzene were present might show differences to studies where it was completely absent. If this were so it was of considerable importance to know what these differences were.

The rate of fading of 1,4-diaminoanthraquinone in ethanol by a Vitan lamp was found to be intermediate between the fastest and slowest rates of those compounds whose fading in ethanol to this radiation source was investigated. It also had a characteristic absorption system in the visible region consisting of twin peaks preceded by an inflection. Its fading product in ethanol also exhibited this unmistakable, characteristic absorption. It was therefore decided to use this compound in studies on the effect of benzene and water on the fading of ethanol dye solutions by a Vitan lamp especially as the fading products would be more readily noticeable than for compounds exhibiting only a single absorption band.

Two ethanol solutions of the dye were made up, one of which contained 10%, v/v, benzene and the other 10%, v/v, distilled water. They were degassed and scaled off in the normal manner. Their spectra were measured against pure ethanol in the wavelength region 300 to 800 mu. Experimentally it would have been extremely difficult to seal off identical comparison solvent blanks since the amount of evaporation of the solvent

during degassing could not be controlled to the fine limits required. The positions of the band maxima for these solutions are given in Table V. They do not differ from the locations of the same bands in pure ethanol (Table IV). These solutions were exposed only to the Vitan lamp.

The rate of destruction of the peaks in the visible region on exposure was found to be much greater for the solution containing water (Fig.37) than that containing benzene (Fig.38). Furthermore, the rate of fading of the ethanol/water solution was much faster than that of the solution containing no added water (Fig.33). The time taken to produce 50% degradation of the band at 557.5 mu was 1.5 minutes for the ethanol/water solution, 18 minutes for the untreated solution and 47.5 minutes for the ethanol/benzene solution (Fig.32). Similar fading rates were observed for the band at 592.5 mu.

New absorption maxima were recorded for all three solutions, after exposure, at 437.5 (inflection), 457.5 and 487.5 mu and in this respect the fading was not different. However additional maxima were built up in the ethanol/water and ethanol/benzene solutions. In the former(Fig.37) solution weak peaks were formed at 345 and 365 mu and in the latter (Fig.38) extremely strong bands were created at 335, 350 and 370 mu. After 90 minutes total irradiation of the ethanol/benzene solution the intensities of the two shorter wavelength bands were too great to measure. Previously their shape had strongly resembled that of the characteristic absorption bands of benzene in the 255 mu region. It was thought that they might have arisen through a complex reaction of benzene with ethanol.

From the rate of fading of the ethanol/water solution it seems likely that the water enters directly into the reaction. It is possible therefore that the reaction scheme suggested by Cooper[33] for the photo-sensitised oxidation of aqueous ethanol requires modification to include water. Water increases the rate of light fading of many dyed fabrics yet in the gas phase water is a deactivator of excited states, albeit a poor one. Wells[35] has studied the role of water on the rate of uptake of oxygen by propan-2-ol, containing anthraquinone 2-sodium sulphonate, under the influence of light. He found that for increasing concentration of propan-2-ol the rate of oxygen uptake increased to a maximum but thereafter it decreased. The maximum rate of uptake was found to occur at an alcohol concentration above which the structure of water/alcohol solutions changes markedly[59]. It is possible that in predominantly aqueous media the excited dye is deactivated by water but in predominantly alcoholic media changes in the solvent cage by hydration of the alcohol will aid the attack of the photo-excited sensitiser. Although the system of an anaerobic ethanol dye solution exposed to a Vitan lamp is dissimilar in many respects to the system studied by Wells[35] it is possible that the role of water is the same in both cases. It may be that in the complete absence of water the fading of ethanol dye solutions exposed to a Vitan lamp is very slow, and under these conditions the fading rate may approach that in n-hexane.

The fading of a dye in aqueous ethanol by a Vitan lamp is most probably due to a photosensitised reaction. As benzene absorbs strongly radiation of a wavelength of 253.7 mu a photosensitised reaction involving the fading of a dye in an ethanol/benzene solution is likely

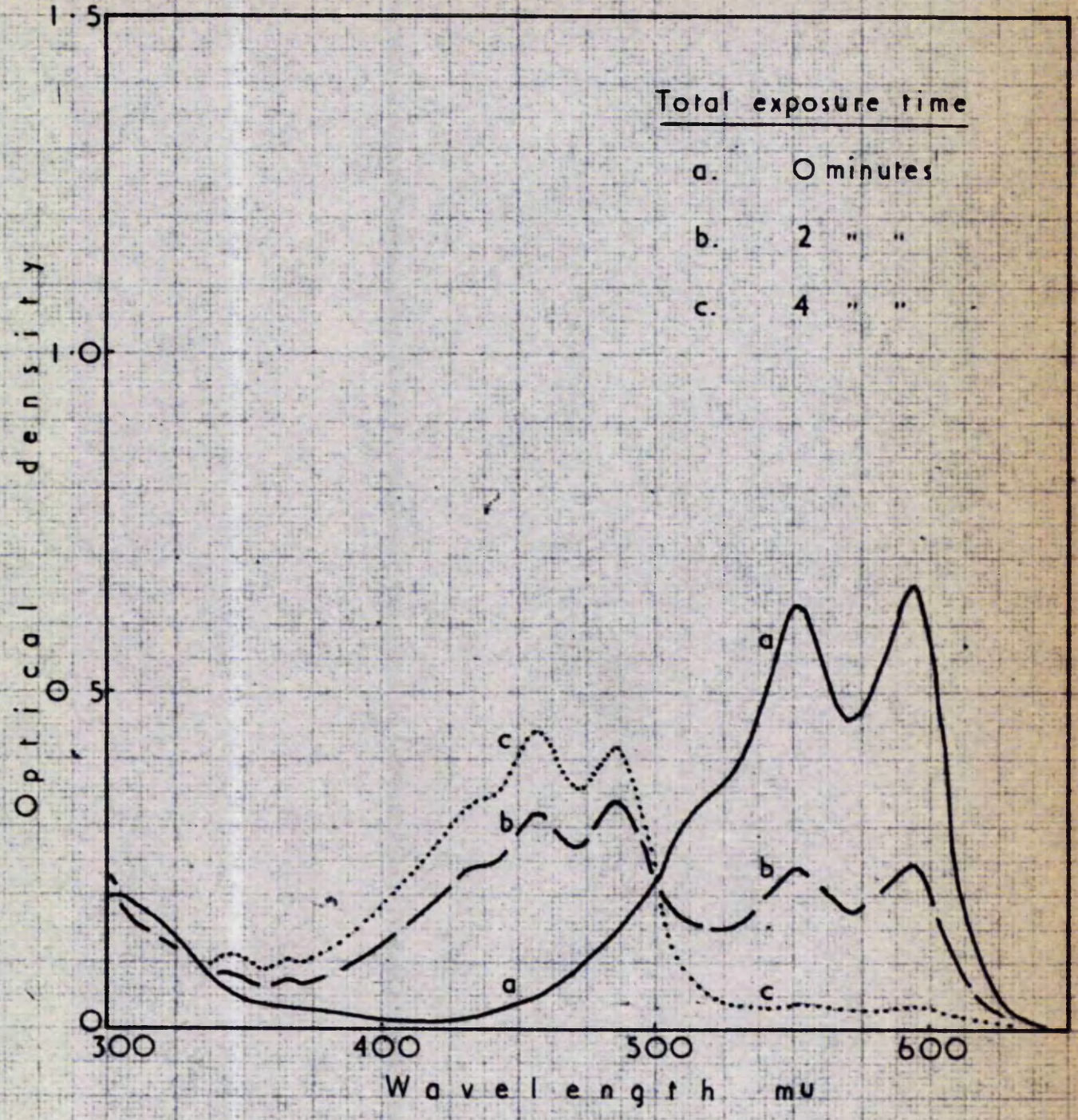
only at the face of the reaction cell exposed to the radiation. The rate of fading of the dye is then dependent on the rate of diffusion of the faded dye molecules into the remainder of the solution and of unaffected molecules to take their place. Other reactions that may occur would involve the photolysis of benzene or an energy transfer from the benzene to the dye followed by hydrogen atom abstraction from the ethanol. Energetically 253.7 mu radiation is not capable of opening the benzene ring directly. Anderton, Chilton and Porter[60] have suggested that the primary reaction of benzene on photolysis in viscous aliphatic solvents is a four centre reaction in which the ring opens and a substituted hexatriene is formed. In fluid solvents polymerisation of these photo-products occurs. The reaction of benzene with ethanol is therefore possible and the bands observed in the 350 mu region after the exposure of the ethanol/benzene dye solution, (Fig.38), may be the result of such a reaction. It is not unexpected that fading of the dye solution is slower in the presence of benzene than in its absence as the radiation is employed for reactions other than direct hydrogen atom transfer.

The unintentional presence of benzene in ethanol in photochemical experiments using 253.7 mu radiation may therefore lead to misleading results both in terms of the rate of reaction and in the photoproducts obtained. There the benzene concentration is low the fading rate may not be greatly affected but the photoproducts formed as a result of benzene photolysis may easily be mistaken for photoproducts from the primary constituents.

1,4-Diaminoanthraquinone in ethanol plus 10% water

Fig. 37

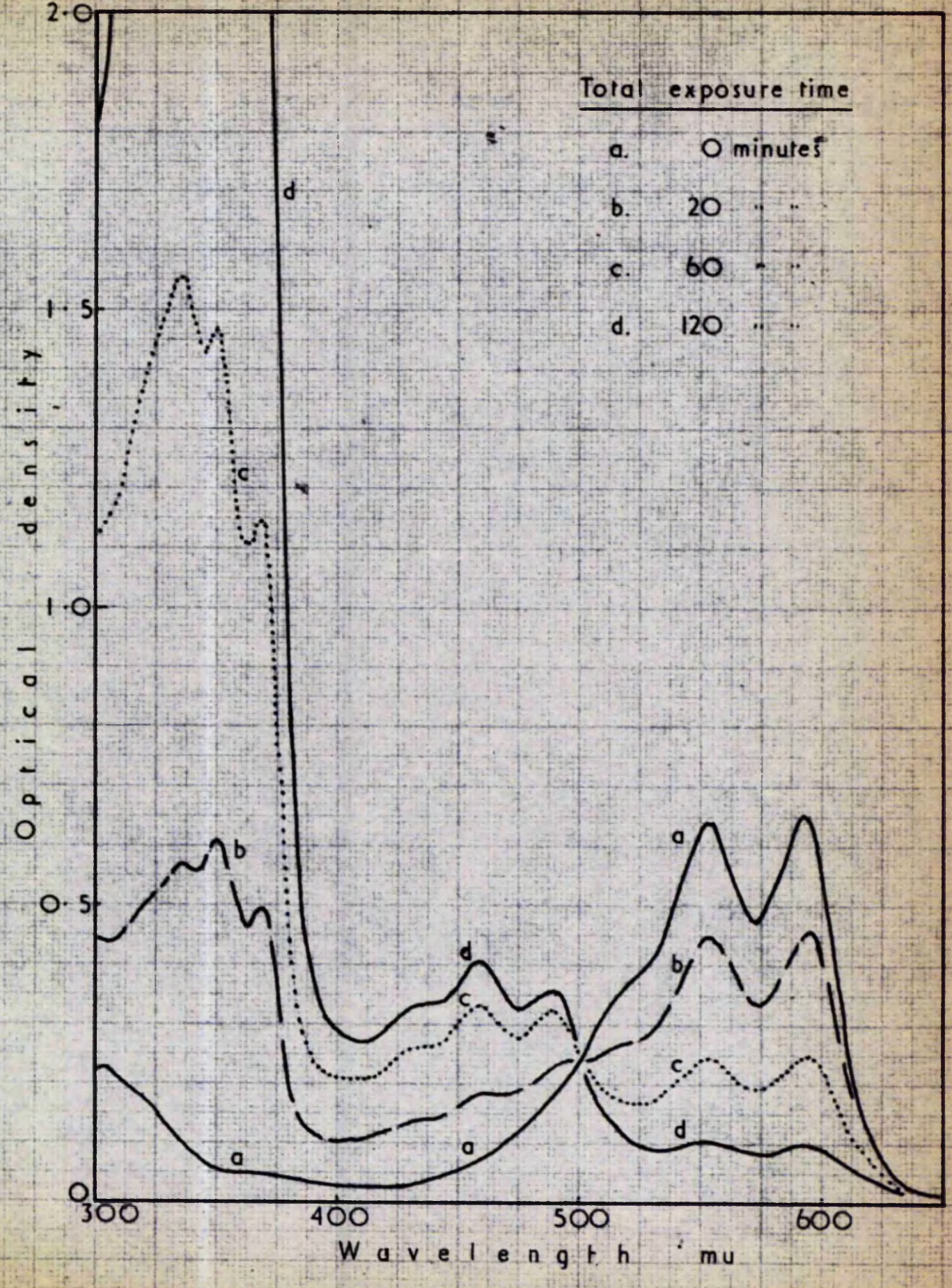
exposed to Vitan lamp



1,4-Diaminoanthraquinone in ethanol plus 10% benzene

Fig.38

exposed to Vitan lamp



1,5-Diaminoanthraquinone

The positions of the band maxima of this compound in ethanol and ethyl acetate together with other data are given in Table VI. The main difference between the spectra of these solutions is that an inflection occurring at 302.5 mu in ethanol exists as a peak at 300 mu in ethyl acetate.

Only one anthrone of 1,5-diaminoanthraquinone exists, it is 1,5-diaminoanthr-10-one.

Fading by Vitan Lamp

As with compounds that have already been dealt with, the rate of destruction of the visible absorption band of 1,5-diaminoanthraquinone was greater in ethyl acetate than in ethanol solution and in this case it was about 6.5 times faster, (Fig. 39). In each solvent new absorbing systems were produced. That in the visible region for the ethanol solution was more complex as more than a single new band was formed.

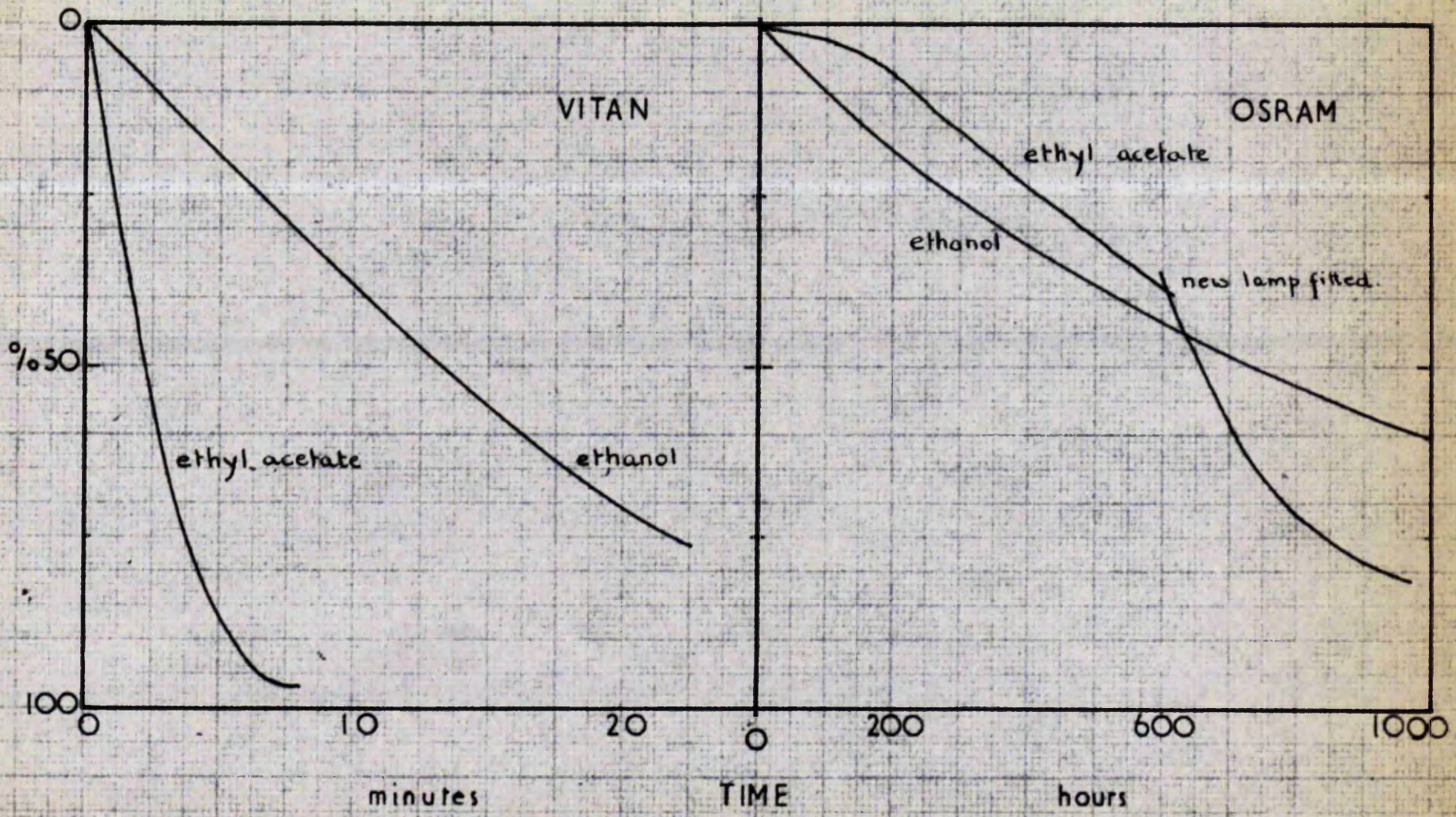
A short exposure of the ethanol solution to this lamp resulted in destruction, but without loss of intensity, of the band at 277.5 mu, (Fig. 40) and the emergence of a new, well defined band at 260 mu. It would seem that this was the result of a bathochromic shift of the band at 232.5 mu since the new band intensified as the latter decreased in intensity on further irradiation. Destruction of the hand at 487.5 mu caused new bands to be formed with maxima at 395, 420 and 447.5 mu, the strongest being that at the shortest wavelength.

The production of these three peaks in the 400 mu region did not occur on irradiating the ethyl acetate solution, (Fig. 41). A single band with maximum at 400 mu was produced, increasing in intensity with

SOLUTION	WAVELENGTH OF ABSORPTION MAXIMA mu						Fig.
ETHANOL	*Inflection						No.
Original	232.5	272.5	302.5*			487.5	40/42
Exposed to Vitan		265		395	420	447.5	40
Exposed to Osram		265		395	420	447.5	42
1,5-Diaminoanthr-10-one	242.5			390			55
ETHYL ACETATE							
Original		275	300			477.5	41/43
Exposed to Vitan		260		400			41
Exposed to Osram		260		397.5			43
1,5-Diaminoanthr-10-one				387.5			55
N-METHOXYMETHYL NYLON							
Original		280	302*			495	Ref.5,6
Exposed to Osram in N_2		265		402.5	437.5	460	

TABLE VI

1,5-DIAMINOANTHRAQUINONE



1,5-DIAMINOANTHRAQUINONE

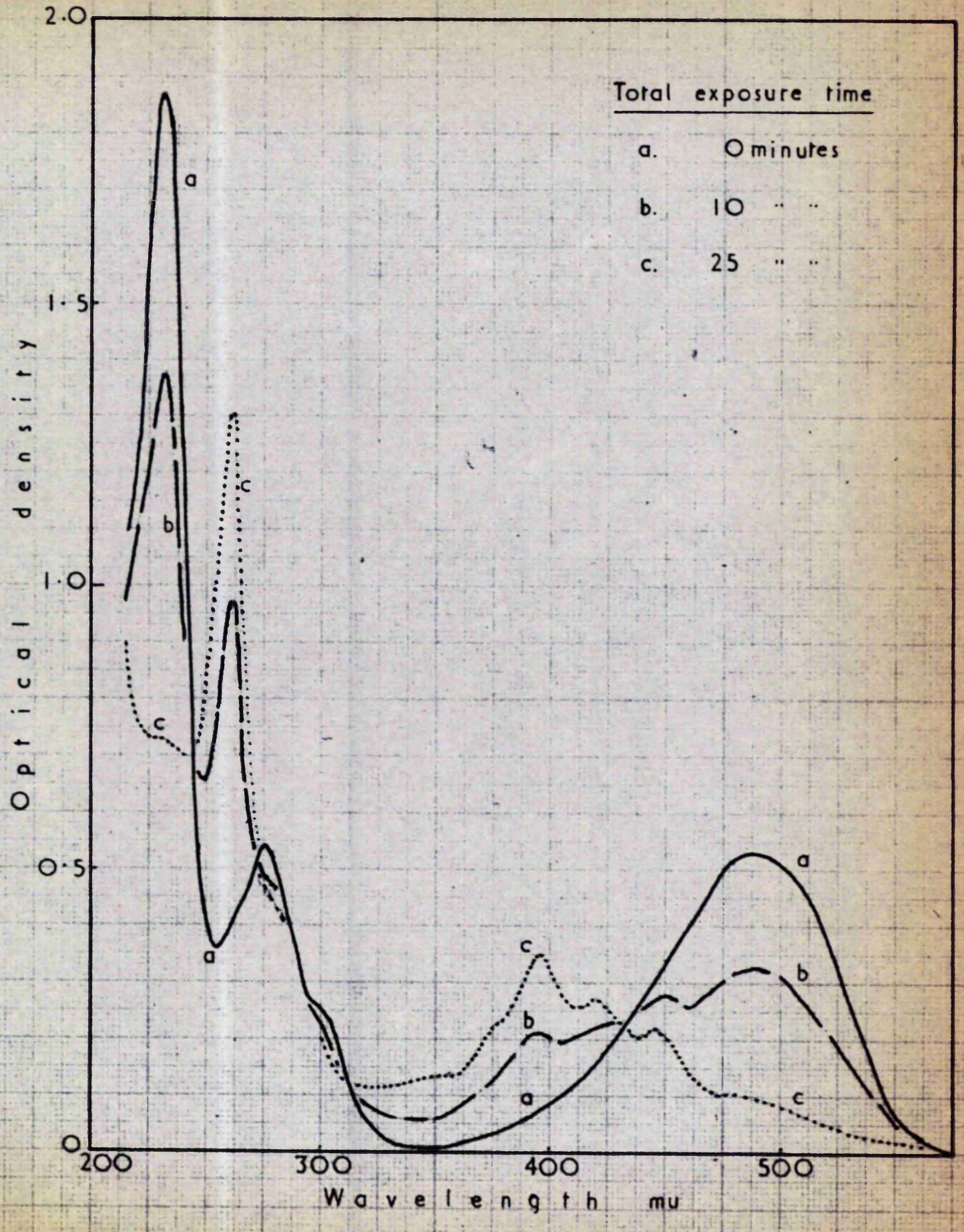
Percentage loss in optical density of the band in the visible region after exposure

Fig. 39

1,5-Diaminoanthraquinone in ethanol

exposed to Viran lamp

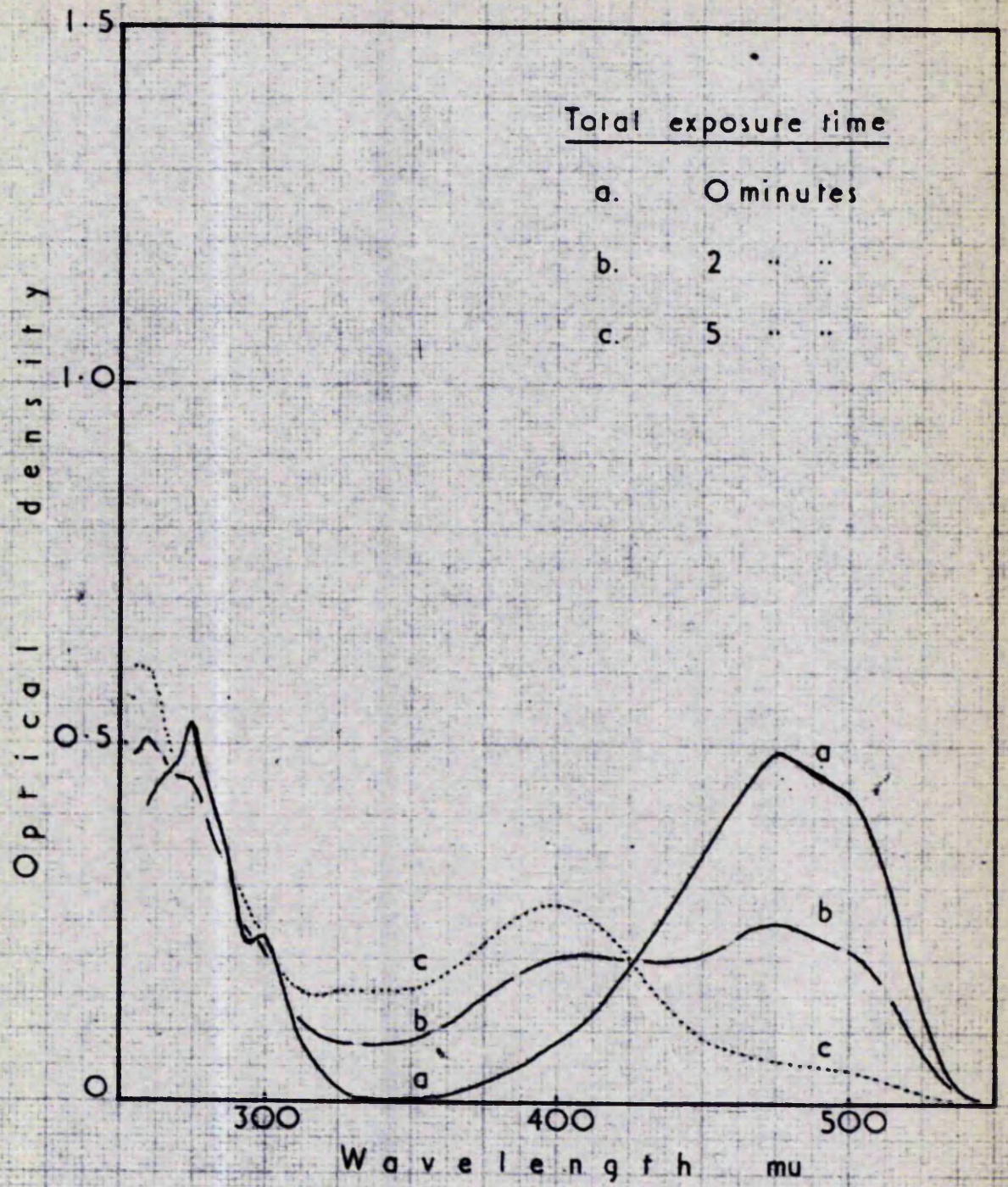
Fig.40



1,5-Diaminoanthraquinone in ethyl acetate

exposed to Vitan lamp

Fig. 41



increased exposure time at the expense of the band at 477.5 mu. The weak band at 300 mu was quickly destroyed. A new peak was formed at 260 mu which increased in intensity with continued irradiation, presumably arising from a bathochromic shift of the peak in the far ultra-violet, as had occurred with the ethanol solution.

Fading by Osram Lamp

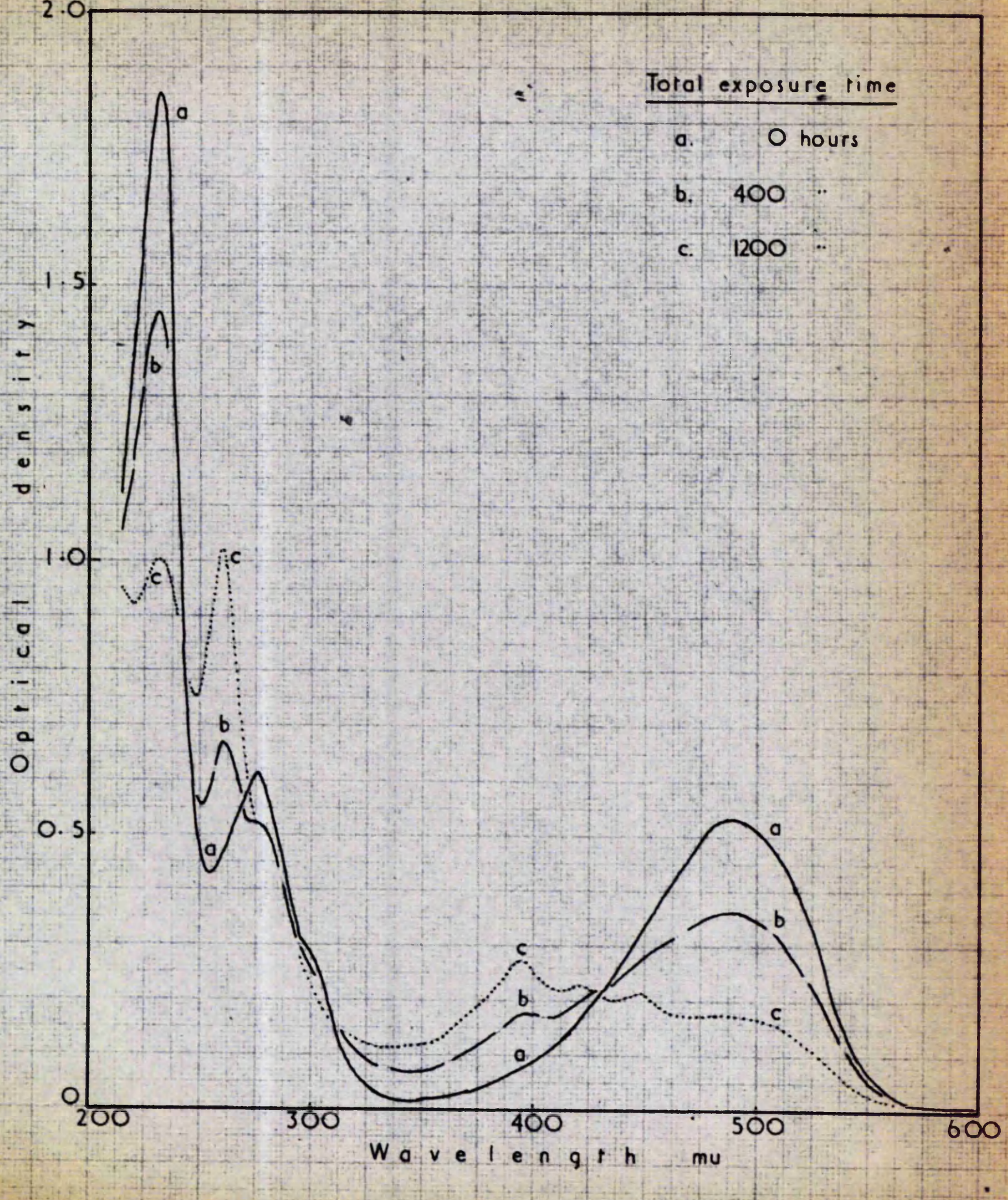
The changes induced in the ethanol solution (Fig. 42) were identical to those reported for the solution exposed to the Vitan lamp. This was not so for the ethyl acetate solution (Fig. 43). The new absorbing system was not nearly so clearly defined. Absorption in the whole of the region from 255 mu to the isobestic point at 425 mu increased. The band formed at 260 mu was first observed as an inflection and was still ill defined after 1000 hours exposure as was also a band formed at approximately 397.5 mu.

The rate of fading of the ethyl acetate solution was somewhat slower than that of the ethanol solution (Fig. 39). After 600 hours exposure of the former solution the lamp was changed and an increase in the fading rate was observed.

1,5-Diaminoanthraquinone in ethanol

exposed to Osram lamp

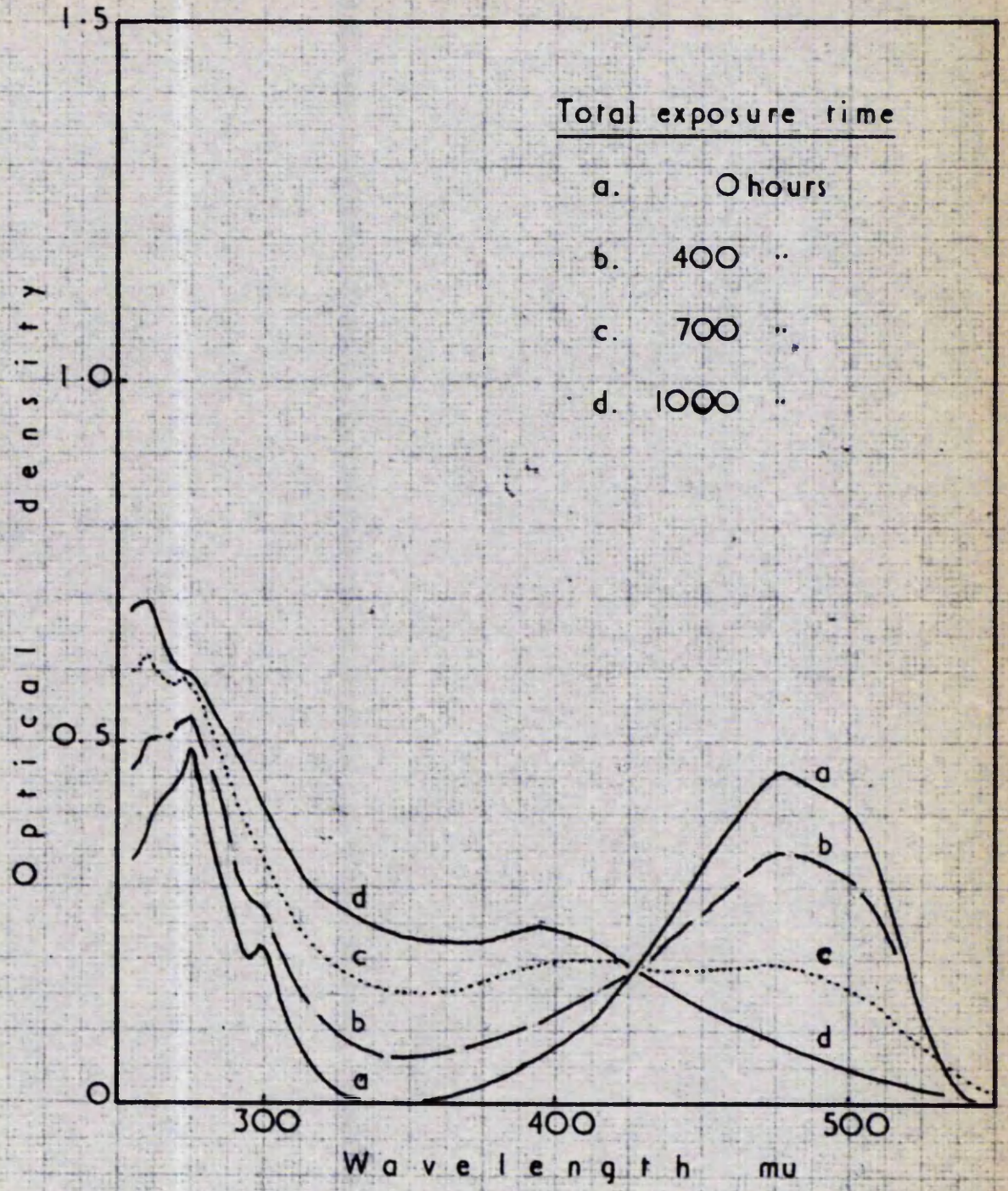
Fig.42



1,5-Diaminoanthraquinone in ethyl acetate

Fig.43

exposed to Osram lamp



Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

The spectra of dyed films of cellulose acetate and nylon showed that on exposure in oxygen to an Osram lamp progressive on tone fading took place[5,6]. The absorption in the region about 350 mu increased slightly for the N-methoxymethyl nylon film and there was also a marked rise at wavelengths below 275 mu. A similar change was noted after 1 minutes exposure of the ethyl acetate solution to the Vitan lamp (Fig.41).

In nitrogen there were spectral changes observed for the cellulose acetate and nylon films which were similar to those occurring in solution. The changes occurring for the nylon film were more noticeable as there was a marked rise in absorption from 250 to 425 mu. Inflections were formed at about 265 and 402.5 mu and these locations corresponded closely to those in ethyl acetate solution exposed to an Osram lamp, (Fig.43). The greatest changes occurred for the N-methoxymethyl nylon film. They were apparently identical to those occurring in ethanol solutions, (Fig. 40,42). Bands were formed with maxima at 265, 402.5, 437.5 and 460 mu. Prolonged exposure was found to suppress the latter two peaks.

2,7-Diaminoanthraquinone

The spectrum of this compound in ethanol differs markedly from the other simple aminoanthraquinone compounds in that the most intense band recorded in the ultra-violet is not that at the shortest observed wavelength. The band maxima positions are given in Table VII.

Theoretically it is possible to prepare two anthrones from 2,7-diaminoanthraquinone. One is the 2,7-diaminoanthr-10-one and the other 3,6-diaminoanthr-10-one. It is to be expected that they will have slightly different absorption spectra. The locations of the peaks for an ethanol solution of 2,7-diaminoanthr-10-one are given in Table VII.

Fading by Vitan Lamp

Up to a total of 30 minutes intermittent exposure carried out over an experimental period of 18 hours the absorption spectra had undergone changes similar to those recorded peviously for other aminoanthraquinone derivatives, (Fig. 44). The most intense band in the ultra-violet region, at 297.5 mu, was slowly degraded on irradiation as were also the bands at 227.5, 345 and 477.5 mu. A new band with maximum at 260 mu was steadily formed, apparently from the band at 227.5 mu. The character of the absorption curve in the region of 395 mu altered, the band maximum at that point moving hypsochromically to about 370 mu. Isobestic points occurred at 240, 357.5 and 387.5 mu.

A post-irradiation effect was observed when the irradiated solutions were stored in the dark for several weeks, and some experiments were carried out to study this effect. After 30 minutes exposure the cell was stored in the dark for four weeks and then the absorption spectrum remeasured, (Fig. 45). It was found that the new curve passed through

SOLUTION ETHANOL	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original	227.5		297.5	345	395	477.5	44/45
Exposed to Vitan		255	297.5			370	44
Exposed to Osram		250	315*			362.5	45
2,7-diaminoanthr-10-one		251	317.5*			362.5	56

TABLE VII

2,7-DIAMINOANTHRAQUINONE

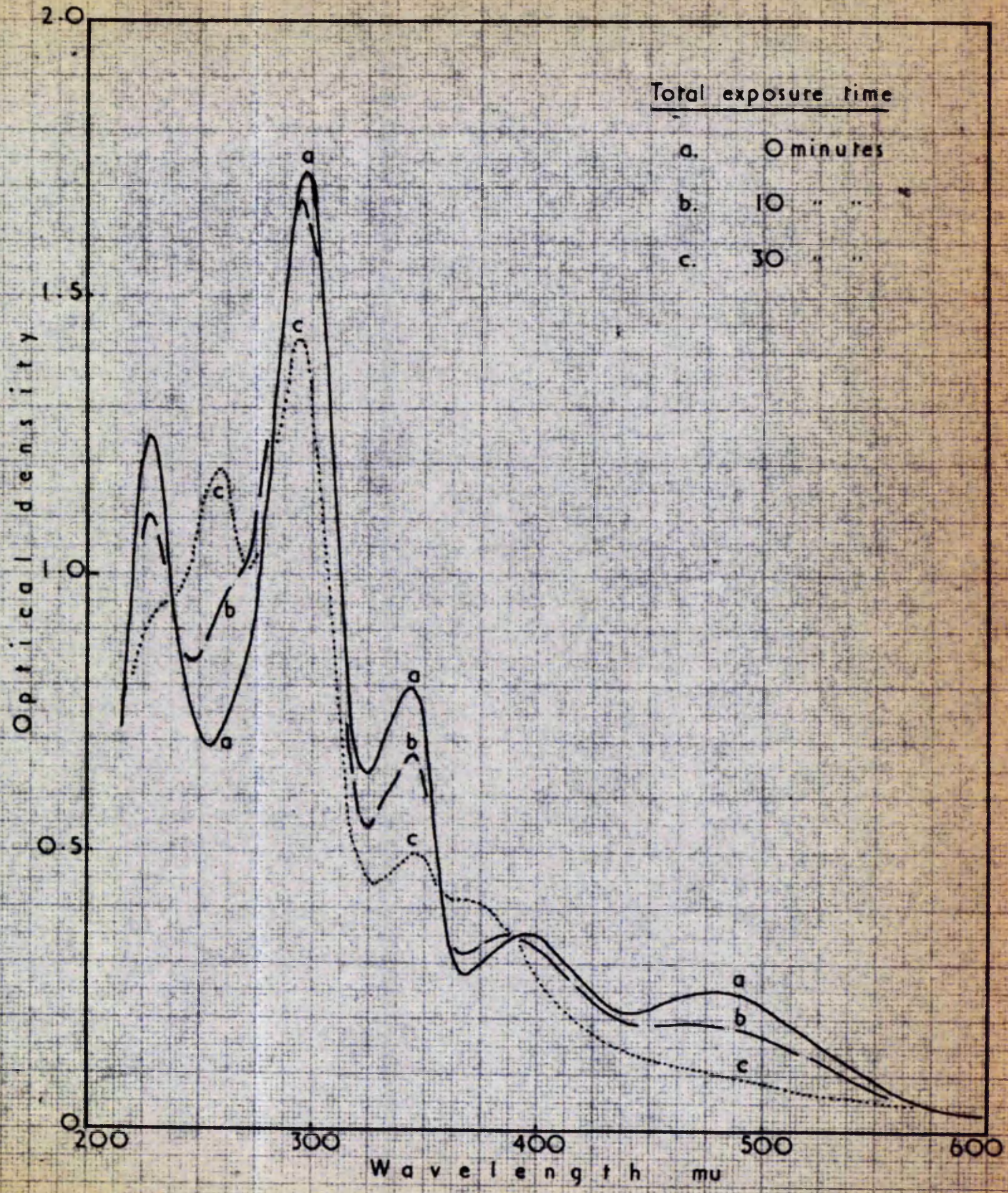
none of the isobestic points on the previous curves. The absorption at 297.5 mu had fallen by about 40% while that between 325 and 425 mu. The band appearing around 370 mu had intensified and centred on 372.5 mu and was then of comparable intensity to the band at 350 mu which had also intensified.

A further five minutes irradiation reversed these trends to a limited extent. The band height of the peak at 295 mu increased by 10% which was the reverse effect of irradiation up to storing. The bands at 350 and 372.5 mu, however, became less intense. On storing the cell in the dark and measuring the absorption spectra at weekly intervals it was found that changes, similar to those recorded after the first storage were still taking place after three weeks. There was a progressive loss of absorption at 295 mu and a slight increase in the region 325 to 400 mu. In addition the maximum at 350 mu existed only as an inflection. New isobestic points also existed at 270, 315, 355 and 400 mu.

2,7-Diaminoanthraquinone in ethanol

exposed to Vitan lamp

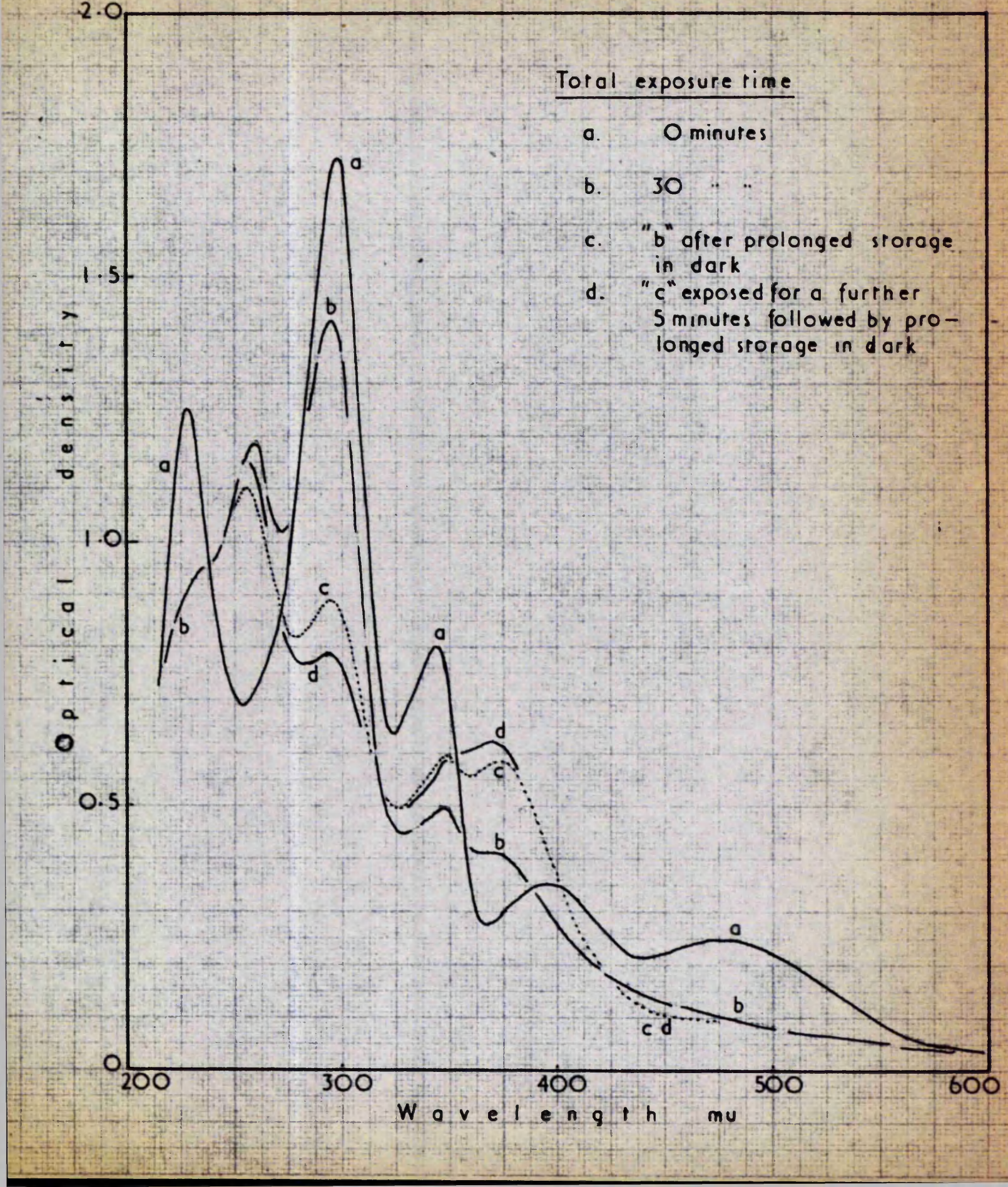
Fig. 44



2,7-Diaminoanthraquinone in ethanol

exposed to Vitan lamp

Fig.45



Fading by Osram Lamp

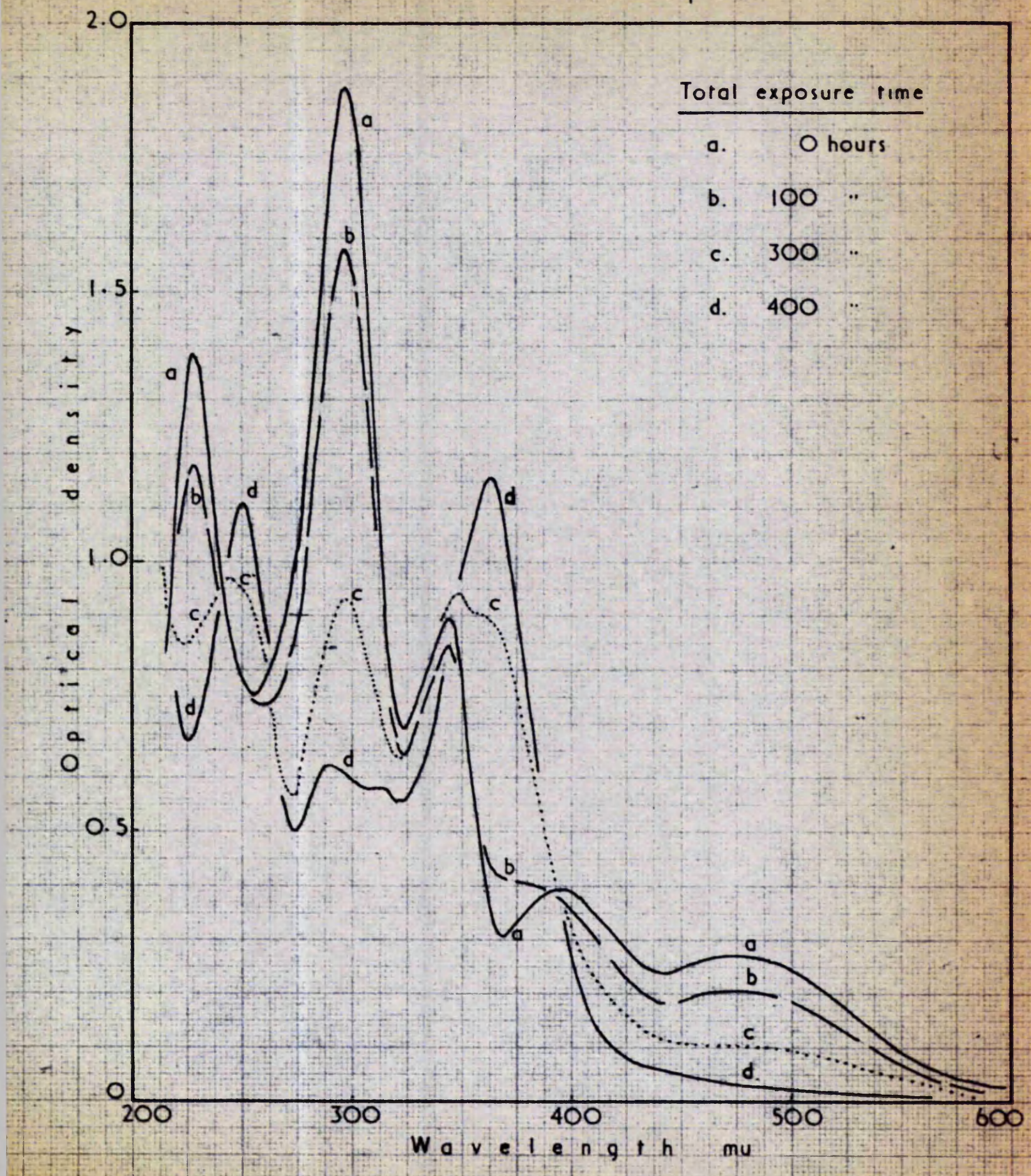
In view of the post-irradiation effect observed when the ethanol solution exposed to the Vitan lamp was stored exposures to the Osram lamp were made as continuous as was practical. The spectral changes were very similar to those recorded for the solution exposed to short-wave ultra-violet radiation. Bands were formed with maxima at 250 and 362.5 mu, the latter being more intense. Again it seemed that the short-wavelength band was the result of a bathochromic shift of the band originally located at 227.5 mu. The peak in the near ultra-violet was formed after absorption in the region of 375 mu had so increased that the peak at 345 mu merged with it, (Fig. 46)

Storage in the dark of the solution after a total of 400 hours exposure caused no alteration to the spectrum.

2,7-Diaminoanthraquinone in ethanol

exposed to Osram lamp

Fig.46



1,4,5-Triaminoanthraquinone

The absorption spectrum in ethanol strongly resembles that of 1,4-diaminoanthraquinone in the same solvent. The band maxima are located at the positions given in Table VIII.

Fading by Vitan Lamp

The exposure to short-wave ultra-violet radiation of an ethanol solution of this compound caused a progressive degradation of the bands at 237.5, 565 and 605 mu, (Fig. 47), but they did not lose their spectral character completely until after a total exposure of one hour. During destruction of the original absorbing system a new one was set up which, in the visible part of the spectrum, corresponded exactly to that of the original solution. An inflection existed at 455 mu and peaks at 475 and 507.5 mu. A band was also created with its maximum at 280 mu together with another at 255 mu. An isobestic point existed at 520 mu.

Fading by Osram Lamp

It was found extremely difficult to keep 1,4,5-triaminoanthraquinone in solution when exposing an ethanol solution to the Osram lamp. Part of the fading, (Fig. 48), must be accounted for by a certain degree of permanent adsorption on to the quartz stem of the absorption cell. However alterations to the absorption spectrum were observed on irradiation which were identical to those recorded for exposure of a similar solution to the Vitan lamp. New peaks were observed in the regions of 475 and 510 mu after 1300 hours exposure.

1,4,5-TRIAMINOANTHRAQUINONE

SOLUTION ETHANOL	WAVELENGTH OF ABSORPTION MAXIMA mu *Inflection						Fig. No.
Original	237.5	260*	292.5*	532.5*	565	605	47/48
Exposed to Vitan		255	280	455*	475	507.5	47
Exposed to Osram				457.5*	475	510	48

1,4,5,8-TETRAMINOANTHRAQUINONE

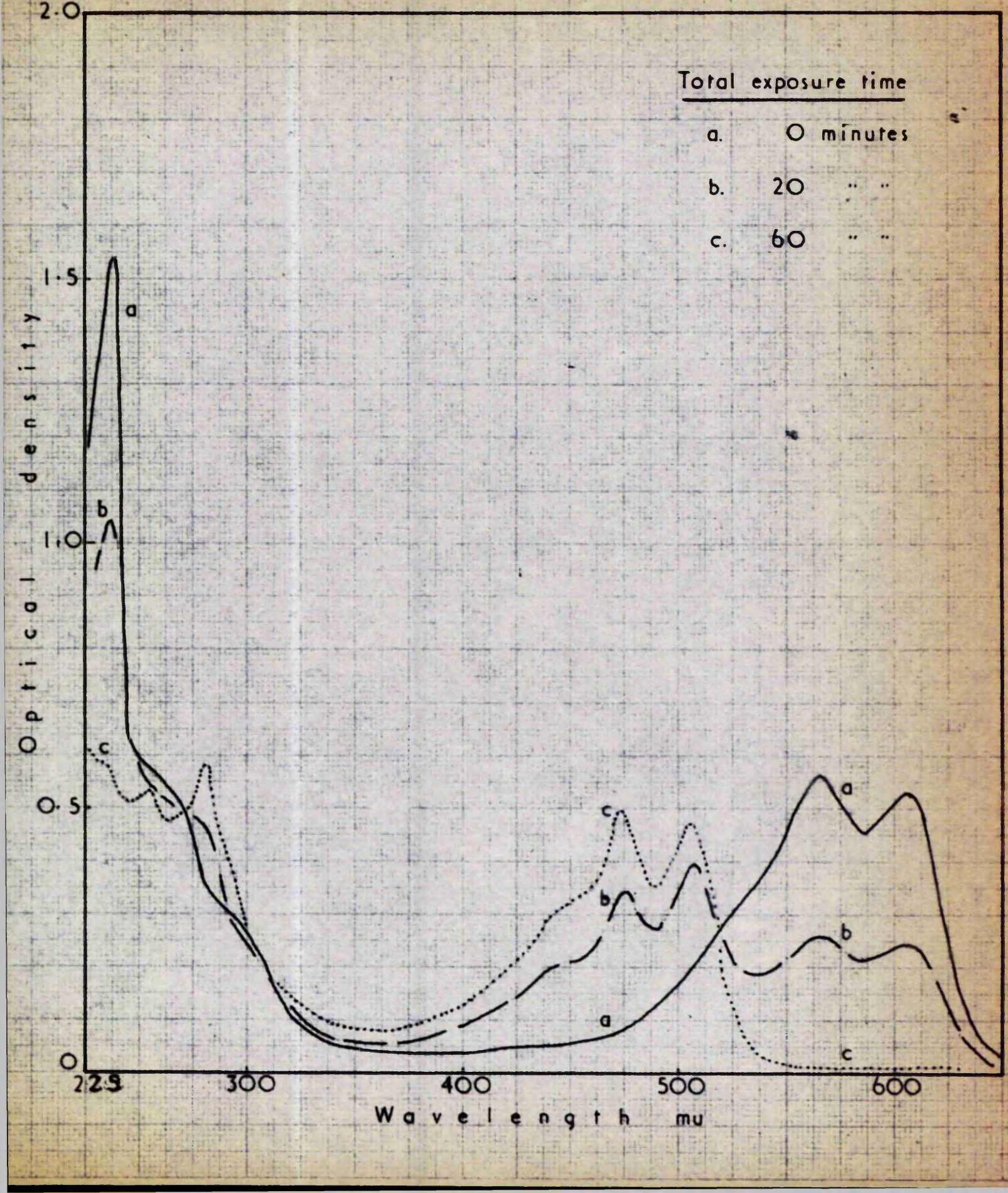
ETHANOL							
Before exposure to Vitan	240	270	307.5*	545*	585	627.5	49
Before exposure to Osram	237.5	270	307.5*	545*	585*	640	51
Exposed to Vitan	240	280		462.5*	485	520	49

TABLE VIII

1,4,5-Triaminoanthraquinone in ethanol

exposed to Vitan lamp

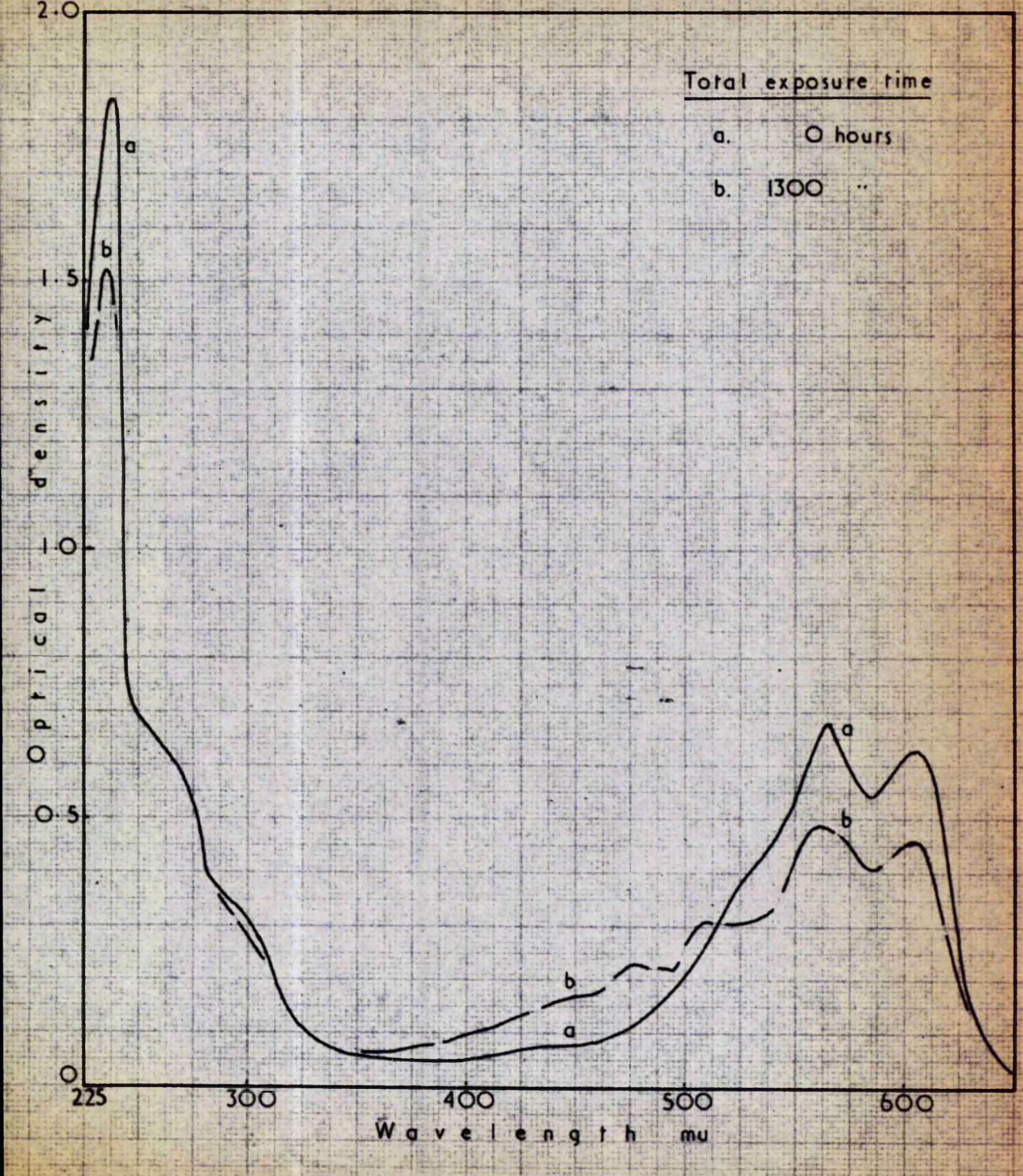
Fig. 47



1,4,5-Triaminoanthraquinone in ethanol

exposed to Osram lamp

Fig. 48



Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

The fading of films of cellulose acetate, nylon and N-methoxymethyl nylon, dyed with 1,4,5-triaminoanthraquinone, on exposure to an Osram lamp in an atmosphere of oxygen was found [5,6] to be spectrally very similar to that recorded for these films dyed with 1,4-diaminoanthraquinone. The first two films showed slight increases in absorbance between 300 and 450 mu on exposure and a greater increase was recorded for the N-methoxymethyl nylon film. The twin peak system occurring between 550 and 650 mu was progressively degraded, the longer wavelength band being more sensitive. For cellulose acetate and nylon this system remained after a long exposure only as an ill defined band with maximum at the shorter wavelength. For N-methoxymethyl nylon, however, was located at 550 mu and not at 575 mu. These changes are completely dissimilar to those occurring in solution where a new absorbing system in the visible region, identical to the first, was set up. Fading of the original twin peak system occurred without loss of spectral character.

1,4,5,8-Tetraminoanthraquinone

There were differences existing in the spectra of the two ethanolic solutions used. The solution exposed to the Vitan lamp (Fig. 49) exhibited a peak at 585 mu which occurred only as an inflection in the solution exposed to the Osram lamp (Fig. 51). The longest wavelength peak was located at 627.5 mu for the solution exposed to the Vitan lamp and at 640 mu for the other. Two absorption maxima existed in the ultraviolet region. The most intense was located at 240 mu and the weaker at 270 mu. The positions of these peaks are summarised in Table VIII.

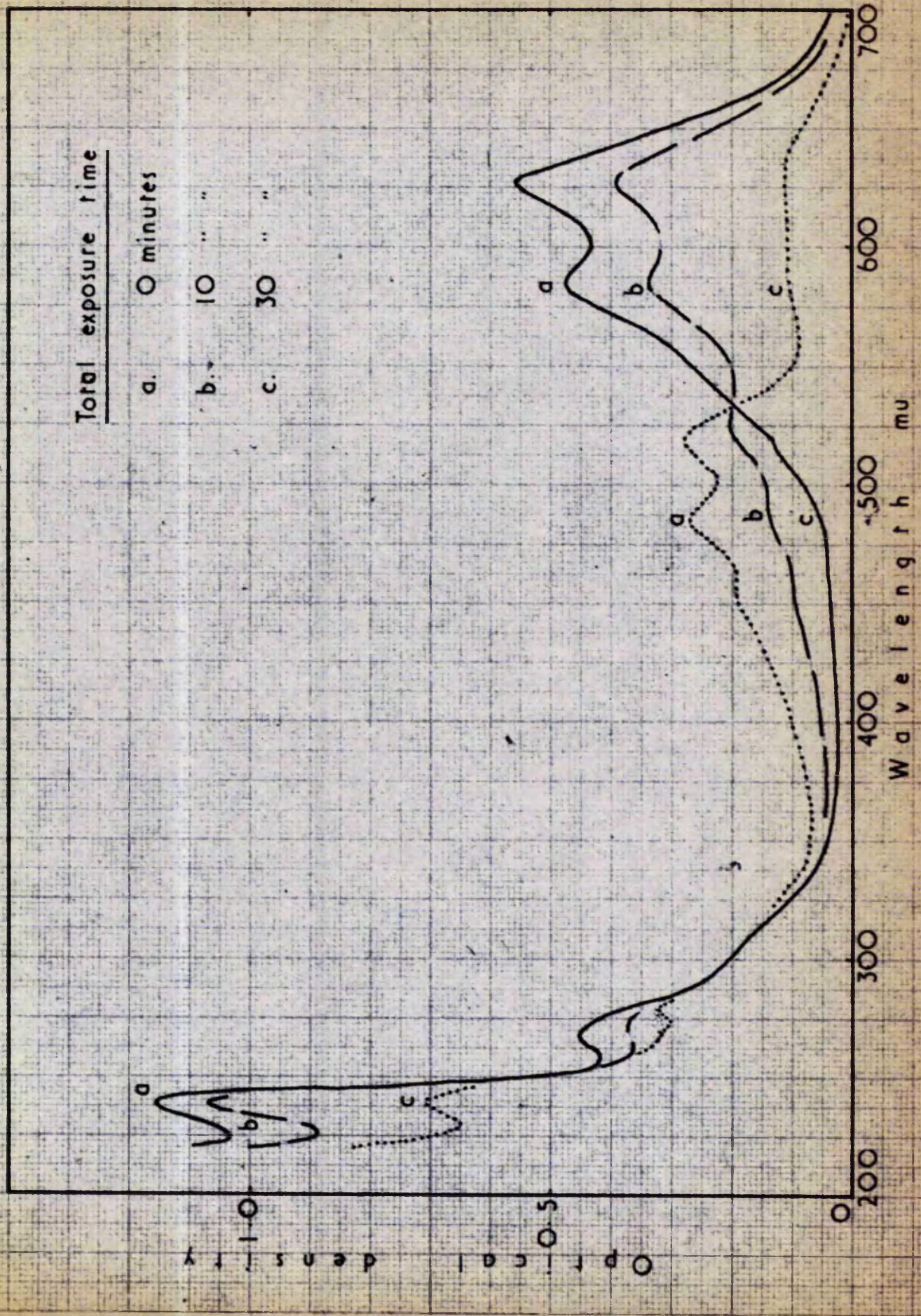
Fading by Vitan Lamp

On exposure to this radiation source similar changes in the absorption spectrum of the ethanol solution were observed, (Fig. 49) to those recorded for 1,4-substituted aminoanthraquinone compounds. The original bands in the visible part of the spectrum were slowly destroyed but maintained their spectral character, while new peaks were formed at 485 and 520 mu. An inflection was produced at 462.5 mu and an isobestic point at 535 mu. The bands at 240 and 270 mu were steadily degraded, little original structure remaining after 60 minutes irradiation. The latter peak appeared to undergo a bathochromic shift to 280 mu. After a total of 120 minutes exposure, (Fig. 50) the new twin peaks in the visible region had merged, together with a slight loss in intensity, while the band at 240 mu existed only as an inflection at about 237.5 mu.

1,4,5,8-Tetraminoanthraquinone in ethanol

exposed to Vitan lamp

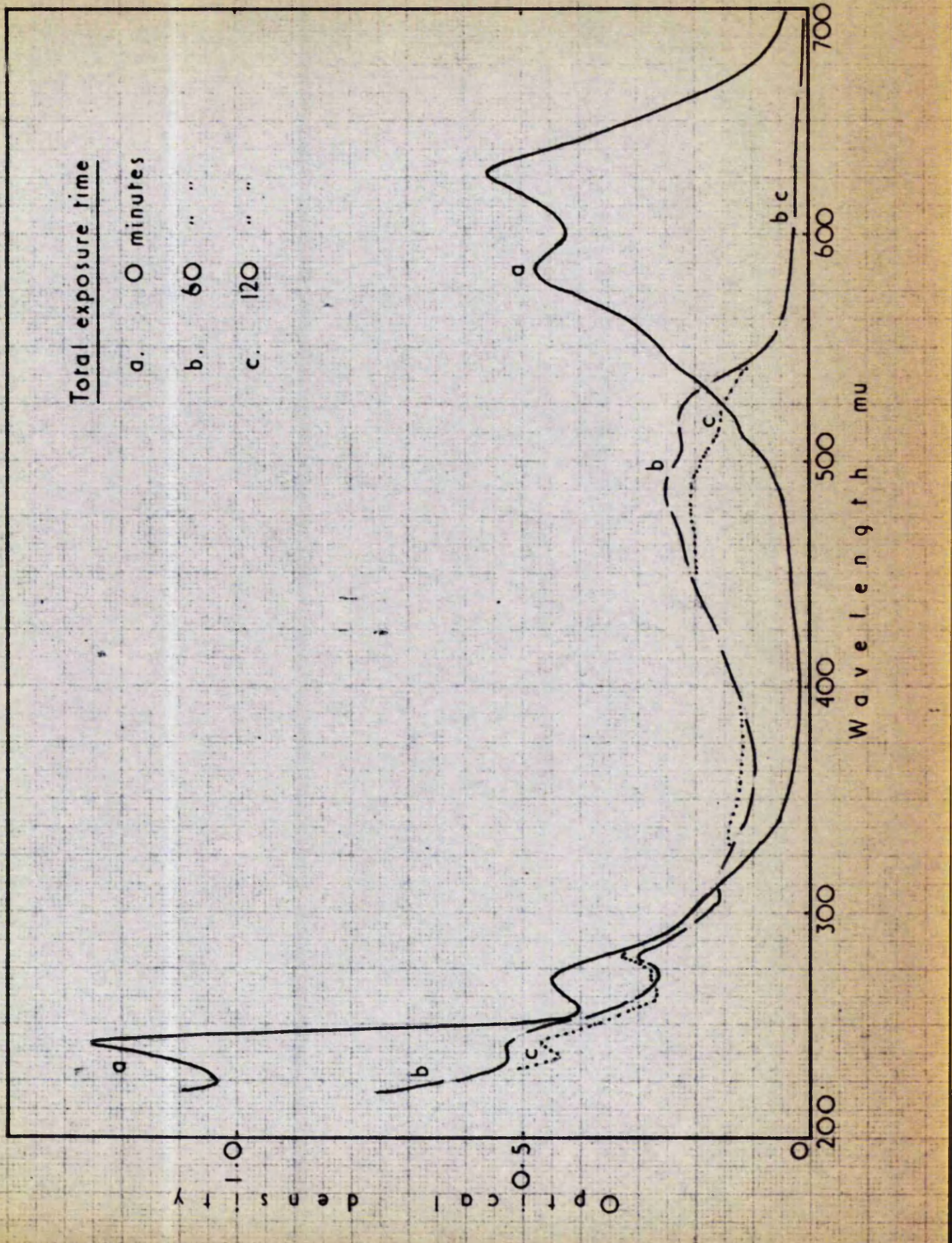
Fig. 49



1,4,5,8–Tetraminoanthraquinone in ethanol

exposed to Vitan lamp

Fig 50



Fading by Osram Lamp

2000 hours exposure to this lamp produced negligible fading. The change

Fading by Osram Lamp

in spec

2000 hours exposure to this lamp produced negligible fading. The change out of solution and depositing itself on the stem of the cell from which it was extremely difficult to remove and redissolve.

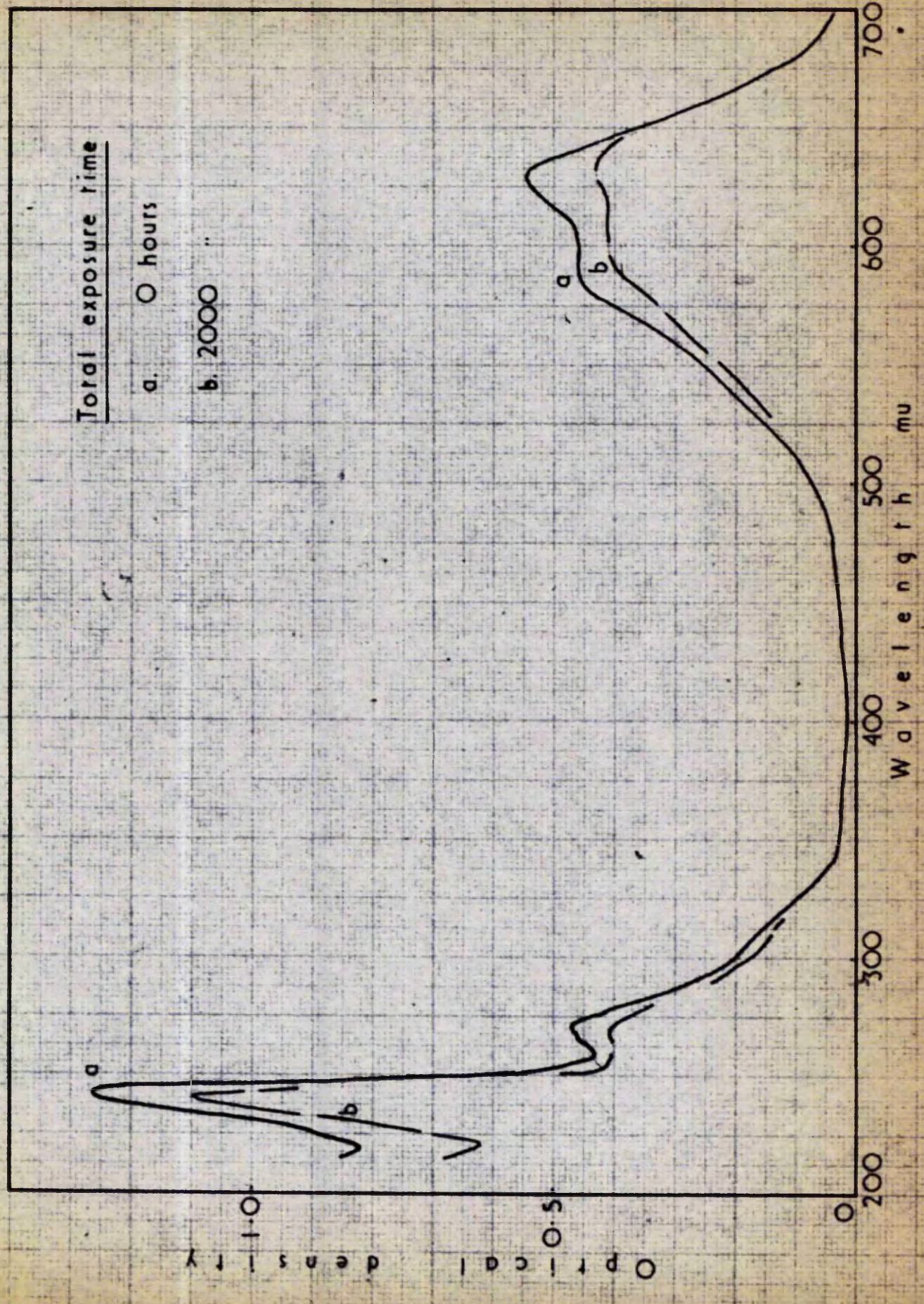
Comparison of the changes in absorption spectra taking place on irradiation of degassed solutions and dyed polymer films.

The fading of dyed polymer films on exposure to an Osram lamp in an atmosphere of oxygen, observed by Egerton and Roach [5,6], does not resemble that occurring in solution. A new absorbing species was produced in solution but the films exhibited only progressive loss of absorption. As was noted for the 1,4- and 1,4,5- derivatives on polymer substrates, the twin peak system lost its character to give a single band at the shorter wavelength of the two peaks. Whereas before, N-methoxymethyl nylon in most cases finally exhibited this peak at a shorter wavelength than this, it did not do so in this instance.

1,4,5,8-Tetraminoanthraquinone in ethanol

exposed to Osram lamp

Fig.51



PART II

Absorption spectra of anthrones and their relation to the absorption spectra of the photoproducts.

Since anthrones are capable of tautomerism to give the corresponding anthranol it cannot be certain that the spectra recorded in this section are completely free from anthranol interference. To minimise the possibility of a tautomeric change solutions were prepared in the cold and spectra recorded as quickly as possible afterwards. All the anthrones examined were found to exhibit a marked fluorescence in ethanol but not in ethyl acetate and other non-polar solvents. Anthr-10-one is said to be non fluorescent but it is believed that traces of anthr-10-01 can cause fluorescence to be exhibited by this compound[61].

In general the absorption spectra of the photoproducts were less well defined than the parent compounds and their anthrones. This is probably due to the presence of secondary fading products which would cause an apparent general rise in absorption. They, together with slight changes in the nature of the solvent induced directly by irradiation or as a result of a photo-sensitised reaction, probably modify the observed positions of the band maxima to some extent.

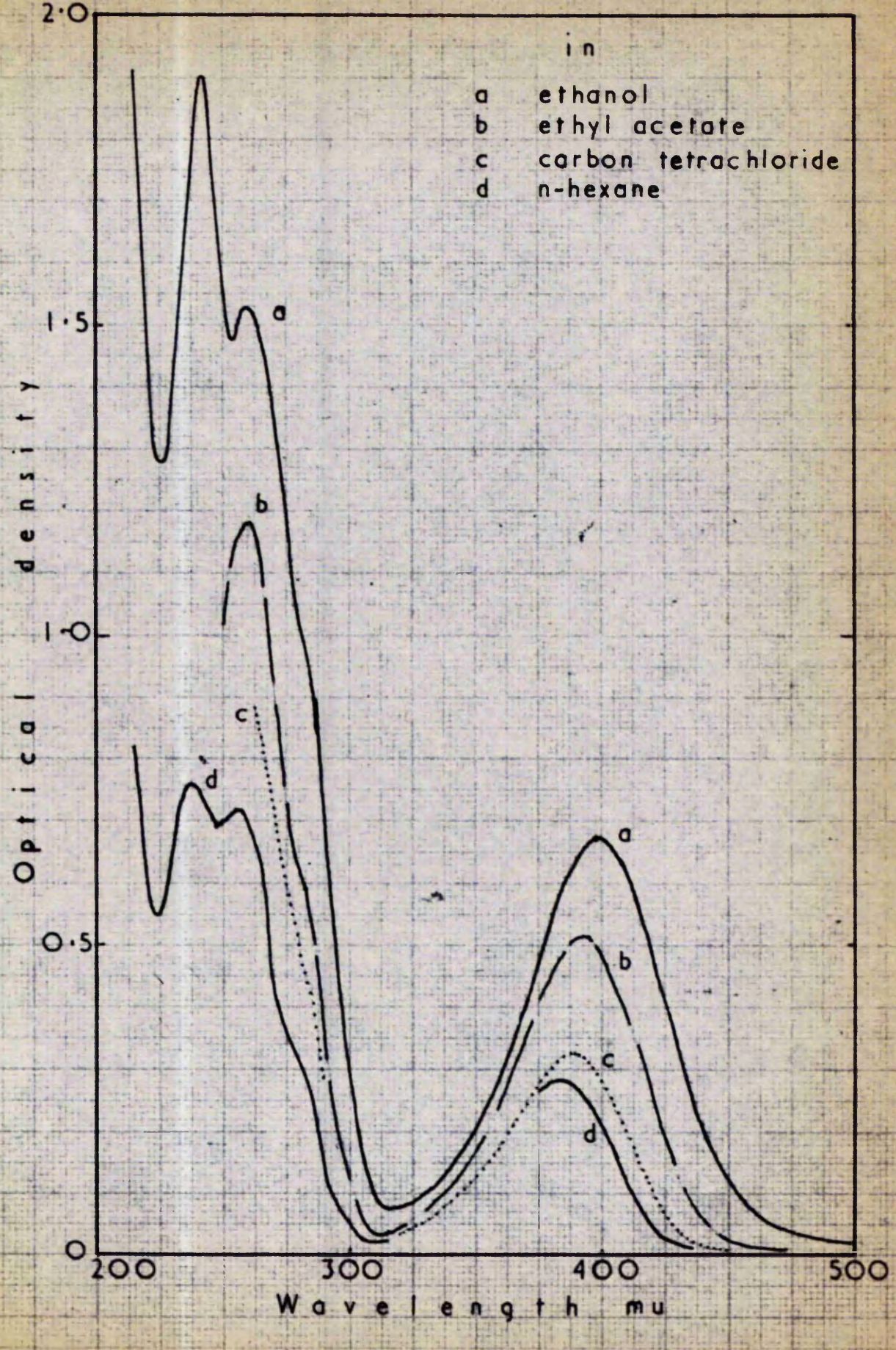
4-Aminoanthr-10-one

The absorption spectra in the four solvents considered, namely ethanol, ethyl acetate, carbon tetrachloride and n-hexane, are given in Fig. 52. In all a sharp band occurs at about 400 mu, depending on the polarity of the solvent. The hypsochromic shift of the visible absorption band of the parent quinone to this wavelength decreases for decreasing polarity of the solvent, from about 4200 cm^{-1} for ethanol to 3700 cm^{-1} for n-hexane. In the two ultra-violet transparent solvents, ethanol and n-hexane, this anthrone is found to exhibit two further peaks. In ethanol they are located at 241 and 260 mu, and in n-hexane at 239 and 256 mu. There is evidence that in ethyl acetate there exists a maximum at 259 mu. A summary of the positions of the band maxima in the various solvents is given in Tables I and II.

Comparing the spectrum in ethanol of the anthrone with that of the fading product 1-aminoanthraquinone in ethanol solution produced by either lamp, it is seen that the ultra-violet region corresponds closely with that of the photoproducts half-way through the total irradiation recorded in Figs. 15, 20. Prolonged irradiation destroyed the similarity since the twin peak system gave way to a single band with maximum at 262.5 mu, midway between the two. Storage of the irradiated solutions led however to a direct or indirect return to the twin peak system depending on the light source. The solution exposed to the Osram lamp, (Fig. 21), also showed a rise in absorption in the region of the original band maximum at 477.5 mu. It was possible that this was due to one of the following:-

4-Aminoanthr-10-one

Fig. 52



(i) reformation of the original compound by a disproportionation reaction,

(ii) tautomeric change of the photoproduct, reversible on re-exposure,

(iii) oxidation of the reduced dye by another photoproduct,

(iv) instability of the photoproduct.

The band maximum of the anthrone at 397.5 mu is 10 mu to longer wavelengths than that of the photoproduct; the peak of the latter under-went no change in position on storage. It has been suggested [44] that the structure of the anthrone obtained by the reduction of a mono-substituted anthraquinone compound with alkaline dithionite depends on the degree of chelation between the substituent and the carbonyl group. Where chelation occurs the carbonyl group removed is that remote from the substituent. It is likely therefore that if an anthrone is formed by the irradiation of an ethanol solution of 1-aminoanthraquinone the isomer favoured is 1-aminoanthr-10-one since there is little, if any chelation between the amino and the carbonyl group in the parent compound. It is to be expected that the absorption band exhibited by 4-aminoanthr-10-one in ethanol at 397.5 mu will for the 1-10-isomer be at a shorter wavelength as the electron donating effect of the substituent will not be so great for the latter form. The anticipated position at a shorter wavelength than 397.5 mu would be nearer to the location of the peak at 387.5 mu for the photoproduct. It is also possible that the photoproduct exists before storage as either the anthranol, anthrahydroquinone or oxanthrone. The first would probably exhibit a band at a shorter wavelength than the corresponding anthrone and it is also likely that the

ultra-violet spectrum would be different from that of the anthrone or the parent quinone and correspond more closely with the ultra-violet spectrum of the fading photoproduct before storage. It is difficult to predict the spectra of the other two reduced forms but it is likely that the positions of the K bands, located at 397.5 mu for 4-aminoanthr-10-one, would be at longer wavelengths. The spectra of the irradiated solutions appear to show bands at about 425 mu which would lend support to this suggestion.

In ethyl acetate it was possible to record only the spectrum above 260 mu with any degree of accuracy, (Fig. 52). The anthrone shows a peak at 392.5 mu, some 5 to 7.5 mu to shorter wavelengths than that of the photoproducts, (Fig. 17, 22). This shift in band location is the reverse of that observed for the ethanol solution.

In carbon tetrachloride the anthrone exhibits a peak at 387.5 mu (Fig. 52) but thiswas not observed in the spectra of the irradiated solutions, (Figs. 18, 23) although absorption in that region was much greater after irradiation than before. If the changes on irradiation so far observed have been due to a process of hydrogen atom abstraction then it is not surprising that the anthrone has not been found to be present in this particular instance.

There was evidence that continued irradiation of the n-hexane solutions of 1-aminoanthraquinone would have led to complete destruction of all the peaks in the far ultra-violet region (Figs. 19, 24). The anthrone shows a twin peak system in this region, one band at 237.5 mu and the other at 255 mu. These locations are close to those of the corresponding peaks

of the unreduced form. The photoproducts also show an absorption band at about 392.5 mu which is some 10 mu to longer wavelengths than the corresponding peak in the anthrone. This difference is comparable to that observed for the ethyl acetate solutions.

The fading product, observed by Egerton and Roach[5,6], resulting from the exposure in nitrogen of a film of N-methoxymethyl nylon dyed with 1-aminoanthraquinone to an Osram lamp, as stated earlier, bore a strong resemblance to the initial fading products in ethanol solution. The spectra of these products at that stage were also very similar to that of the anthrone in the same solvent. It cannot be certain, however, that the spectrum shown is not the resultant of two absorbing systems as is likely for the ethanol solutions. The position of the absorption band is at a shorter wavelength than would have been expected from the relative positions of the K bands of the parent quinone in ethanol and N-methoxymethyl nylon and thus exhibited behaviour similar to that occurring for the irradiated ethanol solutions.

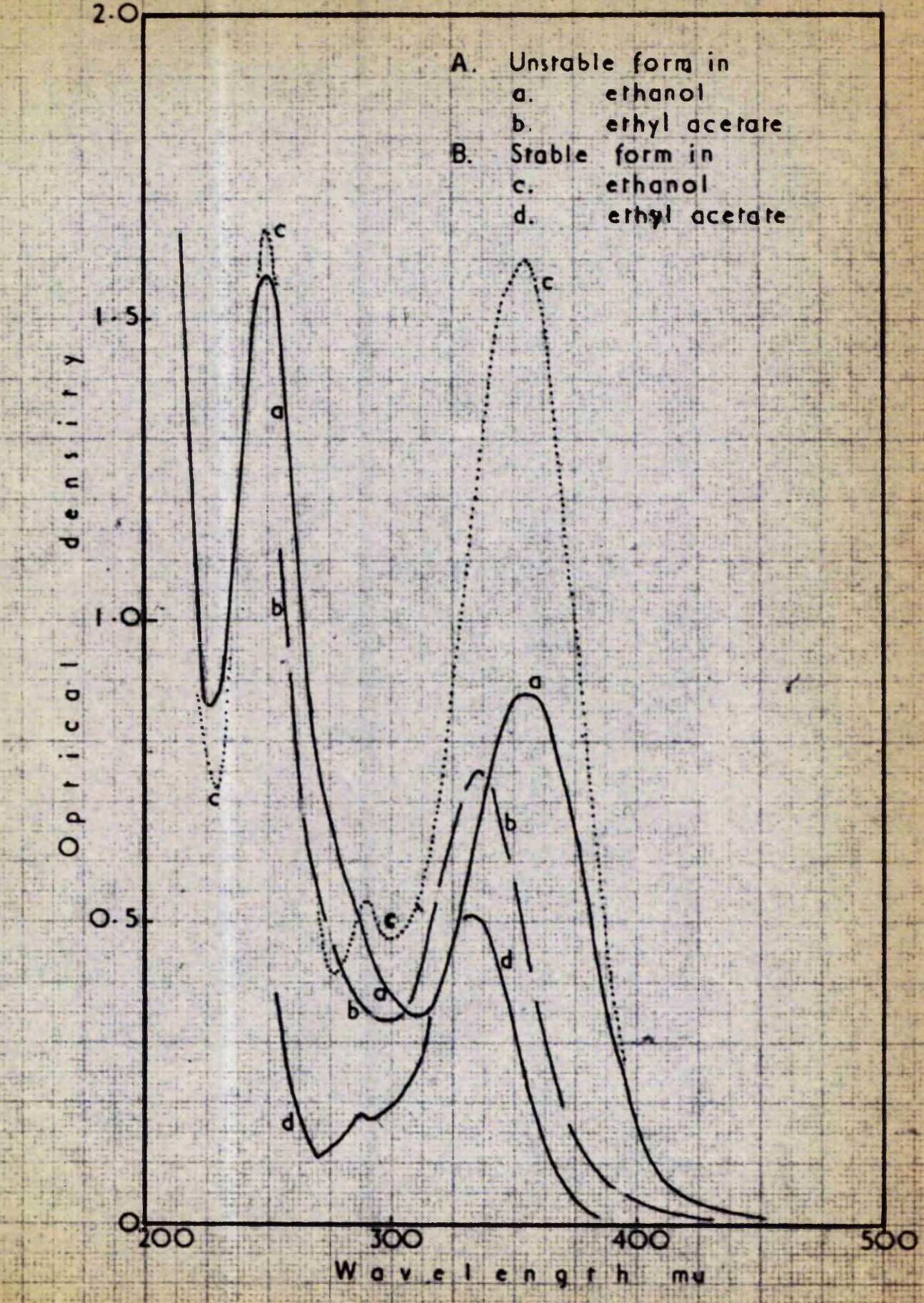
2-Aminoanthr-10-one

The reduction of 2-aminoanthraquinone by the method of Bradley and Maisey[46] gave an anthrone presumed on their results to be 2-aminoanthr-10-one. In ethanol it exhibited well defined bands at 250 and 355 mu (Fig. 53). In ethyl acetate the latter peak was located at 336 mu (Fig. 53). As reported, in the experimental section on anthrone preparation, on one occasion a slightly different product was obtained by the reduction of 2-aminoanthraquinone by alkaline dithionite by using a different method to that of Bradley and Maisey[46]. This second form was more stable to heat than the first and also possessed a slightly different spectra. It showed peaks at approximately the same wavelengths as the first form and in addition a weak one at 290 mu in ethanol, (Fig. 53), and 286 mu in ethyl acetate. The band at about 355 mu in ethanol was found to be almost as intense as that at 250 mu whereas for the first form the longer wavelength band was only of half the intensity.

Exposure of a degassed solution of 2-aminoanthraquinone in ethanol (Fig. 26), to short-wave ultra-violet radiation caused the twin peaks in the ultra-violet part of the absorption spectrum to coalesce and give a band midway between the two. A similar change was noted for 1-aminoanthraquinone under the same conditions (Fig. 15). Storage in the dark of the exposed solutions of 2-aminoanthraquinone caused the new peak to move back to its original location at 245 mu. The intermediate band was not observed in the changes recorded on the exposing of a similar solution to an Osram lamp (Fig. 30). The band at 297.5 mu did not coalesce with that at 245 mu to give a single peak at about 262.5 mu but appeared to move

2-Aminoanthr-10-one

Fig. 53



hypsochromically to 245 mu to give a spectrum similar to that of the solution exposed to the Vitan lamp after storage. The position of this maximum was very close to that in both forms of the anthrone.

The ethanol solution of 2-aminoanthraquinone exposed to a Vitan lamp, (Fig. 26), also initially gave a small peak at 377.5 mu. The energy difference between the location of the new peak and the corresponding peak for the unexposed solution was of the same order as that between the positions of the corresponding maxima for 1-aminoanthraquinone and 4-aminoanthr-10-one in ethanol. Prolonged exposure of the ethanol solution of 2-aminoanthraquinone to the Vitan lamp moved the peak at 377.5 to 350 mu equivalent to an energy shift of half the first. The ethanol solution exposed to the Osram lamp did not show a peak at 377.5 mu but one at 351 mu. The spectra of the final forms of the photoproducts in ethanol corresponded very closely with the spectrum in ethanol of the Bradley[46] form of the anthrone. It is possible that the first photo-product formed in the solution exposed to the Vitan lamp is an oxanthrone or the anthrahydroquinone and in view of the marked difference in the ultra-violet spectrum to that of the unexposed solution more probably the latter.

The spectra of the photoproducts in ethyl acetate produced by the two lamps differed considerably from each other and only that formed through exposure to the Vitan lamp, (Fig. 28) resembled that of the Bradley form of the anthrone. The changes in spectra of the solution exposed to the Osram lamp, (Fig. 31), resembled closely the initial changes in the ethanol solution exposed to the Vitan lamp, (Fig. 26). The band

originally at 427.5 mu moved to 365 mu which involved a similar frequency shift to that for the ethanol solution. In addition the band at 295 mu moved hypsochromically. This fading product might also be an oxanthrone or the anthrahydroquinone. Two forms of an oxanthrone are possible as the amino group can be in either the 2- or 3- position to the carbonyl group.

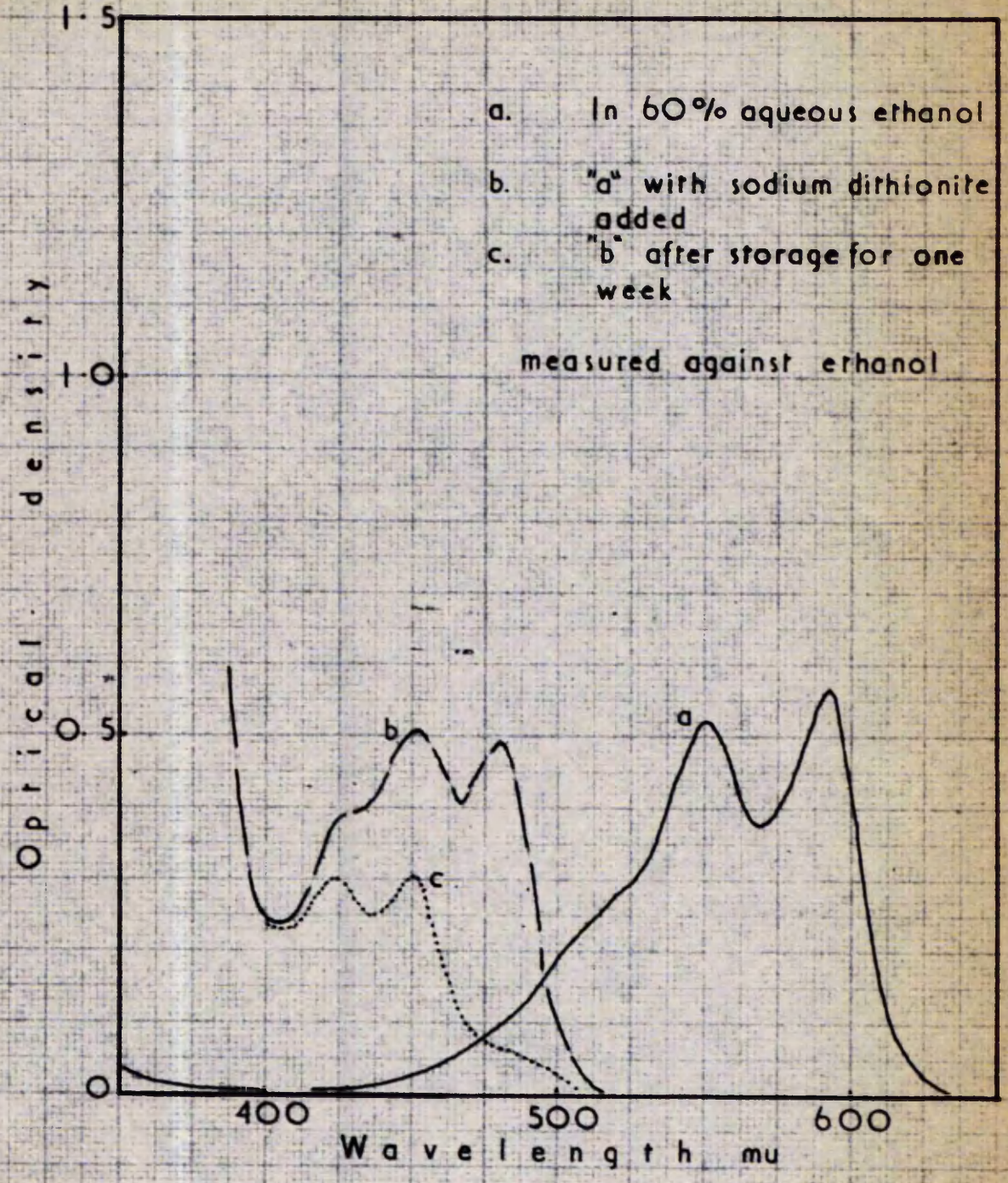
Leuco-1,4-diaminoanthraquinone

The absorption spectrum of this compound could be recorded only in ethanol and also only in the region above 400 mu since a pure sample could not be isolated, the contaminants being sodium dithionite and degradation products of the dye.

The absorption spectrum of a solution of 1,4-diaminoanthraquinone in ethanol and water was determined against a pure ethanol light path, (Fig. 54). The solution was made up of 5 ml of a stock solution of the dye to which was added 10 ml of distilled water and 10 ml of pure ethanol. When the spectrum had been determined a few grains of sodium dithionite were added to the remainder of the solution which was then allowed to stand for two minutes during which there was a marked colour change. The spectrum of this solution was rapdily determined. After one week the spectrum of the remaining solution was again determined. The spectrum of the untreated solution showed maxima at 551 and 591 mu, with an inflection at 522.5 mu. These values corresponded very closely with those obtained for the degassed ethanol solution prior to irradiation, (Table IV). The first reduced form had absorption maxima at 427.5 (inflection), 450 and 480 mu, and on storage gave a second reduced form with peaks at 425 and 452.5 mu. The shift to the latter form was accompanied by a loss of absorbance. There was evidence to suggest that further storage led to another hypso-

1,4-Diaminoanthraquinone

Fig. 54



chromic shift to give bands at about 395 and 415 mu.

The locations of the peaks in the first reduced form correspond very closely to those of the photoproduct formed on exposure of an ethanol solution of 1,4-diaminoanthraquinone to a Vitan lamp (Table IV). The final set of values (395 and 415 mu) are very similar to those given by a sample of leuco-quinizarin in ethanol. The progressive shifts are, therefore, most probably due to formation of leuco-1,4-diaminoanthraquinone followed by the successive loss of amino groups to give leuco-quinizarin.

The product obtained as a result of heating ammonia and leuco-quinizarin under pressure showed absorption bands in ethanol corresponding in position to those of leuco-quinizarin and also to leuco-1,4-diamino-anthraquinone.

While the absorption spectrum of the photoproduct in ethanol corresponded exactly with that of the first reduced sample it cannot be categorically stated that the photoproduct is leuco-1,4-diaminoanthraquinone without a knowledge of the ultra-violet absorption spectrum of that compound. It is said that this compound probably exists in a diketoimine form[44] and it is possible that its ultra-violet spectrum is the same as the original conpound as was observed for the photoproduct. No change occurs in the location of the most intense ultra-violet absorption band of quinizarin on reduction to leuco-quinizarin. This suggests that in solution that the diquinone structure postulated by Zahn and Ochwatt[45] for the latter compound is less in evidence than either an oxanthrone structure or a structure where the hydrogen atoms added on reduction are only in the 2 and 3 positions . This may also occur for leuco-1,4-diaminoanthraquinone.

It seems likely that the oxanthrone form of this compound predominates in solution as the structure of the absorption system in the visible region is identical to that of the unreduced compound. The change of an amino group to an imino group would probably have had a marked effect on the absorption bands in the visible region. Couper[21] records that 1,4-diiminoanthraquinone and 1-imino-4-methyliminoanthraquinone do not have twin peaks in the visible spectrum unlike the diamino compounds. It is believed that the twin peak is associated with the possibility of a mesomeric shift of electrons from a 1,4 pair of amino groups towards the anthraquinone nucleus[62]. 1,4-diiminoanthraquinone is said to possess a single band with maximum at 520 mu in ethanol[21], a location considerably different to the twin peak system observed for the present photoproduct.

The spectra of the photoproducts in ethyl acetate solutions, (Fig. 34, 36), were much less well defined than those in ethanolic solutions. The twin peak system was much less evident although not entirely absent. The positions of these bands were, however, in the region to be anticipated from the ethanol results and it seemed likely that the photoproducts in the solvents were the same.

The general trend found in the fading in oxygen by an Osram lamp of the polymer films dyed with 1,4-diaminoanthraquinone[5,6] was the production of a single absorption band in the visible region as a result of degradation of the original twin peak system. The position of this band was usually to shorter wavelengths than either of the two original bands. For N-methoxymethyl nylon the shift was from 560 and 600 mu to 540 mu. This is consistent with the formation of a diimino compound as postulated by Couper[21] although the location of the peak is at a longer wavelength

than would be expected from its location at 520 mu in ethanol.

1,5-Diaminoanthr-10-one

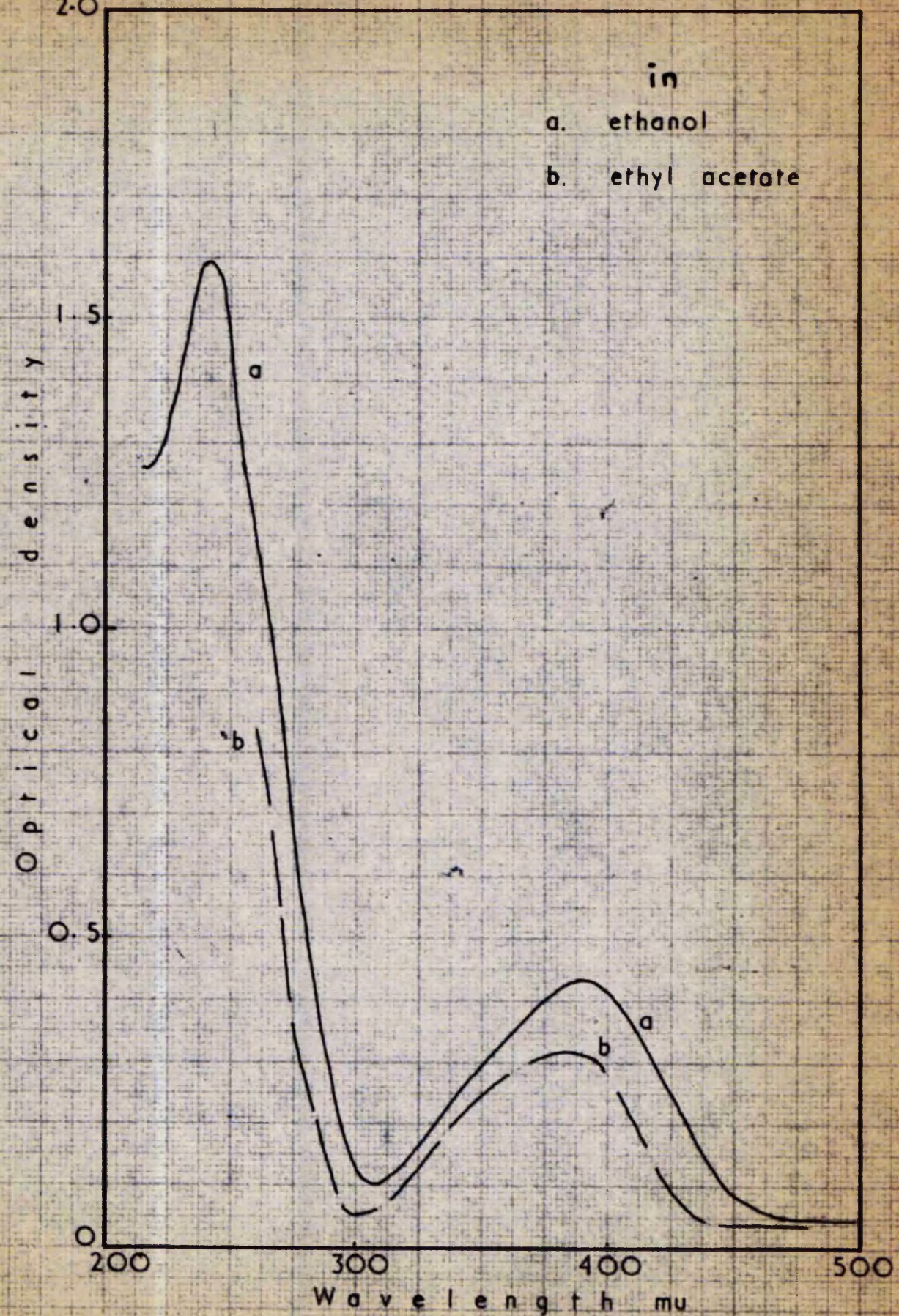
In ethanol this compound possesses only two absorption bands in the region 200 to 600 mu. Their peaks are at 242.5 mu and 390 mu, (Fig.55). In ethyl acetate the latter band is centred round 387.5 mu. Even after recrystallisation there was evidence of a small amount of the band structure of 1,5-diaminoanthraquinone in the region of 480 mu but the concentration was estimated at less than 2%. A summary of the positions of the bands is given in Table V.

The effect of both short-wave ultra-violet and visible radiations on a degassed solution of 1,5-diaminoanthraquinone in ethanol was the production of a number of bands in the region 395 to 447.5 mu, (Fig.40,42), whereas the anthrone displayed only one in this solvent. The photoproducts also possessed an extremely well defined band at 260 mu, not exhibited by the anthrone which possessed a peak at 242.5 mu not shown by the photo-product. Clearly the spectrum of the photoproduct was not attributable solely to anthrone formation. It is quite likely that the presence of other absorbing species with maxima apparently at 420 and 447.5 mu affected the location of the band at 395 mu causing it to be positioned at longer wavelengths. The ultra-violet spectrum was probably modified also by the presence of the other fading products but it is questionable that it was affected to any great degree. The lack of correspondence of the ultra-violet spectrum of the fading product with the anthrone suggests that the peak at 395 mu is more likely due to the anthranol. The other absorbing species may be the anthrahydroquinone and oxanthrone.

In ethyl acetate the spectrum of the photoproduct showed a single band at about 400 mu. This location is about 10 mu to longer wavelengths

1,5-Diaminoanthr-10-one

Fig. 55



than that of the corresponding peak of the anthrone. A similar difference was noted for the photoproducts and the anthrones of 1- and 2-amino-anthraquinone in ethyl acetate.

The spectrum of a film of N-methoxymethyl nylon dyed with 1,5-diamino-anthraquinone after exposure, in nitrogen to an Osram lamp[5,6] was initially identical to that obtained for an ethanol solution exposed to the same lamp, (Fig. 42). It is possible therefore that the fading products in the two systems were the same. The result of prolonged exposure of the dyed polymer film was the elimination of the two longer wavelength peaks leaving only that of the anthranol or anthrone. The changes in the ultra-violet region were masked and thus the final position of the band at one time located around 265 mu could not be ascertained. For this product to have been the anthrone it was required that this peak should have moved hypsochromically by about 20 mu which would have involved a large energy change.

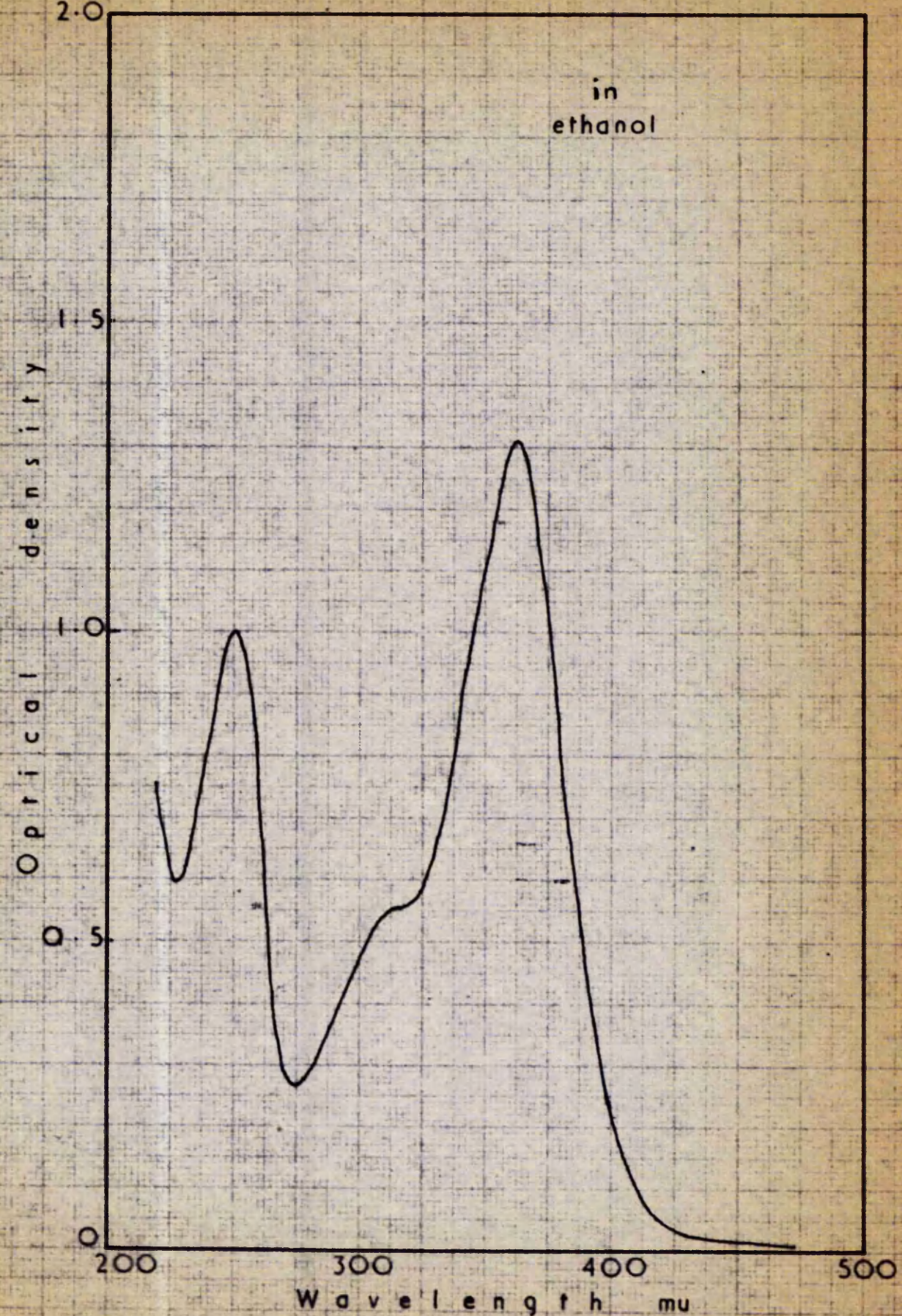
2,7-Diaminoanthr-10-one

It was observed for the absorption spectrum of 2,7-diaminoanthraquinone in ethanol, (Fig. 44), that it was unusual for the most intense absorption band not to be that at the shortest wavelength. This was also true for the anthrone which in ethanol displayed well defined bands at 251 and 362.5 mu, the latter being more intense, (Fig. 56). An inflection existed at 320 mu.

The post-irradiation effect noted for the ethanol solution of 2,7-diaminoanthraquinone exposed to the Vitan lamp did not affect the positions of the band maxima as it did for 2-aminoanthraquinone. The correspondence between the absorption spectra of the anthrone and the fading product was excellent.

2,7-Diaminoanthr-10-one

Fig. 56



PART III

GENERAL DISCUSSION

Changes in spectra on fading

The fading of anaerobic solutions of simple aminoanthraquinone compounds in organic solvents by short-wave ultra-violet radiation or near ultra-violet and visible light gave similar photoproducts but the rate at which fading occurred was considerably greater for the higher energy radiation.

The irradiation of ~~o~~ the solutions resulted in a progressive decrease in optical density of the absorption peaks in the visible region of the spectrum. Coupled with this there was a rise in absorbance in the formerly non-absorbing region between the ultra-violet and visible absorption bands resulting in the formation of new bands. The new absorption peaks were usually located at a position of about 100 mu (in most cases equivalent to a wave-number shift of 4000 to 5000 cm^{-1}) to shorter wavelengths than the original absorption maxima and were apparently related to them. This was most strikingly demonstrated by the 1,4- substituted derivatives and in particular for 1,4-diaminoanthraquinone in ethanol exposed to a Vitan lamp, (Fig. 33). The original absorbing system in the visible region for this dye was unusual in that it exhibited twin peaks. On irradiation these peaks and the inflection preceding them were degraded and reformed at shorter wavelenghts. The spectral shift involved was greatest for the inflection and least for the longer wavelength band and as a result there was a slight spreading of

the new absorption system compared to the original. The character of the latter system was maintained during fading and there was no displacement of the peaks other than that described. The original absorption bands in the visible region of some other compounds did, however, show a slight hypsochromic shift during fading (e.g. Figs.15,20).

For 1-amino- and 1,5-diamino- anthraquinone the difference in frequency between that of the new band and that of the original was found to be about 1000 cm^{-1} greater in ethanol than in ethyl acetate and as a result the photoproduct exhibited an absorption band at longer wavelengths in the relatively non-polar solvent. This was the reverse of the trend observed for the unexposed compounds, (c.f. Tables I, II & V), where decreasing polarity of the solvent caused a hypsochromic shift of the visible maxima. The positions of the peaks in the spectra of the photoproducts for solutions of 2-amino- and 1,4-diamino- anthraquinone, (Tables II & IV) were found to be at shorter wavelengths in ethyl acetate than in ethanol.

For all the ethanol solutions irradiation caused a loss in optical density of the shortest observed wavelength bond and with the exception of the 1,4-substituted derivatives a new band was simultaneously produced. The new peak was located approximately 20 to 30 mu to longer wavelengths which involved an energy change comparable to that occurring in the shift of the original visible absorption band to its position at shorter wavelengths. Storage in the dark of the ethanol solutions of 1-aminoanthraquinone after exposure to the Osram lamp, (Fig.21), and 2-aminoanthraquinone after exposure to the Vitan lamp, (Fig.27), both exhibiting the shift of the initial for ultra-violet peak to longer wavelengths on irradiation, caused the new band to decrease in intensity, and become less marked as a peak

and for the original band at the shorter wavelength to bereformed. Further irradiation of the solution of 2-aminoanthraquinone caused reversal of this post-irradiation effect, (Fig.27), but for the solution of 1-aminoanthraquinone this was not apparently so. The post-irradiation effect shown by the latter solution involved an increase in absorption of the degraded original band in the visible region and this probably accounted for a major part of the change. It seems likely that the change exhibited for the solution of 2-aminoanthraquinone was due to an internal molecular rearrangement of the photoproduct and while this was possible for the solution of 1-aminoanthraquinone a chemical reaction involving the photoproducts, or photoproduct and original quinone was more probable. 2,7-diaminoanthraquinone in ethanol exposed to the Vitan lamp, (Fig.45), displayed a different post-irradiation effect to those observed above. The spectral changes caused by irradiation were found to continue on storage in the dark but this behaviour was not observed for the solution exposed to the Osram lamp. The irradiated ethanol solutions of 1,4-di-, 1,5-di-, 1,4,5-tri- and 1,4,5,8-tetra aminoanthraquinone were found to be completely stable on storage.

Nature of the fading products

With the exception of 2,7-diaminoanthr-10-one the spectra of the anthrones in ethanol showed that there were no radical changes in locations of the shortest observed wavelength bands of the parent quinones on reduction and in this respect many of the fading products differed from the anthrones.

On anthrone formation the absorption band in the visible region for the parent quinone was found to undergo a hypsochromic shift, the

magnitude of which depended on whether the substituent was originally in an α or β position to the carbonyl group. For example, the frequency change in the formation of 2-aminanthr-10-one was about 5800 cm^{-1} and in the formation of 4-aminoanthr-10-one about 4200 cm^{-1}. This was probably connected with the greater reduction in electron donating power of the substituent when in the 2-10- position rather than the 3-10- position and a similar effect might be expected for formation of a 1-10- substituted compound compared to the 4-10-isomer. The reduction of 1,4-diaminoanthraquinone in ethanol to the leuco form caused an energy shift in the visible absorption system comparable to that in the formation of 4-aminoanthr-10-one from aminoanthraquinone but was less than that for formation of an anthrone from 1,5-diaminoanthraquinone.

The locations for the anthrones of the absorption maxima in the region of 400 mu were dependent on the solvent, moving hypsochromically for decrease in solvent polarity, as had been observed for the parent quinones (c.f. Tables I & II). The locations of the corresponding peaks for the photoproducts were also dependent on the solvent but for 1-amino- and 1,5-diamino- anthraquinone they were at longer wavelengths in ethyl acetate than in ethanol. This indicated that a different final species of photoproduct was formed in the two solvents and possibly that an entirely different overall reaction mechanism was involved.

For only three compounds could the result of the irradiation of the dye solutions be said to give a reduced form of the dye comparable to that prepared in the laboratory. They were 2-amino-, 2,7-diamino- and 1,4-diaminoanthraquinone. It is interesting to note that anthraquinone dyes with substituents in the β-position are said to show a greater tendency to promote the photo-tendering of textile materials[63]. It has been

suggested that this may be due to the freedom of the carbonyl group from internal chelation and steric hindrance caused by substituents in the α-position and the subsequent ease of electronic transitions which could disrupt any linkage that existed between the carbonyl group and the substrate.

Leuco-1,4-diaminoanthraquinone is not an anthrone but there is evidence to suggest that in the solid state it possesses a diketoimine structure[47]. It seems likely that this is not strictly so in solution and that an oxanthrone form is favoured. The fading products of other 1,4 substituted derivatives (Figs.47,48,49) would appear to be the result of the formation of similar compounds.

The two intermediate peaks in the region 400 to 450 mu exhibited by the faded ethanol solutions of 1,5-diaminoanthraquinone (Figs.40,42), were probably due to the presence of the oxanthrone and anthrahydroquinone. The third peak, located at a shorter wavelength than the other two, was probably that of the anthranol since the ultra-violet spectrum did not correspond to that of the anthrone.

The variable post-irradiation effects on the ultra-violet absorption of the fading products of 1-amino-anthraquinone in ethanol, (Figs.16,21), and 2-aminoanthraquinone in ethanol and ethyl acetate, (Figs.27,29), may have been due to a tautomeric change from anthranol to anthrone, or a disproportionation reaction giving the anthrone. 1-aminoanthraquinone may fade in ethanol to give 1-aminoanthr-10-one.

In view of the alterations to the ultra-violet spectra of the ethanol solutions on irradiation, the lack of information on the changes in that part of the spectrum for the ethyl acetate solutions prevents final

analysis of the fading products of 1-amino- and 1,5-diamino- anthraquinone in this solvent. The positions of the long wavelength bands relative to their locations in ethanol suggests that the photoproducts were not the same in the two solvents and also were not anthrones in ethyl acetate. Both 2-amino- and 1,4-diamino- anthraquinone appeared to give the same photoproducts in ethyl acetate as in ethanol, the former compound giving an anthrone and the latter the leuco-compound.

The statement that anthrones are colourless[30] would appear to be misleading. Their colour will depend on the structure of the original unreduced quinone and on the type of anthrone produced.

The similarity of the fading by the Vitan lamp to that caused by the Osram lamp is perhaps surprising as many vat dyes are able to reduce the photolysis of cotton cellulose by far ultra-violet radiation yet are able to accelerate the oxidative degradation caused by sunlight and air[26]. Bridge[63] has suggested that the active radiation in photosensitised tendering by many vat dyes is of a wavelength of about 400 mu. It seems probable therefore that the reduction in photolytic degradation caused by the presence of the dye is due to the dye acting as a filter by absorbing most of the incident radiation and a subsequent inability to use up the energy in promoting a chemical reaction. The mechanism of photosensitised tendering apparently involves a hydrogen atom abstraction reaction in which the dye forms a semi-quinone radical. In the presence of oxygen this radical is reoxidised to the parent quinone but in the absence of oxygen it can proceed to a stable reduced state. It does not seem unreasonable to suppose that in the absence of oxygen the rate of reduction of the dye and hence the fading will depend to a considerable extent on the presence

of radiation of a wavelength of the order of 400 mu. The Osram lamp emits strong radiation in this region but the Vitan lamp does not[64] and it would be expected on the above reasoning that the fading caused by the Osram lamp would be greater than that by the Vitan lamp. However it has been shown that the rate of fading of anaerobic solutions of dyes is far greater to the Vitan lamp. It is possible that the Vitan lamp can promote photosensitised reactions in solution to give photoproducts similar to those observed for exposures made to the Osram lamp.

Rate of fading

The fading of the ethanol solutions of the dyes exposed to a Vitan lamp was less rapid than that of the ethyl acetate solutions and generally this was true for solutions exposed to the Osram lamp. The rate of fading caused by short-wave ultra-violet radiation was for all solutions much greater than that caused by near ultra-violet and visible light. This is in agreement with the rate of fading of dyed fabrics on exposure to these radiations[65,66].

For 1-aminoanthraquinone exposed to the Vitan lamp the fading in carbon tetrachloride was almost as rapid as in ethyl acetate and faster than the rate in ethanol or n-hexane. Fading in the latter solvent was found to be the slowest. The exposure of similar solutions to the Osram lamp did not follow the same pattern; the most rapid fading occurred in n-hexane and the slowest in carbon tetrachloride.

An ethanol solution of 1,4-diaminoanthraquinone exposed to the Vitan lamp was found to fade more rapidly when water was added and more slowly when benzene was present than the untreated solution.

The light fastness of the dyes was different in different solvents

for exposures made to the same lamp and also differed for exposures of the same solutions made to the two lamps. In ethanol the order of increasing stability to the Vitan lamp was 1-mono- < 1,5-di- < 1,4-di- < 2-mono- and to the Osram lamp 1-mono- < 2-mono- < 1,5-di- < 1,4-di-. In ethyl acetate the stabilities were 1,5-di- < 1-mono- < 2-mono- < 1,4-di- to the Vitan lamp and 2-mono- < 1,4-di- < 1-mono- < 1,5-di- to the Osram lamp.

The nature of the fading products showed that reduction of the quinone was the most likely reaction during fading and was probably due to hydrogen abstraction from the solvent. The ease with which a reaction of this sort can occur depends on the nature of the medium surrounding the sensitiser. A primary consideration is that a hydrogen atom should be available and that the sensitiser should be in reasonably close contact with it. Modification of the composition of that medium, for example, by the addition of water to an ethanol solution will change the nature of the solvent cage around the dye. Thus Moran and Stonehill[41] observed a decrease in the induction period for the photosensitised polymerisation, by active vat dyes, of methyl methacrylate in ethanol by the addition of water. Berthoud and Porret[67], however, found that the reaction between p-benzoquinone and propan-2-ol under the influence of light decreased by 50% when the alcohol concentration was reduced from 5 molar to 0.02 molar. Wells[35] has shown for the photosensitised oxidation of propan-2-ol that with increasing water concentration the rate of oxygen uptake increased to a maximum and thereafter decreased. The maximum rate of oxygen uptake occurred at an alcohol concentration where marked changes were known to occur in the structure of the solvent. The increased rate of fading of 1,4-diaminoanthraquinone in ethanol by short-wave ultra-violet radiation in the

presence of about 10% of water was probably due to a similar effect to that noted by Wells and for larger concentrations of water the rate of fading might be less. In predominantly aqueous media the excited dye molecule is deactivated by the water but in predominantly alcoholic media the changes in the solvent cage aid the attack of the sensitiser on the solvent. It should however be pointed out that by the action of light and air and in the absence of organic material aqueous suspensions of pigments such as zinc oxide and vat dyes are capable of producing hydrogen peroxide[26], which is one of the photoproducts from the photosensitised oxidation of ethanol and dyed fabrics. It is possible, therefore, that phototendering does not always involve hydrogen atom abstraction from an organic substrate by an excited dye molecule.

The inhibiting influence of benzene on the fading of an ethanol solution of 1,4-diaminoanthraquinone by a low-pressure mercury-vapour lamp may be due to (a) the preferential absorption of the radiation by the benzene followed by an energy transfer to the dye or the ethanol, (b) reaction of benzene with ethanol which would account for the formation of peaks in the near ultra-violet region, (Fig.38), and (c) deactivating effect of benzene on the excited dye molecules.

The greater rate of fading in ethyl acetate than in ethanol caused by short-wave ultra-violet radiation may be due to the greater ease of photolysis of the former solvent and a subsequent reaction with the dyes to give photoproducts similar to those arising on exposure to an Osram lamp.

The fading of 1-aminoanthraquinone in carbon tetrachloride on exposure to the Vitan lamp, (Fig.18), may involve solvent photolysis

followed by a reaction with the dye. Owing to the strong absorption by the solvent of the radiation emitted by the Vitan lamp a photosensitised reaction was likely to occur only at the cell face, and the fading of the solution as a whole would have been dependent on the rate of diffusion of the dye molecules through the solvent. An internal hydrogen abstraction reaction of the type observed by Bridge and Porter[36] for duroquinone in carbon tetrachloride might occur in the present work through an energy transfer from the solvent to the dye rather than by direct excitation of the dye. Bridge and Porter also found that the addition of chloroform to the carbon tetrachloride solution of duroquinone greatly facilitated the photoreduction of the duroquinone. Traces of chloroform were not thought to be present in the solvent used in the present work. Its presence would not however explain the differences in the degree of fading of the solutions, prepared from the same ampoule of solvent, exposed to the two light sources. The fading of the solution exposed to the Osram lamp reached a maximum after only 50% of the original band in the visible region had been destroyed yet the same absorbing system was completely destroyed in the solution exposed to the Vitan lamp.

The slow rate of fading of 1-aminoanthraquinone in n-hexane relative to that in ethyl acetate on exposure to the Vitan lamp compared with the relative rates of fading of these solutions on exposure to the Osram lamp (Fig. 14) lends support to the suggestion that the primary fading reaction in ethyl acetate is different for the two lamps. Solvent photolysis is unlikely for the n-hexane solution exposed to the Vitan lamp and the fading probably occurs through a photosensitised reaction, as would seem likely for the fading caused by the Osram lamp. The fading of the ethyl acetate

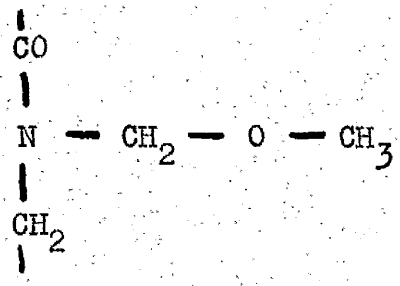
solution exposed to the Vitan lamp is likely to involve solvent photolysis whereas the fading by the Osram lamp probably involves a photosensitised reaction. The differences in the fading rate of these solutions exposed to the Vitan lamp would then be dependent on the relative speeds of solvent photolysis followed by reaction with the dye for the ethyl acetate solution and of the photosensitised reaction in n-hexane.

The different rates of fading for exposures made of the solutions to the Osram lamp may be the result of the mode of bonding of the dye to the solvent and the availability of a hydrogen atom for abstraction.

Fading of dyed polymer films

The modifications to the absorption Spectra of anaerobic solutions of 1-mono-, 2-mono- and 1,5-di- aminoanthraquinone during irradiation showed a marked similarity to those observed by Egerton and Roach[5,6] during the light fading of these dyes on N-methoxymethyl nylon film in an atmosphere of nitrogen. There was also a limited resemblance to the fading of 2-amino- and 1,5-diamino- anthraquinone or cellulose acetate and nylon film under the same conditions. The considerable changes during fading in nitrogen for dyed N-methoxymethyl nylon at first did not appear to occur in oxygen but a close examination of the spectral changes showed that there were similarities in the two systems. This was not the case for the other polymer films.

The greater ease with which the modified nylon film promotes the photoreduction of the dyes considered, compared to other substrates, is probably connected with the presence of the N-methoxymethyl side group



in the polymer chain. It is possible that by the action of light either this side group is split off to leave an N-methyl substituent with the evolution of formaldehyde which could react with the dye to give an intermediate, as Egerton and Roach have suggested, or, as now seems more likely, is able to donate a hydrogen atom to the activated dye molecule. The fading in nitrogen and oxygen would therefore occur more rapidly than for other polymer films and the dye in the reduced state would be able to enter into further reactions involving decomposition. The presence of oxygen apparently does not prevent the initial photoreduction of the dye, as is seen from the spectral changes, but the rate of reoxidation of this form to the parent quinone will depend on the rate of diffusion of oxygen into the polymer film.

The polymer films dyed with 1,4-substituted derivatives appear to fade in oxygen by the eventual formation of a diimino compound.

Conclusions

(i) The fading of anaerobic solutions of simple aminoanthraquinone compounds in ethanol and ethyl acetate by short-wave ultra-violet or near ultra-violet and visible radiations gives photoproducts which appear to be reduced forms of the dyes.

(ii) The rate of fading is much greater for exposures made to the high

energy radiation and is usually faster in ethyl acetate than in ethanol for both types ofradiation. The light fastness of the dyes depends both on the solvent and on the radiation employed and there are no general trends.

(iii) The presence of a small quantity of water in an ethanol solution of 1,4-diaminoanthraquinone exposed to short-wave ultra-violet radiation can greatly increase the rate of photoreduction of the dye. The presence of benzene can reduce the rate.

(iv) The fading products would appear to be anthrones for the 2-substituted compounds and some form of a diketoimine for 1,4-substituted derivatives. Other fading products may include oxanthrones, anthrahydroquinones, anthrones or anthranols.

(v) The fading of dyed films of N-methoxymethyl nylon in nitrogen by an Osram lamp gives fading products spectrally very similar to those arising on exposure of anaerobic ethanol solutions of the dyes. It seems possible that in oxygen these products are either reoxidised to the parent quinone and then undergo fading reactions with other photoproducts, or, undergo further fading while still in the reduced state. The rate of reoxidation of the first fading product will depend on the rate of diffusion of oxygen into the polymer.

(vi) The photoreduction of the dyes on other polymer films, for example cellulose acetate and nylon, does not take place so readily and as a consequence the fading is slower.

Suggestions for future investigations

The work presented in this thesis could be extended to a study of

the fading of N-substituted aminoanthraquinone compounds and purified commerical vat dyes both in suitable organic solvents under anaerobic conditions and on polymer films. The analysis of the fading products would show whether photoreduction of the dyes occurred in these systems, and it would be possible to determine the wavelength of the radiation most active in producing the change. If photoreduction were found to occur, the ease with which it did might be related to the tendering activity of these dyes. A study of the fading of dyed cellophane films under carefully controlled atmospheric conditions could include measurements of the tendering produced for different degrees of fading.

SUMMARY

A spectrophotometric study has been made of the light fading of anaerobic solutions of some simple aminoanthraquinone compounds in ethanol and in ethyl acetate and for 1-aminoanthraquinone also in carbon tetrachloride and in n-hexane. The sources of radiation used were a low-pressure mercury-vapour lamp (Vitan) emitting short-wave ultra-violet radiation and a high-pressure mercury-vapour lamp (Osram) emitting near ultra-violet and visible light.

Solutions exposed to the former light source were found to fade much faster. For both sources fading was normally more rapid in ethyl acetate than in ethanol. The stabilities of the dyes followed no definite trends either for exposures made in the two solvents to the same lamp or for exposures made in the same solvent to the two lamps. The addition of about 10% of water to an ethanol solution of 1,4-diaminoanthraquinone was found to increase greatly the rate of fading by the Vitan lamp but the addition of about 10% of benzene was found to decrease the rate of fading by the same radiation source.

The fading of all the solutions involved a progressive decrease in absorption of the peaks in the visible part of the spectrum coupled with a rise in absorption at shorter wavelengths. With the exception of solutions of 1-aminoanthraquinone in carbon tetrachloride the increase in absorption in the formerly non-absorbing region led to the formation of new peaks which were closely related to the original absorbing systems at longer wavelengths. The locations of the new peaks in ethyl acetate

were to longer wavelengths than in ethanol for 1-mono and 1,5-diamino-anthraquinone but to shorter wavelengths for 2-mono- and 1,4-diamino-anthraquinone. Irradiation of the ethanol solutions also caused destruction of the main ultra-violet absorption bands and, with some exceptions, there were corresponding rises in absorption at slightly longer wavelengths resulting in the formation of new peaks. For the mono-substituted compounds prolonged storage in the dark tended to reverse the changes in the ultra-violet spectra. In the presence of benzene an ethanol solution of 1,4-diaminoanthraquinone exposed to a Vitan lamp was found to give additional absorption bands in the region 300 to 400 mu. They bore a strong resemblance in shape to the characteristic benzene absorption bands in the region 250 to 275 mu and probably arose from complex reactions of benzene with ethanol.

Dyes with substituents in the β-position were found to give fading products whose spectra were very similar to those of anthrones prepared from the unexposed compounds. Where substituents were present in the 1,4-position the spectra of the fading products strongly resembled the spectra of the corresponding leuco-compounds. The fading products of other compounds were not identified but were thought to be either oxanthrones, anthrahydroquinones, anthranols or anthrones.

The fading of the ethanol dye solutions was found to give photoproducts spectrally similar to those produced when the same dyes on N-methoxymethyl nylon were exposed, in an atmosphere of nitrogen, to an Osram lamp.

REFERENCES

1.	Joffre,	Bull.Soc.chim.,	1, 553, (1889).
2.	Bolis,	Rev.gen.Mat. Col.,	13, 73, (1909).
3.	Gebhard,	J. Soc. Dyers & Col.,	26, 173, (1910).
4.	Ackerman,	J. Phys. Chem.,	36, 780, (1932).
5.	Egerton & Roach,	J. Soc. Dyers & Col.,	74, 401, (1958).
6.	Roach,	Ph.D.thesis, Victoria Univ. of Manchester,	(1957).
7.	Gebhard,	J. Soc. Dyers. & Col.,	34, 74, (1918).
8.	Egerton,	ibid	64, 336, (1948).
9.	idem.,	Textile Res. J.	18, 659, (1948).
10.	idem.,	J. Textile Inst.,	39, T305, (1948).
11.	Haller & Ziersch,	Z. Angew Chem.,	43, 209, (1930).
12.	idem.,	Melliand Textilber,	10, 951, (1929).
13.	Gillet & Giot,	Compt. rend.,	176, 1402, 1558, 1894, (1923).
14.	Sandoz,	J. Soc. Dyers & Col.,	50, 13, (1934).
15.	Seibert & Sylvester,	Am. Dyestuff Reptr.,	33, 311, (1944).
16.	Mounier,	Tiba,	9, 5, 121, 237, 353, 469, 585, (1931).
17.	Hodgson & Smith,	J. Soc. Chem. Ind.,	56, 108T, (1937).
18.	Iwamato,	Bull. Chem. Soc. Jap.,	10, 420, (1935).
19.	Hibbert,	J. Soc. Dyers & Col.,	43, 292, (1927).
20.	Scholefield, Hibbert & Patel,	ibid,	44, 236, (1928).
21.	Couper,	Textile Res. J.,	21, 720, (1951).
22.	Hartley,	J. Chem. Soc.,	633, (1938).
23.	Mechel & Stauffler,	Helv. Chim. Acta.,	24, 151E, (1941).
24.	Egerton,	J. Soc. Dyers & Col.,	63, 161, (1947).
25.	idem.,	J. Textile Inst.,	39, T293, (1948).
26.	idem.,	J. Soc. Dyers & Col.,	65, 764, (1949).
27.	Turner,	ibid	63, 372, (1947).
28.	Sunthankar & Venkataraman,	Proc.Indian Acad.Sci.,	32A, 240, (1950).
29.	Blaisdell,	J. Soc. Dyers & Col.,	65, 618, (1949).
30.	Bamford & Dewar,	ibid ,	65, 674, (1949).
31.	Ciamician & Silber,	Ber.,	34, 1530, (1901).
32.	Meyer & Eckert,	Monatsh.,	39, 241, (1918).
33.	Bolland & Cooper,	Proc. Roy. Soc.,	A225, 405, (1954).
34.	Wells,	Nature,	177, 483, (1956).
35.	idem.,	Trans. Faraday Soc.,	57, 1703, (1961).
36.	Bridge & Porter,	Proc. Roy. Soc.,	A244, 259, 275, (1958).
37.	Bridge & Maclean,	J. Soc. Dyers & Col.,	75, 147, (1959).
38.	Bridge & Reed,	Trans. Faraday Soc.,	56, 1796, (1960).
39.	Schenk & Koltzenburg,	Naturwiss.,	41, 452, (1954).
40.	Scholefield & Turner,	J. Textile Inst.,	24, P131, (1933).
41.	Moran & Stonehill,	J. Chem. Soc.,	788, (1957).
42.	Meyer,	O.S.C.V.,	1, 60.

43.	Feiser & Putnam,	J. Amer. Chem. Soc.,	69,	1038,	(1947).
44.	Coffey,	Chem. & Ind.,		1068,	(1953).
45.	Zahn & Ochwatt,	Annalen,	462,	72,	(1928).
46.	Bradley & Maisey,	J. Chem. Soc.,		274,	(1954).
47.	Flett,	ibid ,		1441,	(1948).
48.	Beilstein, Prager & Jacobson,	Organische Chemie,	14,		(1931).
49.	Elliot & Telesz,	J. Soc. Dyers & Col.,	73,	8,	(1957).
50.	Maki,	J. Soc. Chem. Ind. Jap. Suppl.	36,	44,	(1933).
51.	F.I.A.T.	1313, 2, 51.			
52.	D.R.P.	598, 476.			
53.	Beckman & Liesche,	Ber.,	56B,	17,	(1923).
54.	B.P.,	314, 804.			
55.	Weissberger et al.,	Technique of Organic Chem., Interscience Publishers	7,	341,	1955.
56.	Bowen,	Nature,	177,	889,	(1956).
57.	Barnes & Forsythe,	J. Opt. Soc. Amer.,	27,	83,	(1937).
58.	Gillam & Stern, (Ed. Arnold, 1960)	An introduction to electronic absorption spectroscopy in organic chemistry. App. 2.			
59.	Braude & Stern,	J. Chem. Soc.,		1976,	(1948).
60.	Anderton, Chilton & Porter,	Proc. Chem. Soc.,		353,	(1960).
61.	Jones,	J. Amer. Chem. Soc.,	67,	2141,	(1945).
62.	Allen, Wilson & Frame,	J. Org. Chem.,	7,	169,	(1942).
63.	Bridge,	J. Soc. Dyers & Col.,	76,	484,	(1960).
64.	Cooper & Hawkins,	ibid ,	65,	586,	(1949).
65.	Hill,	ibid ,	43,	296,	(1927).
66.	Taylor,	Illum. Eng.,	41,	35,	(1946).
67.	Berthoud & Porret,	Helv. Chim. Acta.,	17,	694,	(1934).
68.	Flett,	Private communication.			

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