LATENT IMAGE FORMATION
IN THALLOUS BROMIDE - GELATIN SYSTEMS.

Thesis Presented for the Degree of
Doctor of Philosophy
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May, 1944.

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INTRODUCTION.

General.

In spite of the mass of experimental evidence concerning latent image formation in silver halides it had not been possible, until recently, to correlate the facts into a satisfactorily consistent theory. In 1938, however, Gurney & Mott[1,2.] proposed, on theoretical grounds, a mechanism of latent image formation which has been very successful in explaining the observed effects.

Briefly, two essential processes are recognised; one the liberation of electrons from lattice bromide ions by illumination and their subsequent trapping by certain sensitivity specks in or on the crystal; and the other the movement of the positively charged silver ions to these negatively charged centres. The net result of suitable illuminations is thus the production of small specks of silver and the liberation of bromine.

Under ordinary conditions of illumination and of temperature, the electronic and ionic processes proceed simultaneously at rates such that experimental separation of their effects is not easily demonstrated. In this respect, however, considerable evidence in support of the Gurney-Mott theory has been provided by experiments at low temperatures[3], at which ionic movement is considerably reduced while electronic movement remains practically unaffected. Also, at very high intensities of illumination conditions may be reached where, in comparison with the rate of the ionic process, the rate of electron release may be considered instantaneous. Under such extreme conditions however other circumstances arise which introduce complexity in the application of the theory.

The darkening, under the action of light, of metallic halides other than silver has been known for many years, but it was not until 1936 that Farrer[4,5.] described the formation of a latent image in thallous bromide, closely similar to that in silver bromide. While the absolute sensitivity was much less, wedge spectrograms showed a somewhat similar region of spectral sensitivity which could be extended into the red by suitable dye sensitisation. Characteristic H & D curves (see p. 19) were obtained of similar form, and in certain other respects also a comparable similarity to the silver bromide system was in evidence.

The latent image so produced, while capable of development in a physical developer, could not be developed by a normal photographic developer, a difficulty overcome by Farrer by double decomposition in silver nitrate solution. The thallous bromide grain with its latent image was thus converted into a corresponding silver system which could, after removal of excess silver nitrate by washing, be developed in the usual manner.

It seemed probable that further examination of this system in relation to the Gurney-Mott theory might prove profitable from two points of view. First, the essential difference between silver and thallous systems is the replacement of the silver ions by the relatively larger thallous ions which, under similar conditions, have a lower ionic mobility. The system might on this account be expected to approximate to the low temperature silver conditions, with a partial separation, at ordinary temperatures, of the electronic and ionic processes, and a consequent accentuation of the problem of disposal of surplus electrons and bromine atoms. If a general similarity between the thallous and the silver systems can be established any divergence depending on the substitution of thallium for the silver of the latent image may be expected to yield information regarding both systems. Secondly, the technique of development allows in some respects a differentiation between latent image and developed product which is absent in the silver system; e.g. fog associated with the latent image may be distinguished from that produced by overlong development.

Further, thallium is above silver in the electropotential series and will thus tend to lose electrons more easily by reverting to thallous ions. Regression of any latent image will thus take place more readily. In as much as reversion of the silver image by 'non-actinic' red and green light (Herschel Effect(6)) is well known, parallel effects of a greater magnitude may be expected in the thallous bromide system.

The slow development of a consistent theory which would correlate the mass of experimental evidence on latent image formation and development has been largely due to the lack of a proper recognition of the processes following illumination of crystals. This branch of physical chemistry had to await the remarkable advances in physics in the last two or three decades, which followed upon the introduction by Planck[7] in 1900 of the concept of 'atomicity' in the realm of energy change. In order to account theoretically for the experimentally established laws of heat radiation Planck postulated that an oscillator of a frequency v can only absorb or radiate in units, or quanta, of energy hv where h is a universal constant ('Planck's constant')

The application of the extended quantum theory to the problem of the origin of spectral lines and bands initiated new conceptions of atomic and molecular structure which now furnish the necessary background for the modern theory of latent image formation.

While Planck had, strictly speaking, postulated only a discontinuous <u>interchange</u> of energy in its relation with matter by which it was radiated or absorbed, Einstein[8] in 1905 suggested that radiation energy itself could be profitably considered, particularly from the photochemical point of view, as discontinuous and in the nature of similar quanta of the magnitude $h\nu = \frac{hc}{\lambda}$, Where c is the velocity of light and λ is the wavelength of the radiation in question. Photochemical problems to-day are in general examined on the basis of the Einstein Law of Photochemical Equivalence, first enunciated in 1909, and later re-emphasised by Planck in 1913. According to this law, one light-absorbing molecule should react per quantum of radiation absorbed. Exhaustive examination of numerous photochemical reactions has shown that the law is seldom obeyed as judged by the net overall chemical result of illumination[7]. Its application must be limited to the initial physical process following light absorption, whereby one light activated molecule may be said to be produced per quantum absorbed. The chemical examination of quantum efficiency, i.e. the number of molecules chemically affected by the absorption of one quantum, has naturally been most exhaustively applied to the simpler gaseous molecules which present relatively few complications. Essentially such examinations have dealt with isolated molecules. On the other hand, in a crystal such as the alkali or silver halides, the identity of the single molecule is largely lost and thus necessitates the introduction of certain conceptions which are peculiar to the ionic crystal lattice. These conceptions have made possible the modern theory of latent image formation.

Light Absorption in the Silver Bromide Crystal.

The essential feature of such a crystal from the quantum standpoint may be emphasised by consideration of the potential energy of an electron moving within the crystal lattice. The potential energy curve for an electron moving in the field of a single silver atom has the form shown in figure 1.

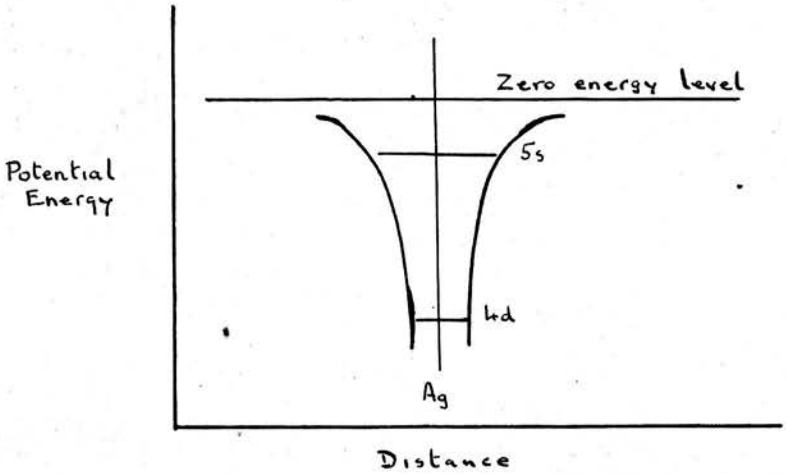


Figure 1.

The potential energy approaches an infinite negative value as the electron approaches the nucleus and rises to the value zero at large distances from the nucleus. The horizontal lines shown in the diagram represent two permissible energy levels of electrons in the atom. The level marked 5s represents the level occupied by the single valence electron in the outermost O-shell of the silver atom. The level of the electrons in the next lowest shell (i.e. the 4d level of the N-shell) is represented by the lower horizontal line 4d.

This treatment can be extended to a one-dimensional crystal lattice. Consider an array of silver and bromine ions arranged alternately as in a crystal. The potential energy curve for an electron constrained to move along a straight line passing through the nuclei will be of the form shown in figure 2.

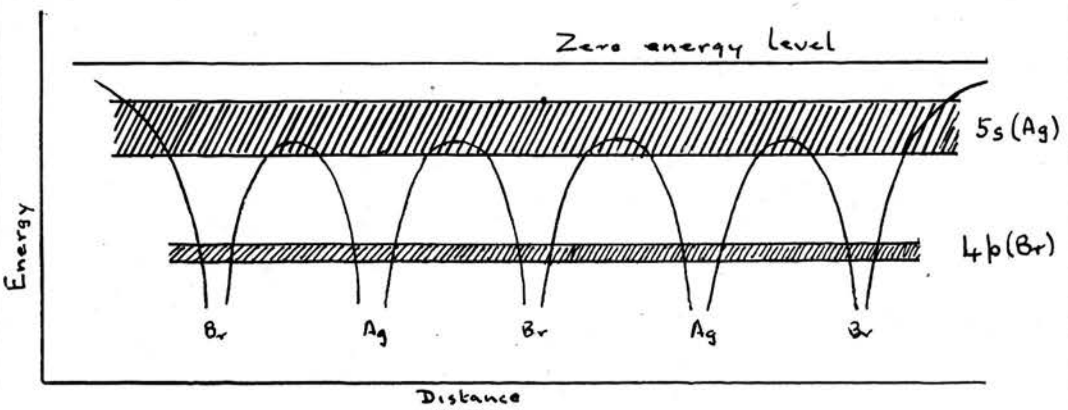


Figure 2.

An electron leaving a bromine nucleus does not lose its potential energy entirely before encountering the field of the neighbouring silver nucleus. The energy curve thus takes the form of a series of humps.

In the formation of the crystal of silver bromide the loosely bound 5s electron of the silver atom transfers to the bromine atom to occupy the one vacant space in the 4p level. The 5s level is thus completely empty while the 4p level is completely full. This is true only at the absolute zero of temperature since at normal temperature thermal agitation will excite a few electrons into the upper level.

It has been shown mathematically[9] that the permissible levels of an electron in a periodic force field (such as a crystal lattice) broaden out into bands. Thus the 5s and 4p levels are shown in figure 2 as bands of finite width. An electron moving in a discrete level of a potential valley will have a certain probability of appearing at the corresponding energy level of the neighbouring valley, provided the energy barrier between them is not too high nor too wide. (Tunnel effect).

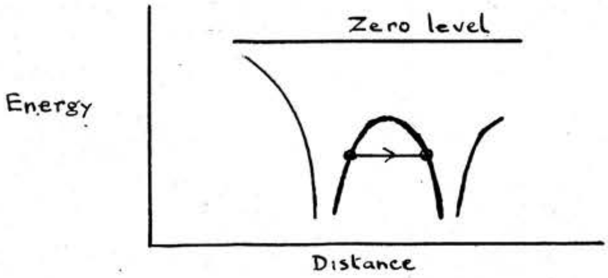


Figure 3.

The energy bands are thus shown in figure 2 as continuous bands extending throughout the crystal. In the case of the 5s band the energy 'hump' for an electron in the lower part of the band is quite low and the probability of this electron penetrating this obstacle is correspondingly high. For electrons in the upper part of the 5s band the obstacle has entirely disappeared and such an electron is free to move unhindered throughout the lattice. This energy level is usually referred to as the conductivity level of the crystal.

The formation of the latent image is considered to involve the transference under the action of suitable light of an electron from the 4p band to the 5s band. Webb[10] identified the latent image with the electron concentration thus formed in the upper conductivity level of the crystal. This view has undergone considerable modification (notably by Gurney and Mott) but the electronic transference pictured above is still considered to be the first stage in the series of processes initiated by light absorption.

In the light of the above discussion, absorption should show as a well defined band in the absorption spectrum. While this is so in most ionic crystals, the absorption spectrum of silver bromide shows a marked 'absorption tail' in which absorption falls off slowly towards longer wavelengths.[11] The presence of this absorption tail is of very great importance from the point of view of photographic latent image formation. It is accounted for by the assumption that it is due to surface ions only[12] which assumption is supported by the fact that the tail is easily altered by impurities, presumably adsorbed at the surface of the grain. These surface ions are not so firmly bound by lattice forces as are those in the interior. The electrons will therefore occupy different levels depending upon their actual situation at the surface and the proximity of neighbouring ions, and their elevation to the conductivity level of the crystal will include transitions over a wide range of energies. It is this range of energies of the absorbed quanta which gives rise to the absorption tail. Practically this means that latent image formation can occur over a wide range of wavelengths instead of being confined to monochromatic absorption, which in picture making would render true representation impossible. The marked nature of the absorption tail in the case of silver bromide has been accounted for by the assumption that a normal crystal is built up of a mosaic of small ideal crystals with thus a greatly increased number of surface ions.[13]

Any theory of latent image formation must take into account two main facts. First, the silver formed in the photodecomposition of silver bromide is always found in colloidal specks or aggregates of silver atoms, whereas the light is absorbed uniformly throughout, or over the surface of the grain. Second, as shown by Eggert and Noddack[14] the quantity of halogen set free during photolysis indicated that the Einstein Law of Photochemical Equivalence is obeyed.

Certain experimental observations on pure silver bromide crystals have furnished information useful in the elucidation of the mechamism of latent image formation, and two of these will now be discussed in more detail.

Photoconductivity.

At a sufficiently low temperature, and in the absence of light, silver bromide will not conduct an electric current.[15] If illuminated by light of a suitable wavelength (e.g. within the region of the absorption tail) conductivity appears. This may then be identified with the production of free electrons in the conductivity level of the crystal. If the applied potential is sufficiently high it is found that for each quantum absorbed one electron is discharged at the anode.[16] For lower potentials this unit quantum efficiency drops off markedly, showing that some of the electrons are trapped in some way. This trapping of electrons is very much more pronounced when the crystal contains small colloidal particles of silver. The conduction levels of metallic silver are thus regarded as below those of the silver bromide.[17]

Ionic Conductivity.

While a crystal of silver bromide at low temperatures is an insulator in the dark, at normal temperatures a conductivity is found of the order of 10^{-8} ohm^{-1} cm^{-1}. This conductivity is regarded as due to the passage of metallic ions.[18] A certain fraction of the metallic ions is displaced from the normal lattice positions into interstitial positions where they are not subject to the normal lattice forces. They are in fact mobile, requiring an activation energy of some 8000 calories.[19] A certain amount of energy is also required to bring these ions into the interstitial positions, their concentration being given by a formula of the type

$$C = C_0 e^{-W/kt}$$

where W for silver bromide is of the order 20,000 calories per mol.[20] At room temperature the concentration of interstitial ions is thus very low; calculation indicates that in an emulsion grain of 10^9 ion pairs, there are only 1,000 such interstitial ions, although there are indications that, by reason of impurities, this figure is rather to be regarded as a minimum.[20]

When a normal ion moves into an interstitial position a "hole" is left in the lattice structure. This hole has also a certain mobility due to a replacement mechanism, whereby a neighbouring ion occupies the vacant space. The activation energy for this process is of the same order of magnitude as that of interstitial ion movement, holes and interstitial ions contributing nearly the same amount to the ionic conductivity. Such movements under the influence of an applied field are illustrated in figure 4.

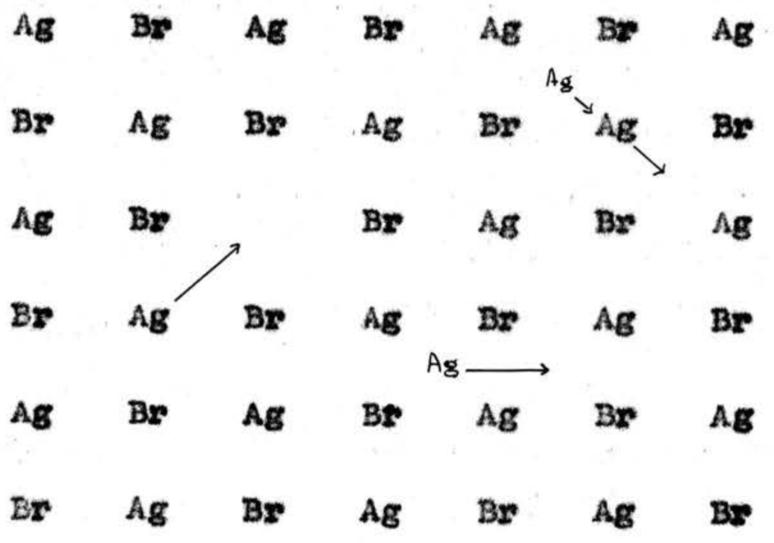


Figure 4.

It is possible for the negative bromine ions to occupy interstitial positions also, but in this case the energy required is regarded as considerably higher than that for the metallic ion, mainly because of the greater size of the bromine ion. The fraction contributing to the ionic conductivity is thus regarded as negligible.

The Mechanism of Latent Image Formation.

The work of Sheppard and collaborators[21] has shown that the sensitivity of an emulsion depends largely on the presence on the surface of the grain of specks of silver sulphide. These sensitivity specks are formed during digestion of the emulsion and are believed to result from the decomposition of various complexes of silver bromide and certain sulphur compounds which are present in the gelatin in minute quantities. Notable among these is allyl thiocarbimide ($C_3H_5-N=C=S$), of which 1 part in 10^6 will activate inert gelatin. Other compounds, e.g. silver selenides and tellurides[21], as well as impurities or lattice imperfections in the grain are similarly regarded as effective in promoting sensitivity. Latent image silver is also found in the interior of the grain[22,23]. as well as on the surface. The formation of silver sulphide in the interior of the grain is regarded as unlikely.[24]

In the theory of latent image formation advanced by Gurney and Mott[1] these sensitivity specks are assumed to act as electron traps with energy levels below that of the conductivity level of the lattice. Electrons are liberated by the initial light absorption and appear in the conductivity level where they move about with thermal energy and have a calculated velocity of 10^7cm/sec. Their rate of diffusion through the crystal is of the order of 1 cm/sec. The sensitivity specks now act by trapping the mobile electrons, thereby becoming negatively charged and attracting the interstitial metallic ions which migrate towards the speck and are there discharged. Metallic silver is thus deposited upon the centre and the resultant aggregation, if sufficiently large, constitutes the latent image. Sheppard[25] concludes that the latent image as made evident by development contains on an average some few hundred silver atoms and that the sensitivity speck of silver sulphide consists of not more than ten molecules.

<u>Positive Holes.</u>

When the photoelectron leaves its bound state in the bromine ion under the action of light, the resulting bromine atom has a certain mobility due to the transference of an electron from a neighbouring ion into the so-called "positive hole" associated with the atom. The ion in this case becomes an atom, the effect being equivalent to the transport of a halogen atom into an adjacent position. Because of the wave-mechanical tunnel effect no activation energy is required for this electron transfer and the atom may be as mobile as an electron in the conductivity level and unless it is removed from the grain will attack the latent image. If positive holes are attracted towards the charged sensitivity specks (i.e. if electrons are repelled into the holes, this in effect amounting to an attraction of the holes) as fast as positive metal ions move towards the speck, then latent image formation would not occur. Gurney and Mott[1] therefore assumed that positive holes in a silver bromide lattice are relatively immobile, possibly because of polarisation of the surrounding lattice.[26] There is evidence that some of the bromine leaves the crystal and is taken up by the surrounding gelatin; further information as to the fate of such bromine atoms is however required.

Development.

In as much as development is by far the most sensitive detector of a latent image and as theoretical considerations of latent image formation are largely extrapolated from and interpreted in terms of the resultant developed density a brief account of the development process of reduction in given here. The latent image itself is lost during the development, the final product being found in the form of tangled filaments of silver.[27,28.] The developing solution is essentially a solution which can supply electrons and according to the Gurney-Mott theory may be assumed to charge negatively the latent image specks with which it comes in contact. The interstitial positive ions in the grain move to the speck and are discharged as before. A deposit of silver is thus formed on the latent image which is pushed outward from the grain in the form of a silver filament. Essentially the developer continues the process of light action, the electrons however now coming from the developer

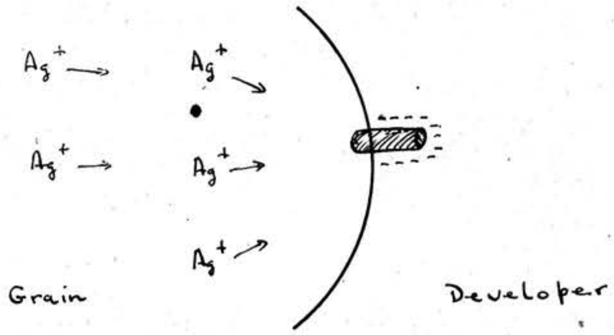


Figure 5

According to this view the rate of development would depend upon the rate of production of interstitial ions. Arrested development, however, reveals that there are very few grains which are partially developed. In general a grain is either developed completely or not at all. There is evidently an induction period during which the rate of development is slow followed by a period in which development proceeds very rapidly. The rate of production of interstitial ions is much too slow to account for the rapid rate of this second period of development.

Berg[29] explains this by assuming that there are two different stages involved. During the first stage the latent image speck builds up slowly at a rate controlled by the rate of formation of interstitial Ag^+ ions. The growing speck can take up an increasing number of electrons from the developer and the increasing negative charge eventually reaches a value at which the attractive force for Ag^+ ions exceeds the lattice forces. At this point the second stage commences. The neighbouring Ag^+ ions are pulled bodily out of the lattice and the whole grain rapidly breaks down.

The criterion determining whether a grain will develop is therefore the attainment by the growing speck of the critical size necessary for the second process to set in before development is arrested.

Photographic Effects.

In view of certain results on thallous bromide emulsions recorded later, the following paragraphs give a brief review of certain photographic effects observed in silver bromide.

Reciprocity.

In photochemistry generally it has been found profitable to examine reactions from the point of view of the quantum efficiency γ, as defined by the equation

$$\gamma = \frac{\text{Rate of reaction}}{\text{Quanta absorbed per unit time}} = \frac{dx/dt}{I_{abs}}$$

If the rate of reaction is directly proportional to I_{abs} then the quantum efficiency will be independent of I_{abs}. This may be put in the form

$$I_{abs}\, t = \text{const.}$$

where t is the time of exposure, indicating that the same amount of photoaction will occur, regardless of the relative values of I_{abs} and t, provided $I_{abs}\, t$ is constant.

Certain photochemical reactions are however known e.g. the photocombination of hydrogen and bromine[30] where the rate of reaction is proportional to $I_{abs}^{\,n}$, where n is not unity. The same effect will not be produced by the same product $I_{abs}\, t$ regardless of the values of I_{abs} and t. Conversely, if the same effect is not produced by constant values of $I_{abs}\, t$, then the rate of reaction is not directly proportional to the intensity of the light absorbed.

Strictly, this refers, as far as intensity is concerned, to the intensity of absorbed light. In the photographic plate, and with solids generally, exact measurement of absorbed light is difficult by reason of reflection and scattering. For a given series of photographic plates it is usual to deal with incident light I rather then absorbed light I_{abs}. If the product It then produces different effects for different relative values of I and t, this behaviour is known as "reciprocity failure."

The characteristics of a particular photographic plate are conveniently examined by plotting the logarithm of the exposure (i.e. log It) against the developed density. The characteristic H & D curve (Hunter and Driffield) is then usually of the form shown in figure 6, in which reciprocity failure of different kinds is apparent.

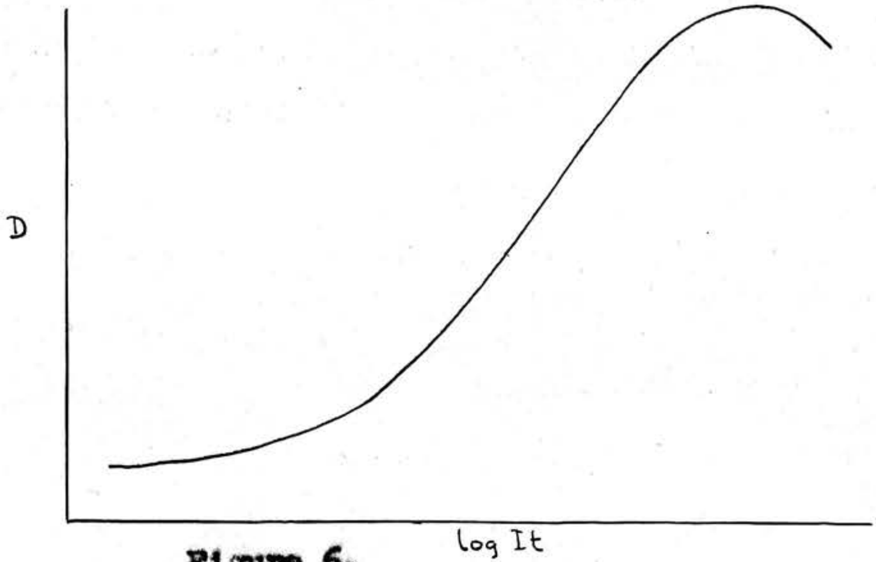


Figure 6.

Variations from true reciprocity are conveniently investigated by measuring the exposure (It) required to produce a given arbitrary density and by plotting log It against log I. For true reciprocity a straight line should be obtained as in figure 7.

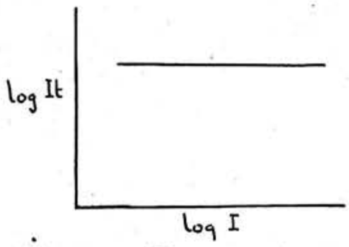


Figure 7.

The type of curve shown by typical photographic plates is of the form of figure 8. Two regions of reciprocity failure are then to be recognised, one at low and one at high intensities.

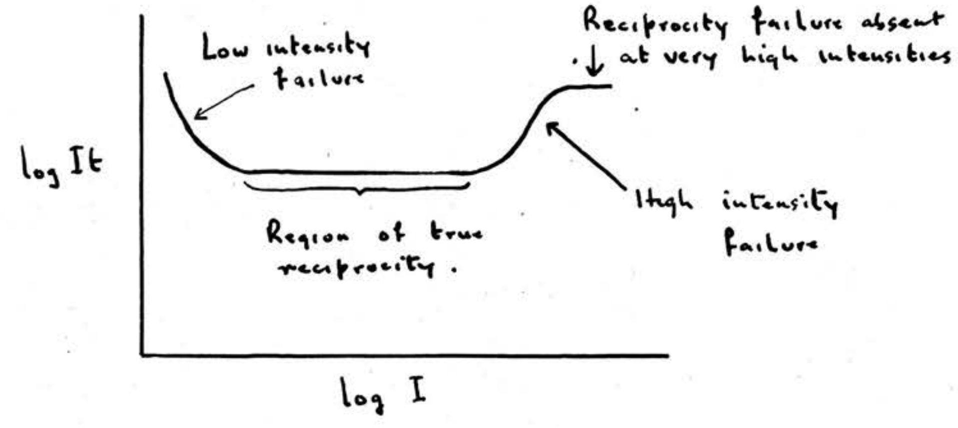


Figure 8

Low Intensity Reciprocity Failure.

Low intensity reciprocity failure is regarded as due to inefficient latent image formation in the first growth stages,[31,32.] a process using up electrons being required. Either the latent image speck does not increase in size unless a certain minimum concentration of electrons is produced in the grain;[1] or a speck of silver which has begun to form may disintegrate by thermal agitation into electrons and interstitial silver ions.[32.]

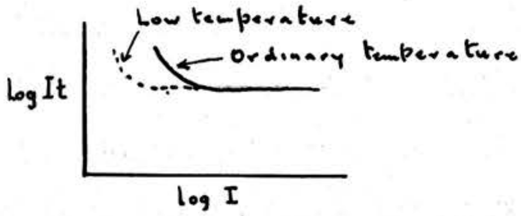
Reciprocity Failure at High Intensities.

At high intensities the ionic mobility is not sufficiently high to ensure the neutralisation of all the electrons formed by the light absorption. The excess electrons may recombine with bromine atoms or may fall into other electron traps, in this latter case ultimately forming specks which may compete with the main speck in development. The density produced for a given It will then be less than before.

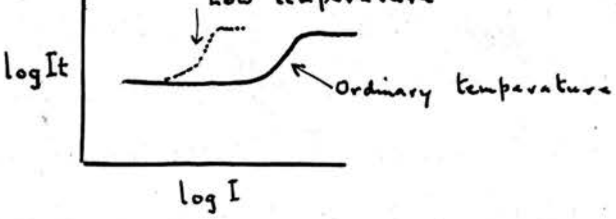
At very high intensities, It being kept constant, t may become so small that the exposure time can be considered instantaneous with respect to the ionic movement. Experiments with certain photographic materials showed reciprocity failure to be absent for exposure times of less than 10^{-5} sec.

The Effect of Temperature on Reciprocity.

The effect of lowering the temperature is, generally, to shift the whole reciprocity failure curve towards lower intensities. This is explained on the Gurney-Mott basis as follows. At low temperatures the small β- speck (p22) is more stable and low intensity failure due to its disintegration does not appear until still lower intensities are reached.



Also, ionic mobility is less, hence high intensity failure occurs, again at relatively lower intensities.



There is thus an analogy between low temperature exposures and high intensity exposures at room temperature.

Post- and Pre- Exposures.

Certain aspects of the relative sizes of possible latent image specks have been emphasised as a result of the application of two different exposures on the same plate. It is convenient to recognise four different stages of speck size, as shown in the following table, where the four different types have been designated $\alpha, \beta, \gamma, \delta$ with the approximate orders of magnitude shown.

Table I.

	Size classification.	Approximate order of magnitude.
α	Sensitivity speck.	$<$ 10 molecules Ag_2S
β	Unstable sub-image speck.	$<$ 50 atoms Ag.
γ	Stable sub-image speck (Not developable).	$>$ 50 atoms Ag.
δ	Latent image speck.	$>$100 atoms Ag.

If an exposure be made at a fairly high intensity there will be a large number of γ-specks formed in addition to the developable δ-image. If now a uniform low-intensity post exposure be given, these γ-specks will grow into developable δ-specks and, if the intensity be suitably chosen, only β-specks will be formed in unexposed grains; these latter will disintegrate spontaneously. This method may thus be considered as an auxiliary method of development.

Similarly a short high-intensity uniform pre-exposure will result in γ-specks being present in some of the grains before the picture exposure is made. Such grains will therefore become developable with a smaller number of quanta than would otherwise be required, this in effect being a means of increasing the plate speed.

That is, the application of a short high-intensity exposure followed by a low-intensity exposure may be considered as an auxiliary method of development or of increasing the plate speed accordingly as the picture exposure is the pre- or post- exposure respectively.

Clayden Effect.

In the following series of applied influences, any preceding influence, if applied as a pre-exposure, desensitises the plate in respect of a subsequent one.[33]

i. Pressure.
ii. X-rays.
iii. Very brief exposure to light.
iv. Normal exposure to light.

It was suggested by Lüppo-Cramer[34] that a brief exposure produces internal latent image specks which compete with those on the surface for the electrons formed by a subsequent exposure. If this is so, the relative distribution of such image specks becomes of the greatest importance.

Herschel Effect.

Reversal of latent image or of print-out density can be accomplished by post-exposure to red or infra-red light.[35.] The action of such light is to eject electrons from the speck, the silver ions reoccupying interstitial positions in the lattice.

The numerous small specks produced by high intensities are more readily destroyed than the larger ones produced by a low intensity exposure.

Solarisation.

With certain photographic materials and certain developers, continued increase in exposure eventually leads to a drop in developed density. This effect is confined to surface latent image[36] and can be minimised by the addition of a halogen acceptor before exposure,[37] or treatment with a silver halide solvent after exposure.[38]. The latent image is regarded as attacked by the bromine atoms set free by the exposure, and protected from the action of a normal developer by the resultant coating of silver bromide.

Iodo-bromide Emulsions.

Ordinary negative emulsions usually contain a small amount of silver iodide, of the order of 5% relative to the bromide, the sensitivity to light being thereby increased to a much greater extent than would be expected from the change in spectral absorption. This is usually attributed to the loosening-up effect of the distortion of the silver bromide lattice by the introduction of the iodide ions, this facilitating an increase in the rate of production and the number of interstitial ions. Solarisation tends to increase with increasing iodisation.[39]. According to Kameyama and Mizuta[40], 1·6 to 2·5% of silver iodide increases the photoconductivity in the spectral range in which pure silver bromide is sensitive and widens the sensitive range to longer wavelengths. A mobility factor is perhaps therefore also concerned.

Thallous Bromide.

The fact that thallous halides undergo decomposition on exposure to light has been known for some time[41] but no systematic examination of thallous bromide emulsions seems so far to have been published except that of W.J.G. Farrer[5,4]. Several papers have however appeared on the effect of the addition of small amounts of thallous salts to the standard silver bromide systems and may be considered in two main groups, relating to addition to the emulsions on one hand and to developing agents on the other.

According to Lüppo-Cramer[42] thallium halides sensitise silver bromide and silver iodide emulsions This effect is more pronounced in the iodide emulsion, the spectral sensitivity of which is extended to red light and the resultant speed of which can be brought up to that of medium bromide emulsions. Sodium nitrite and potassium metabisulphite were found to increase both the sensitivity and the maximum density obtainable, both acting as iodine acceptors. Haidrich[43] found that silver iodo-bromide plates could be sensitised to orange light by erythosin and small amounts of thallous nitrate solutions. A decrease in spectral sensitivity was, however, noted for pinacyanol.

In 1925, Hommel[44] reported the speeding up of hydroquinone development by the addition of thallous salts, a similar effect being noted by Wulff and Seidl[45] and by Lüppo-Cramer[46]. In slow emulsions an increase in threshold speed of development and in density generally was observed, without increase in fog, whereas for fast emulsions fog increased considerably. All these effects were attributed to enhanced absorption of hydroquinone. Haidrich[47] attemped to minimise, by the addition of thallous ions, the considerable regression in threshold rapidity believed to occur during development of silver iodo-bromide emulsions. With certain materials, e.g. Imperial Special Lantern Plate or Ilford Selochrome film, the sensitivity first increased with increasing amounts of thallous nitrate. Further additions however brought about a decrease. Thallous bromide resembles silver bromide in that its absorption spectrum also shows a 'tail'[48]. In the formation of thallous bromide the 6p electron of the thallous atom transfers to the bromine atom to occupy the unfilled position in the 4p shell of the latter. If it is assumed that the absorption of light by thallous bromide results in an electronic transfer analogous to that in silver bromide the excited electron will jump from the 4p band of the crystal to the 6p band. This represents a greater energy intake than is involved in the 4p to 5s transfer in silver bromide. In relation to that of silver bromide the absorption will thus be displaced toward the short wavelength end of the spectrum. The absorption spectrum of thallous bromide does, in fact, exhibit in the ultra-violet a series of bands shaded towards the red.[48] In addition to the absorption bands there is a domain of continuous absorption.[43] In emission a band spectrum extending from 3400 to 4500 with a prominent group at 3950 has recently been reported.[49.]

Farrer[4] prepared thallous bromide emulsions by adding thallous nitrate solutions slowly to potassium bromide in gelatin solution. The formula used gave a 20% excess of alkali halide. The emulsions were washed free from the soluble salt product by coating the plates and washing in running water. Digestion, if desired, was carried out by scraping the emulsion from the plates, digesting and recoating. The final plates contained approximately 0·5 gm. of thallium per whole plate. All operations were carried out in yellow light.

Normal developers were found to be incapable of developing any latent image, but physical development was found suitable except that a long treatment was necessary to produce any reasonable density. Fixation by hypo could be carried out after, but not before, such physical development, this being due to the replacement of thallium by the silver of the developer. The exposed plate was therefore treated with silver nitrate solution and the excess removed by washing. A normal developer was then found to give a reasonable density for appropriate exposures.

The speed of the plates so prepared and examined was very low and application of various procedures (digestion etc.) suggested by silver bromide practice gave no marked increase in sensitivity. The use of normally 'fast' gelatine gave a plate slightly less sensitive than the normally slow gelatine. The addition of small amounts of iodide, which in silver bromide emulsions is found to give increased speed, was found to diminish the speed. Farrer thus concluded that gelatin and iodide have not the same function as in silver systems.

Increases in speed were nevertheless obtained by the addition of bromine acceptors, e.g. sodium nitrite, hydroxylamine and sodium sulphite, being more pronounced with the latter. Fogging however was accentuated. The thallium latent image, once formed, was subject to regression with time in the interval before development, this being much more marked than in the corresponding silver image.

The suggestion that the low speed of such plates might be due to unsatisfactory replacement of thallium by silver in the double decomposition process was examined photomicrographically. Little change in crystal shape was observed. While there was some evidence of an increase in opacity of the larger crystals after treatment, suggesting that aggregates of sub-microscopic particles were formed, there appeared nothing to suggest that the latent image was unable to function due to imperfect contact with the halide.

In thallous bromide therefore we have a system in which a possible partial separation is made of the two physical processes, (a) electronic movement and (b) ionic movement, on which the Gurney-Mott theory is based. If a latent image is formed in thallous bromide in a similar way, then the different size and mobility of the metallic ion should accentuate certain aspects of this theory. This thesis therefore presents the results of an investigation on latent image formation in thallous bromide - gelatin systems carried out with reference to the Gurney-Mott mechanism.

EXPERIMENTAL PROCEDURE.

In the following sections are given details of, and some observations on, the experimental procedures employed in the present research, in some cases reached only after numerous preliminary trials.

Preparation of Thallous Bromide - Gelatin Emulsion.

The emulsions were prepared as required in approximately 100 ml portions. To 6.5 gm. of photographic gelatin in a glass beaker, the same stock of gelatin being used throughout the entire series of experiments, was added 50 ml of distilled water, and the contents raised to 35.0°C in a thermostat (electrically controlled and with a temperature variation of less than 0.1°) When the contents were homogeneous, a process aided by mechanical stirring with a glass stirrer, 2.000 gm potassium bromide were added and dissolved. 50 ml of an aqueous solution containing 8.000 gm thallous nitrate per 100 ml was then added drop by drop from a burette and with vigorous mechanical stirring, this operation being carried out in a dim red light. Stirring was continued for 20 minutes and the emulsion was then kept at 35°C for a further 3 hours, before being chilled in running cold water and set aside until the next day.

Shredding of Emulsion.

The emulsion, now in the form of a solid mass, still contains excess potassium halides together with potassium nitrate formed by the double decomposition

$$TlNO_3 + KBr = TlBr + KNO_3.$$

To eliminate these soluble salts the emulsion was shredded and washed. Shredding was accomplished by gathering the emulsion into a ball in a piece of butter muslin, which had previously been well washed and boiled in distilled water. The ball of emulsion was placed beneath the surface of cold water in a large beaker and steadily squeezed, thus forcing the emulsion through the meshes in the form of shreds. These were allowed to settle and the bulk of the water was removed by decantation.

Washing of Emulsion.

The emulsion was washed by decantation, employing eight five-minute washes with 200 ml of distilled water, the emulsion shreds being gently stirred with a glass rod during each wash. The washed shreds were drained on a muslin filter and transferred to a wide-necked stoppered bottle for remelting, some 10 ml of water being added to bring the total volume to 100 ml approximately. Stirring was continued for 15 minutes and, at this stage, sensitiser and preservative etc. were added if required, such additions being made dropwise and with vigorous stirring. After a further 15 minutes' stirring the emulsion was then ready for coating.

The following observations in regard to the above may here be made.

i. In view of the slight solubility of thallous bromide (.04% at 15°C, as compared with .000011% for Ag Br), whereby washing may remove considerable quantities of bromide, a concentrated solution of thallous nitrate was used, 8.0 gm per 100 cc being practically a saturated solution at room temperature. The amount of potassium bromide used gave an excess of 11% bromide when all the nitrate was added. When potassium iodide was also present this was added to the gelatin with the bromide. Normally in the experiments quoted later the emulsions contained 5% iodide, i.e. 0.100 gm of potassium iodide were added with 2.000 gm of potassium bromide.

ii. Precipitation of thallous bromide began in the presence of all the gelatin and potassium bromide used in the preparation. Both these conditions tend to produce "slow" emulsions in silver bromide systems. The use of less initial gelatin and the simultaneous addition of thallous nitrate and potassium bromide solutions to a medium containing few bromide ions (1/25 of the total number) produced no marked increase in emulsion speed.

iii. The period of 3½ hours digestion after mixing appeared suitable. Emulsions prepared with 9 hours and 19½ hours digestion gave, if anything, a slightly lower density upon exposure.

iv. Some emulsions were prepared at 40°C and others at 50°C; these however showed a pronounced tendency to fog on processing, even without exposure.

v. An emulsion digested for 15 minutes at 100°C was found to become colourless and transparent and to remain so indefinitely after cooling. Plates prepared from this emulsion were transparent and gave no density whatsoever upon exposure and processing.

vi. Earlier emulsions were prepared with the final addition of 5 ml of alcohol to facilitate coating, and a small amount of alcoholic phenol (0.5 ml of 1% solution) to act as preservative. These were later omitted as of little practical advantage, although emulsions containing phenol appeared slightly "faster" than these without, probably on account of acceptor action.

vii. Various other methods of shredding and washing the emulsion were examined: e.g. the emulsion was pressed through perforated porcelain discs and the shreds washed in running tap water (see figure 9). Various practical difficulties however were encountered and reliance was therefore placed on the above simpler methods. Glass or porcelain vessels and spatulae etc. were used throughout.

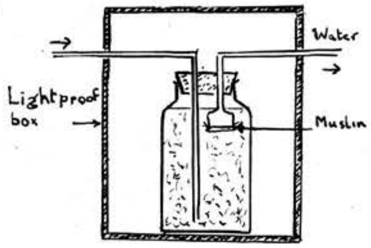


Fig 9.

viii. All additions to the emulsion (acceptor etc.) were made in relatively dilute solution. Uneven densities resulted otherwise.

ix. The earlier emulsions were filtered through chamois leather in a wide glass tube arranged as shown in figure 10. The chamois leather previously well washed, was fastened over the end of the tube and bound securely with string. The emulsion at 35°C was poured into the warmed tube and forced through the leather by compressing the air above the emulsion. No contact with the rubber piston was made, it being only necessary to push the rubber section about half way down the tube. This process was later omitted as unessential.

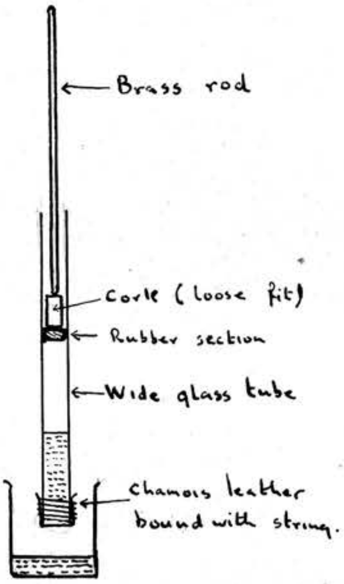


Figure 10.

Coating of the Plates.

The plates used were cut to the size 13 x 8.3 cm from old thin-glass spectrographic plates and thoroughly cleaned by treatment with concentrated nitric acid, scrubbing by muslin, and then by immersion for several days in a mixture of sodium hydroxide and ammonium hydroxide solutions. On removal, they were then scrubbed with cotton wool soaked in the above alkaline solution. The plates were placed in a glass-rod holder and the alkaline solution washed off with running tap water, then immersed again in dilute nitric acid and rinsed thoroughly in tap water and finally in distilled water. They were then set to dry edgewise in a drying cupboard, in which were placed open vessels containing calcium chloride and phosphorus pentoxide. From the time of placing in the glass-rod holder until thoroughly dry, even the edges of the plates were not touched by hand.

When required for coating the plate was placed in a printing frame of the required size (13 x 8.3 cm) so adjusted, on a glass levelling table, that a trial plate appeared exactly level as indicated by a sensitive spirit level. A glass pipette of 7.8 - 8.0 ml volume and large nozzle (0.4 cm diam), cleaned and dried by the above procedure was used to transfer the melted emulsion from container to plate. The emulsion was allowed to flow rapidly but steadily on to the centre of the plate, the plate-holder being then slightly inclined so that the plate was uniformly coated. The frame was then covered with a glass plate cover to exclude dust, and left undisturbed for 5 minutes to allow the emulsion to set. The back of the printing frame was then removed and the plate detached by a porcelain spatula pressed at one edge. The coated plate was then placed horizontally on the glass-rod supports in a light-tight drying cupboard. All the above operations were performed in as dim a red light as possible.

It was found advisable to coat all the emulsion at one time, later results showing that the emulsion proper lost sensitivity very appreciably on standing. Comparison of plates from the same emulsion coated at appreciably different times was found to be difficult (See Results).

The drying box contained shallow dishes of calcium chloride and phosphorus pentoxide and, under these conditions, the coated plates were normally dry in 48 hours.

It was found that, in drying, extreme desiccation was to be avoided as otherwise the emulsion film tended to peel from the plate. In earlier experiments, warm (25°C) dry air was passed slowly into the box (see figure 11). Uneven drying, and subsequently uneven density, was observed in plates near to the air entry.

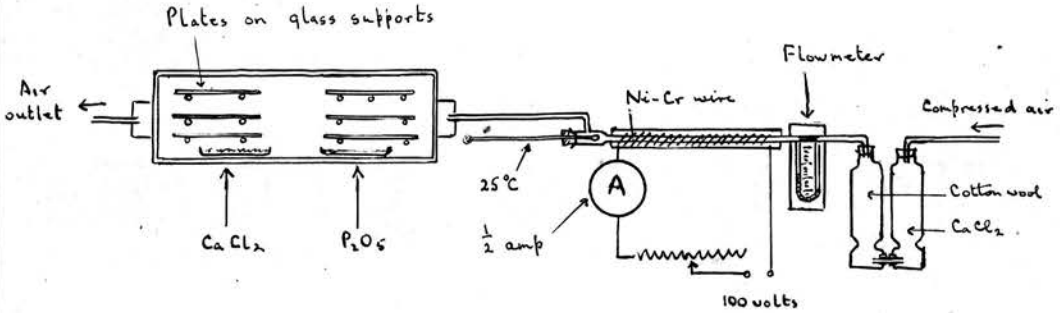


Figure 11.

When dry, half inch edge strips were cut from the plates and rejected, it having been found that these showed a greater density than the other parts of the plate, this being regarded again as due to uneven drying. Thereafter, the plates were cut to the required sizes and stored in lightproof boxes.

As prepared above, the plates contained .0023 gm of thallous bromide per sq. cm. This is equivalent to

0.59 gm of thallium metal per whole plate, which is comparable with Farrer's figure of 0.5 gm thallium for whole plate. The thickness of the undried film was 0.75 mm.

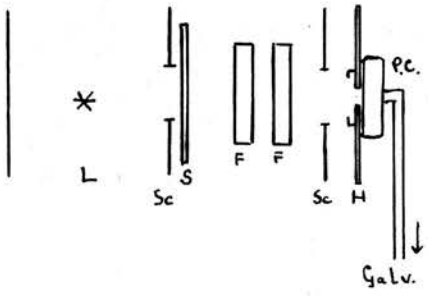
For blue light ($\lambda = 4360$ A) the logarithm of the incident light to transmitted light ratio (see Density measurements) was approximately 0.10. For green light ($\lambda = 5460$ A) it was approximately 0.20, both values being approximately independent of the addition of sensitisers; the effect of iodide, however, was more marked (see page 116).

Exposure.

Preliminary experiments were carried out by exposure at fixed distances to the light of various tungsten lamps, whereby it became obvious that for emulsions free from added sensitisers and acceptors very intense sources were required to produce any appreciable image on development. Daylight was found to be more effective and various carbon arcs were satisfactory, the latter indeed producing visible darkening of the plate prior to development. It was found difficult however to keep such sources sufficiently steady in intensity for accurate comparison. "Photoflood" and "Nitraphot" lamps were somewhat more satisfactory in this respect.

It became necessary (see Discussion) to employ monochromatic light and to distinguish sharply "bleaching" light (e.g. green) from the more actinic blue light. For this purpose the ordinary continuous sources were unsuitable with the light filters available. Mercury vapour lamps were employed, with however the added complications of variation in intensity and the difficulty of ensuring a uniform light flux of sufficient intensity. Finally, an Osira A.C. mercury vapour lamp was used in conjunction with a Solus stabiliser. This gave a very steady light output and was suitable, not only for plate exposures, but also for measurement of developed density. The main theoretical objection to such a system is that the light source is not continuous[50] but fluctuates 100 times/sec. Results were therefore checked, as far as possible, against the continuous Nitraphot and photoflood lamps.

The arrangement finally employed for exposures and density measurements is shown in figure 12.



L. = Light source.
S. = Shutter.
Sc. = Screen with aperture.
F. = Filter.
H. = Plate holder.
P.C. = Weston photronic cell.

Figure 12.

The plates used for exposure were normally approximately 1" x 1½" and were inserted in the plate holder H, this itself being removable, in fixed supporting slides at a constant distance from the light source. Part of the plate remained unexposed.

When required, a wedge of eight steps, constructed from an ordinary silver bromide plate and covered permanently by thin cellophane was supported by a spring in contact with the plate under investigation. The photronic cell was fixed immediately behind the plate and, when connected to a mirror galvanometer - scale system was used to record the incident light intensity on the plate and the intensity transmitted by the plate. A black paper shutter was used to prevent the light reaching the sensitive photo-cell surface if required, as for example at very high intensities. The same portion of the photo-cell surface as determined by a small circular aperture (1 cm diam), was used throughout. Previous calibration had shown that for this set-up at the intensities recorded on the scale, deflection of the light spot was proportional to intensity for monochromatic light.

Every effort was made to exclude all light, except that passed by the filters, by means of black velvet edgings on the filters etc.

<u>Measurement of Developed Density.</u>

The arrangement of the exposure box was suitable for such measurement, density being recorded as $\log \frac{I_o}{I}$, where I_o is the incident light intensity and I is the intensity transmitted by the plate in question. In as much as a clear glass plate reflects and absorbs some part of the incident light, all such densities were greater than zero. Unexposed areas of the plate were similarly recorded. Blue light was generally employed, direct comparison with white light having shown no appreciable differences in recorded densities.

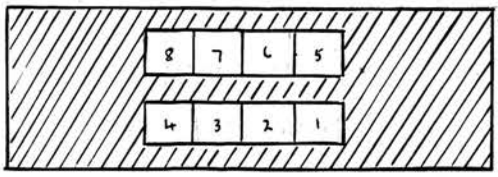
Where the wedge was employed to obtain an H. & D. curve, the small areas of the wedge necessitated the use of a smaller aperture. In general such densities were measured by a separate arrangement, using white light, by which each area of the plate in question was examined in turn.

For example, for one series of plates the values of the incident intensities (I_o) and the transmitted intensities (I) were as shown below, the measurements being in terms of galvometer scale deflections. From these readings, the values of log I_o/I give the densities required.

I_o	40.6	40.5	40.5	40.6	40.4	40.4
I	27.4	18.6	13.6	9.4	4.8	1.6
log I_o/I	.171	.348	.474	.635	.925	1.40

Construction of Wedge.

The H. & D. curve of a thin film Ilford Plate was first determined by exposures at various times under standard conditions (argon lamp at 340 cm distance from plate). From this curve suitable densities were chosen such that an over-all 50-fold variation of transmitted light could be obtained in eight regular density steps, and the corresponding times of exposure calculated. The wedge itself was then made by suitably exposing and developing a second similar Ilford plate, the final wedge pattern being one of eight ¼" squares, thus:



The shaded portions were covered by opaque black paper and the emulsion side of the wedge, which was placed in contact with the thallous bromide plate, was covered with thin cellophane.

Direct calibration of the wedge then gave the following densities.

Table I Wedge Densities.

Area	1	2	3	4	5	6	7	8
$\frac{I_o}{I}$	1.47	2.63	4.17	6.46	11.2	19.9	34.7	67.6
$D = \log \frac{I_o}{I}$	.16	.42	.62	.81	1.05	1.30	1.54	1.83

In view of the possibility that the intensities incident upon the various wedge areas might not be exactly uniform, these were measured directly with the photronic cell. Certain corrections then became necessary, which when applied, gave the following values for the intensities transmitted by the various wedge areas, when illuminated by incident intensities of 190 scale divisions blue light and 31 scale divisions green light, as recorded by the galvanometer

Table II Transmitted Intensities of Wedge.

Wedge Area.	1	2	3	4	5	6	7	8
Incident light 190 s.d. blue.	129	73.7	38.3	21.5	16.7	10.6	4.87	1.91
Incident light 31 s.d. green.	21.1	12.0	6.25	3.51	2.73	1.73	0.795	0.312

Absolute Calibration of Blue and Green Light (Osira lamp).

Blue light predominantly of wavelength 4360A was isolated by means of a 1 cm layer of 2% cuprammonium sulphate, containing a little added ammonium hydroxide, together with, if necessary, a second cuprammonium sulphate cell (3 cm) and several blue glass plates.

Green light of wavelength 5460A was obtained in the first instance by means of the filters recommended by Bowen.[51]

20 cc. of a solution of 1000 gm $CuCl_2 2H_2O$ per litre were added to 80 cc. of a solution of 340 gm $CaCl_2$ per litre, and a 1 cm layer of the mixed solution used in conjunction with a 3 cm layer of neodymium nitrate (100 gm $Nd(NO_3)_2 6H_2O$ per litre). A green glass filter (Chance No.7) and various green glass plates were also employed.

A "neutral" glass filter, transmission approximately 0.2, was also available.

These filters were used when the actual light intensity incident upon the plate could not be determined directly, as for example with very high or very low intensity light, unsuitable for direct measurement by the galvanometer scale system. Thus it was necessary to determine the transmission factors of these filters.

Transmission Coefficients of Filters.

The transmissions to blue light of the various filters were obtained by assembling them together in various combinations and noting the galvanometer deflections produced when they were illuminated with blue light of λ - 4360A produced as described above.

Similarly the transmissions to green light were obtained by corresponding illumination to green light of λ = 5460.

The deflections obtained for the various combinations of filters are shown in the following table, whish also indicates the various groupings selected in the calculation of the transmission factors of the individual filters.

The following abbreviations are used to denote the different filters.

Cup.I. 1 cm cell containing 2% cuprammonium sulphate.
Cup.II. 3 cm cell containing 2% cuprammonium sulphate.
B.G.I. Single blue glass plate.
B.G. Packet. Five blue glass plates bound together.
N. Neutral glass filter.
Chance green. Chance No.7. green glass filter.
$CuCl_2CaCl_2$ 1 cm cell containing mixture of $CuCl_2$ and $CaCl_2$ solutions, prepared as already described.
$Nd(NO_3)_2$. 3 cm cell containing neodymium nitrate (100 gm $Nd(NO_3)_26H_2O$ per litre)
Green glass I. Single green glass plate.
$CuSO_4$. 2 cm cell containing copper sulphate. (40 gm $CuSO_45H_2O$ per litre)

Table III.

Cup I.	$CuCl_2/CaCl_2$	$Nd(NO_3)_2$	$CuSO_4$.	Chance green.	Green glass I.	B.G.I.	B.G.packet.	Cup II	N.		
x								x	x		28.6
x						x		x	x		19.0
x						x			x		39.4
x						x	x		x		3.2
x						x	x				15.85
x				x		x			x		.0
	x	x			x				x		21.3
	x				x				x		24.8
	x		x		x				x		18.1
	x		x						x		42.2
	x		x	x					x		9.6
			x	x					x		27.4
	x		x	x							35.8
	x		x	x		x					1.05
	x	x					x				0.00
x	x		x			x			x		.01

B.G.I.
Cup II
B.C.packet
N.

$Nd(NO_3)_2$.
$CuSO_4$.
Green glass
Chance gree
SB $CuCl_2/CaCl_2$.

B.G.I.

From the above measurements the transmission factors for the various filters are as follows:

B.G.I. Factor (blue) = $\frac{19.0}{28.6}$ = 0.66

Cup II Factor (blue) = $\frac{19.0}{39.4}$ = 0.48

B.G. packet. Factor (blue) = $\frac{3.2}{39.4}$ = 0.08

N. Factor (blue) = $\frac{3.2}{15.85}$ = 0.202

$Nd(NO_3)_2$. Factor (green) = $\frac{21.3}{24.8}$ = 0.86

$CuSO_4$. Factor (green) = $\frac{18.1}{24.8}$ = 0.73

Green glass I. Factor (green) = $\frac{18.1}{42.2}$ = 0.43

$CuCl_2/CaCl_2$. Factor (green) = $\frac{9.6}{27.4}$ = 0.227

N. Factor (green) = $\frac{9.6}{27.4}$ = 0.347

B.G.I. Factor (green) = $\frac{1.05}{35.8}$ = .265

B.G.packet. Factor (green) 0.000

B.G.I.Cup I. Factor (green) $\frac{.01}{45}$

$CuCl_2/CaCl_2$ Factor (blue) $\frac{.01}{39.4}$

To produce an appreciable density on exposure to blue light it was normally necessary, for emulsions lacking added acceptors or sensitisers, to employ the high intensity given by one blue glass plate (B.G.I.) and the 1 cm cuprammonium sulphate cell (Cup I). These in conjunction with the neutral filter N gave a direct galvanometer deflection of 39.4 scale div. Since the transmission, for blue light, of N is .202, the total incident light intensity given by B.G.I. and Cup I. was taken as $\frac{39.4}{.202}$ = 195 scale divisions. This intensity when filtered through the "Chance green" filter of green light transmission 0.227 gave at most a deflection of

0.03 divs. Even if this be considered as all due to green light the amount in 195 scale divisions is only 0.13 div.

When, in fact, the intensity of green light recorded by the standard green filters above, in conjunction with the neutral filter was 42.2 divs, the introduction of B.G.I. and Cup I. gave a deflection of less than 0.01 divs. Since the green transmission factor for the standard green set up was 0.347 x 0.73 x .265 = 0.067 the amount of green in the 195 divs blue light given by Cup I and B.G.I. must be less than 0.15 ($= \frac{.01}{.067}$) scale divisions.

It was required to find (see Discussion) the absolute number of quanta per second incident on 1 sq.cm. of plate surface, i.e. to find the equivalent of 1 scale division in quanta /sec/cm^2, for blue and for green light.

Calibration of Blue Light.

This calibration was carried out by means of the photochemical decomposition of uranyl oxalate, investigated in detail at various temperatures and wavelengths by Leighton and Forbes[52].

Blue light has no effect on oxalic acid solution alone. In the presence of uranyl sulphate, which is thought to form a loose compound with the oxalic acid[53], blue light is absorbed and the oxalic acid decomposes according to the equation

$$(COOH)_2 = CO_2 + CO + H_2O.$$

Leighton and Forbes found that the quantum efficiency at 12°C for = 4360A was 0.60, and this value is adopted in the following calibration.

In a glass vessel, of polished plane faces 2 cm apart, there was placed exactly 100 cc of a solution containing 4.202 gm of uranyl sulphate ($UO_2SO_4 3H_2O$) and 6.24 gm oxalic acid ($(COOH)_2 2H_2O$) per litre, the solution being thus 0.01 M and 0.05 M respectively. The cell was placed in the path of the light beam so that the front of the cell occupied the position normally occupied by the thallous bromide plates. Immediately in front of this was a copper plate with a circular aperture, the aperture again corresponding to the position of the plate during an exposure. Blue light (195 divs galvanometer deflection) was allowed to fall on the solution for a noted time. After illumination the contents of the cell were removed to a conical flask containing 30 ml of dilute sulphuric acid, raised to 80°C and titrated with standard potassium permangnate, in red light. A control experiment of similar procedure, except that the illumination was omitted, was also carried out.

Experiment I. The reflection and transmission coefficients for the cell and solution in question were determined directly by means of blue light of intensity suitable for galvanometer scale measurements.

Readings.

Blue light alone (CupI, B.G.I, B.G.II, N) = 29.05 scale divs.

Blue light plus empty and dry cell = 23.50 scale divs.

Blue light, plus cell containing distilled water. = 25.75 scale divs.

Blue light, plus cell containing uranyl solution = 15.65 scale divs.

Area of aperture. = 4.91 sq.cm.

Time of insolation. = 364 min.

Intensity of illumination. = 195 scale div.

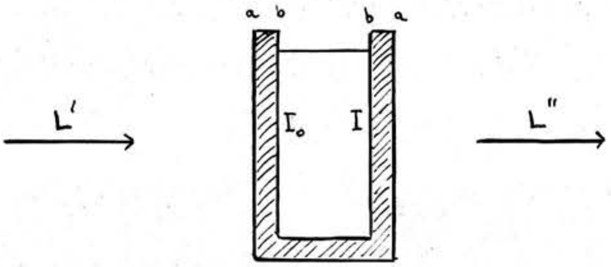
Initial titration with 0.2N.$KMnO_4$ = 49.65 ml.

Final titration with 0.2N.$KMnO_4$ = 49.17 ml.

Difference = 0.48 ml.

Calculation.

Let a, b, s be the transmission coefficients for an air-glass surface, a glass-solution surface and the solution respectively, with L' = incident intensity, I_0 = intensity at front glass-solution surface, I = intensity on rear solution - glass surface, and L" = final transmitted intensity (See diagram).



For empty dry cell, a = b; then after passing through four air-glass surfaces

$$L'' = L'a^4 \text{ (neglecting reflected light)}$$

$$\therefore a = \sqrt[4]{\frac{L''}{L'}}$$

$$= \sqrt[4]{\frac{23.50}{29.05}} = 0.95$$

For water filled cell, a = b, and

$$L'' = a^2b^2L'$$

$$ab = \sqrt{\frac{L''}{L'}}$$

$$= \sqrt{\frac{25.75}{29.05}} = 0.94$$

$$\therefore b = \frac{.94}{.95} = 0.99$$

The transmission b may be assumed to be the same for the solution filled cell as for the water filled cell. Hence light incident on the front surface of solution =

$$I_0 = 29.05 \times .95 \times .99$$

Light transmitted by solution, i.e. incident on second solution - glass surface =

$$I = {}^{L''}\!/_{ab} = \frac{15.6}{.99 \times .95}$$

The transmission coefficient of the solution, s, is then =

$$I/I_0 \quad = \quad 0.610$$

In the general case, where L is the light intensity incident on the front air-glass surface of the cell, the light absorbed by the solution is

$$L\,ab \; - L\,abs.$$

To this must be added light reflected back from rear surface a (neglecting reflection from rear surface b). Total light absorbed by solution in cell = I_{abs} =

$$L\,ab - L\,abs + L\,abs\,(1-a)(1-s)$$

$$= L\,ab \left[1 - s + s\,(1-a)(1-s)\right]$$

$$= .378\ L.$$

For conditions of actual calibration, L = 190 scale divs,

$$I_{abs} = 71.8 \text{ scale divs.}$$

Since 1000 ml N.$KMnO_4$ = 0.5 gm Mol. oxalic acid.

$$0.48 \text{ ml } 0.2 \text{ N.}KMnO_4 = \frac{.5 \times .48 \times .2}{1000} \times 6.06 \times 10^{23}$$

molecules oxalic acid.

But quantum efficiency, $\gamma = \frac{\text{No. of molecules decomposed/sec.}}{\text{No. of quanta absorbed/sec.}}$

Since the concentration, and the quanta absorbed, change during the insolation only by very small amounts, we may take

$$\gamma = \frac{\text{Total number of molecules decomposed.}}{\text{Total number of quanta absorbed.}}$$

as equal to 0.60 from the results of Leighton and Forbes.

Total number of quanta absorbed/sec/sq.cm.

$$= \frac{.48 \times .2 \times .5 \times 6.06 \times 10^{23}}{1000 \times .6 \times 4.91 \times 364 \times 60.}$$

The absorbed light was however equivalent to 71.8 scale divisions;

$$1 \text{ scale div} = \frac{.48 \times .2 \times .5 \times 6.06 \times 10^{23}}{1000 \times .6 \times 4.91 \times 364 \times 60 \times 71.8}$$

$$= 6.3 \times 10^{12} \text{ quanta blue light/sec/sq.cm.}$$

<u>Experiment 2.</u> The experiment was repeated with a smaller cell (thickness approximately 0.9 cm) and a different aperture, thus:-

Area of aperture. = 2.76 sq.cm.

Time of insolation. = 309 min.

Difference in initial and final titrations. = 0.23 cc .100N. $KMnO_4$.

The transmission factors were calculated from the following galvanometer readings:

Blue light: no cell = 10.15 scale divisions.

Blue light: dry empty cell = 8.17 " "

Blue light: cell + water = 8.96 " "

Blue light: cell + solution = 7.27 " "

Here $a = \sqrt[4]{\frac{8.17}{10.15}} = 0.95$, as before.

$ab = \sqrt{\frac{8.96}{10.15}} = 0.94$

$b = .99$, as before.

Giving $s = \frac{I}{I_o} = \frac{L''}{ab} / L'ab.$

$$= \frac{7.27}{10.15 \times .94^2} = 0.81$$

$$I_{abs} = L\,ab\left[1 - s + s(1 - a)(1 - s)\right]$$

$$= 0.185\ L.$$

With L = 190 scale divisions, as before,

I_{abs} = 35.2 scale divisions.

and 1 scale division $= \frac{0.23 \times .1 \times .5 \times 6.06 \times 10^{23}}{1000 \times .6 \times 2.76 \times 309 \times 60 \times 35.2}$

$= 6.45 \times 10^{12}$ quanta blue light/sec/sq.cm. of plate.

This value is in agreement with the value 6.3×10^{12} obtained in the first experiment.

It may be noted that the above air-glass and glass-water surface transmission factors may be calculated by the formula:

$$F = 1 - \left(\frac{n - n'}{n + n'}\right)^2$$

when n and n' are the refractive indices of the two media.

Taking the refractive indices, to blue light, of glass, water and air as being:

Glass	1.60
Water	1.33
Air	1.00

we have for the transmission factors of the surfaces,

Air-glass: a = 0.95

Glass-water: b = 0.99

which values are in agreement with those obtained by experiment.

Calibration of Green Light.

This determination was based on the preceding blue light calibration. Two fixed sets of filters, one for blue light and one for green light, were chosen to give suitable intensities as recorded by the photronic cell. The photocell was then replaced by a thermopile, and the two light intensities again recorded. From the photocell measurements can be calculated the number of quanta of blue light corresponding to 1 division of the thermopile scale. This in turn can be expressed in ergs. Since, in contrast to the photocell, the thermopile records energy directly in ergs, irrespective of wavelength, the thermopile reading for green light will give the number of ergs, and hence the number of quanta, for green light. Hence, from the photocell-galvanometer deflection for this green light, is found the number of quanta corresponding to 1 scale division.

The two types of illumination were obtained by the use of the following filters:

Blue (λ = 4360A) = B.G.I., CupI., N., B.G.II.

Green (λ = 5460B) = Chance green, $CuSO_4$, N.

With the photronic-cell galvanometer system the following mean deflections were obtained:

λ = 4360A: Deflection = 27.63 scale divs.

λ = 5460A. Deflection = 27.81 scale divs.

With the thermopile -galvanometer system the corresponding deflections were 0.6 for blue light and 0.3 for green light. As these were too small for accurate measurement the neutral filter N was removed in each case and the mean deflections there obtained were 3.055 for blue light and 1.21 for green. Since the transmission factors for N to blue and green light are 0.202 and 0.265 respectively, the deflections obtained with N in position would therefore more accurately be:

$\lambda =$ 4360A. Thermopile deflection $= 3.055 \times .202$
$= 0.615$ scale divs.

$\lambda =$ 5460A. Thermopile deflection $= 1.21 \times .265$
$= 0.320$ scale divs.

For blue light, 27.63 scale divs (photocell) = $27.63 \times 6.4 \times 10^{12}$ quanta of blue light/sec/sq.cm. of plate. This intensity registered as 0.615 scale divs (thermopile)

i.e. 1 scale div (thermopile) $= \dfrac{27.63 \times 6.4 \times 10^{12}}{.615}$ Quanta blue light/sec/sq.cm.

$= \dfrac{27.63 \times 6.4 \times 10^{12}}{.615} \times \dfrac{hc}{\lambda_b}$ ergs/sec/sq.cm.

$= 2.88 \times 10^{14} \times \dfrac{hc}{\lambda_b}$ ergs/sec/sq.cm.

But, for green light illumination the thermopile galvanometer deflection is 0.320, which is thus equivalent to

$$0.320 \times 2.88 \times 10^{14} \times \frac{hc}{\lambda_b} \text{ ergs/sec/sq.cm.}$$

$$= 0.320 \times 2.88 \times 10^{14} \times \frac{hc}{\lambda_b} \times \frac{\lambda_g}{hc} \text{ quanta (green)/sec/sq.cm.}$$

$$= \frac{.320 \times 2.88 \times 10^{14} \times 5460}{4360} \text{ quanta (green)/sec/sq.cm.}$$

This records on the photocell-galvanometer system as 27.81 scale divs.

1 scale div. (Photronic cell) $= \dfrac{.320 \times 2.88 \times 546 \times 10^{14}}{436 \times 27.81}$ quanta

$= 4.1 \times 10^{12}$ quanta (green)/sec/sq.cm. of plate.

Development.

The principles of the development procedure normally exployed were, in principle, as described by Farrer,[64] the actual details being as follows:

At the end of the predetermined time of exposure, the light was cut off, by closing the shutter, and switching off the lamp. In darkness, the exposed plate was removed from the plateholder, immersed immediately in 25 ml 10% silver nitrate solution and covered by an opaque cover. The time between the end of the exposure and the immersion was normally about one minute. After two minutes the dim darkroom light was switched on and the plate was gently moved vertically, by means of nickel tongs, to agitate the solution, this agitation being repeated each minute until five minutes had elapsed. The plate was then immersed, for one minute each, in each of three separate 25 ml portions of distilled water, and was then washed in running tap water for 45 minutes.

"Normal" development was carried out for 3 minutes at 16°C in 30 ml of a standard metol-hydroquinone developer (Appendix 1; Developer A.). The plate was rinsed briefly in distilled water and fixed for 12 minutes in 30 ml of a solution of sodium thiosulphate containing added potassium metabisulphite (Appendix I). A 30 minute wash in running water completed the process.

The following observations may here be made:

i. Experiment showed that the latent image decreased in intensity on standing prior to immersion in silver nitrate solution. This effect, however, was inappreciable unless some hours were allowed to elaps. Hence, for the actual variations encountered in practice in the time between exposure and immersion, this effect can be neglected.

ii. The actual transfer from plateholder to silver nitrate solution was carried out in darkness, as experiment showed that the latent image, in certain systems, was appreciably sensitive to reversal. When on one occasion the plate floated on the surface of the silver nitrate solution and was only partly immersed, the resultant lens effect of the liquid-solid boundary showed, for a few minutes exposure to red light, a decided bleaching of the final image. Results (later) showed that the dim blue light was equally sensitive in its bleaching effect. The lamp was therefore switched off immediately after exposure.

iii. Thallous bromide is not appreciably soluble in sodium thiosulphate solution. The 5 minutes immersion in 10% silver nitrate solution gave eventually a perfectly clear plate for no previous exposure and therefore was judged adequate for the purpose.

iv. Porcelain basins ($3\frac{1}{2}$" diameter) were used for all processes except that of washing, each basin being always reserved for a particular solution. Nickel tongs were however used to transfer the plate from one basin to another, one pair being reserved for all operations involving possible silver nitrate.

During washing the plate was supported at an angle on a perforated porcelain disc on a glass rod table situated within a glass bowl to which was supplied a constant head of tap water, and which was enclosed in a lightproof cupboard (see figure 14)

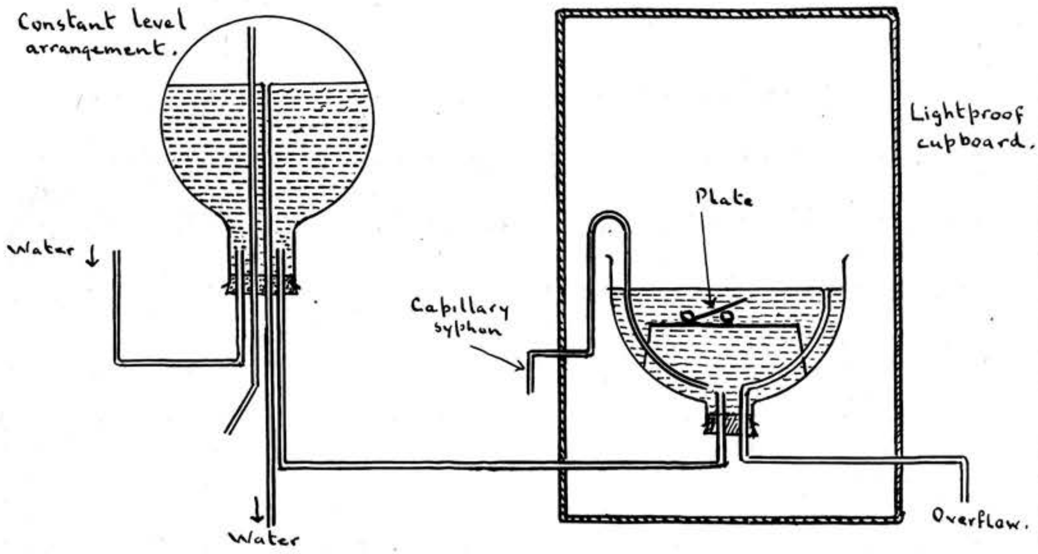


Figure 14.

v. Under the above conditions it was found that 45 minutes washing was required to remove the excess silver nitrate from the plate. Any appreciable reduction in this time resulted in blackening of the plate, when placed in the developing solution, due to the reduction of unremoved silver nitrate. As the entire process requires about 100 minutes for each plate a method was developed which reduced this time to 60 minutes. In this latter method the 45 minute washing process was replaced

5

by a 5 minute immersion in 2% potassium bromide solution, which converted the excess silver nitrate into silver bromide. Eleven small basins were used in this method of processing the sequence of which is indicated below.

Basin	1	2	3	4	5	6	7	8	9	10	11	
Contents	$AgNO_3$ 10%	H_2O dist	H_2O dist	H_2O dist	KBr 2%	H_2O dist	H_2O dist	H_2O dist	Dev. 16°C	H_2O dist	Fixing soln.	Wash.
Time (mins)	5	1	1	1	5	1	1	1	3	Rinse	12	30

It was found that this method of processing produced no appreciable differences in the final developed densities. The longer method was, however, generally adopted as being simpler and the shorter method was only employed when circumstances rendered it advantageous.

vi. Provided the coating of the plates was carried out on plates properly cleaned by the procedure described earlier, there was little tendency for the film of emulsion to become detached from the surface as a result of the somewhat lengthy processing. Final washing could indeed be prolonged for several hours (overnight) without any deleterious effects being observed. The temperature of the tap water used for washing seldom, however, rose above 12°C.

EXPERIMENTAL RESULTS.

The procedures outlined in the preceding section were adopted only after much preliminary work, to some of which brief reference is now made.

Early Emulsions.

The first emulsions, containing no iodide and made by simple (rapid) mixing of thallous nitrate and potassium bromide - gelatin solutions, were found to be very "slow". Variations in the period and method of washing (e.g. coating the unwashed emulsion and washing the coated plates) did not result in any marked speed increases, indicating that the low sensitivity was not due to the presence of unremoved soluble salts. Attempts were made to obtain better images and these may be divided into four main groups:

(a) Variations in preparation of emulsion.

(b) Different developers.

(c) Additions to emulsions.

(d) Different sources of illumination.

(a) Variations in Preparation of Emulsion.

Emulsions subjected to periods of "ripening", before shredding and washing, varying from 15 minutes to 3½ hours at 35°C showed no evidence of speed increase. Prolonged digestion of a thallous bromide emulsion at 35°C, after shredding and washing, appeared to result in a slight decrease in speed; one hour digestion at 35°C gave a developed density of 0.22 under standard conditions, while the same emulsion digested for 16½ hours gave a density of 0.20. As already mentioned, a short digestion at 100°C rendered the emulsion transparent and insensitive.

In view of the lengthy processing, chrome alum was added to the early emulsions (0.1 gm per 100 ml emulsion) as a hardening agent. Reduction of chrome alum to .05 gm per 100 ml resulted in a slight speed increase. Addition of the chrome alum before shredding rendered the emulsion so stiff as to make shredding through muslin very difficult. After setting this emulsion could not be remelted even at 45°C and with the addition of alcohol. After 4 months, however, it was remelted at 62°C and, when coated, gave a plate speed somewhat higher than that obtained with later emulsions containing no acceptor. Emulsions containing no chrome alum were found to be sufficiently hard to withstand the processing operations and accordingly chrome alum was omitted in later preparations.

Slow addition of thallous nitrate (dropwise over a period of 20 minutes) gave faster emulsions than rapid addition. As already reported, simultaneous addition of thallous nitrate and potassium bromide solutions and the use of less initial gelatin gave no greater sensitivity than the "dropwise" method.

(b) Different Developers.

In the early experiments extensive fogging was encountered with the normal M.Q. developer (Appendix I, developer A), and hence experiments with other developing solutions were carried out. To check whether fogging was due to low fog potential of thallous bromide emulsion, a low-potential ferrous oxalate developer was tried. (Appendix I, developer B). Fogging, however, was still extensive. Physical development using Odell's developer (Appendix I, developer C) was next investigated. In this experiment the exposed plate was treated directly with developer without pre-treatment with silver nitrate. After development the unwanted thallous bromide was removed by prolonged washing: a distinct but weak image was obtained. An attempt was then made to develop the latent image after fixation by treating an exposed plate with silver nitrate, washing, and then fixing and rewashing before development. In this case no image was obtained.

In silver bromide practice the addition of potassium bromide to the developing solution helps to restrain fog. Experiments were carried out using a metol-hydroquinone developer in which the bromide content was increased twenty-fold (Appendix I, developer D). Fogging was considerably reduced by this method and well-defined densities were obtained. The development time however was increased to about 16 minutes.

The fine-grain borax developer Kodak D.76 (Appendix I, developer E) and the corresponding buffered-borax developer D.76d (Appendix I, developer F) gave similar results to developer D. Development time was again about 16 minutes.

Certain organic compounds, such as aniline, thioacetanilide and various substituted benzimidazoles, added to the developer, are known to act as anti-fogging agents in silver bromide systems.[54] A number of exposed plates were therefore developed in developer D; developer D containing 1 part in 10,000 of aniline, and developer D containing 1 part in 1,500 of analine. Little difference was discernible in the three series; visible images were obtained but fog in each case was present in equal amount.

In these experiments, low exposing illuminations were employed, e.g. 5 min. exposure at 17 inches from a 100 watt tungsten lamp.* It was later found (vide infra) that higher intensities gave greater developed densities with shorter times of development and consequent reduction in fogging. Developer A was then found to be the most satisfactory.

(c) Additions to Emulsions.

Attempts were made artificially to introduce development centres into the emulsions. An emulsion was prepared to 100 ml of which was added, dropwise over a period of 20 minutes and with vigorous mechanical stirring, 0.5 ml of $\frac{N}{100}$ sodium thiosulphate. Plates from this emulsion were irregular in performance, fogging being encountered in some and not in others.

Mercury sensitisation, in the manner applied to silver bromide plates, was attempted by storing a number of normal thallous iodo - bromide plates in a closed box containing an open vessel of mercury.

Plates tested at intervals up to 2 months, revealed no measurable increase in sensitivity.

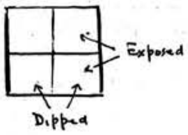
A further attempt to introduce sensitivity centres was made by dipping part of a plate into a very weak solution of sodium sulphide (.001%), drying and exposing. The dipped part gave a slightly greater developed density than the undipped part. This effect may have been due to the acceptor action of the slightly alkaline solution.

Further experiments with bromine acceptors were carried out by partially dipping a series of bromide-iodide plates in various solutions for 2 minutes, rinsing in distilled water, drying and finally exposing to a 150 watt tungsten lamp at 10 inches distance. Visible darkening was observed in the case of the following, arranged in decreasing order of effect; normal M.Q. developer, 5% sodium sulphite solution, 5% sodium hydrosulphite solution, 5% sodium nitrate solution, 5% sodium arsenite solution, 10% sodium carbonate solution. Various other solutions had no effect, e.g. 4.5% sodium hydroxide, 1% borax, 5% lead acetate, 20% sodium thiosulphate, 1% alcoholic phenol, 50% alcoholic phenol, aniline, 1% hydrogen peroxide. In these experiments the time of immersion must not be so long that double decomposition occurs to any appreciable extent. For example, it was found with sodium nitrite that, whereas a 2 minute immersion in 5% or 10% solution resulted in pronounced blackening on exposure to light, a 30 minute immersion in 20%

·ite?

solution caused the coated film to swell (the grain apparently undergoing structural alterations) and to become white in colour. On exposure, this white layer (possibly thallous nitrite) did not blacken except after drying and on very prolonged exposure to sunlight. These dipping experiments suggested that a more extended investigation was necessary.

A number of different solutions were prepared, in each of which was dipped for 2 minutes a thallous iodobromide plate, so that half of the plate only was immersed. The plate was then rinsed briefly in distilled water, allowed to dry and then exposed under standard conditions for 30 minutes to blue light ($\lambda = 4360A$) and processed in the normal manner. The exposures were arranged so that half each of the dipped and undipped portions was illuminated (see diagram). Four areas of each plate were thus available for examination.



Sodium Arsenite. Three solutions were used, viz. 1%, 0.1% and 0.01", and the densities obtained were approximately

	Dipped & Exposed	Dipped	Exposed	Blank
1% Na_3AsO_3	1.05	0.75	Clear	Clear
0.1% Na_3AsO_3	0.20	0.16	Clear	Clear
0.01% Na_3AsO_3	Clear	Clear	Clear	Clear

Treatment with the 1% solution thus markedly increases the sensitivity but is accompanied by considerable fog in the unexposed areas. The effect of the 0.1% is similar but much less pronounced. The experiment with 0.1% Na_3AsO_3 was repeated using plates made from an emulsion containing 0.5 ml of $\frac{N}{100}$ sodium thiosulphate per 100 ml. Distinct densities, accompanied however by fogging in the dipped-unexposed area, were obtained.

	Dipped Exposed	Dipped Not exposed	Exposed Not dipped	Blank
1st experiment.	.65	.35	.25	Clear
Repeat "	.63	.35	.25	Clear.

Ammonium Cinnamate. 0.1% and 1% solutions were found to have no effect. With a 5% solution however pronounced fog was produced in the dipped-unexposed area, the density of the dipped-exposed area being only discernible above this fog.

Dipped Exposed	Dipped Only	Exposed Only	Blank
.95	.92	Clear	Clear.

Sodium Citrate. 5%, 1% and 0.1% solutions were used and the densities obtained were approximately:

	Dipped Exposed	Dipped Only	Exposed Only	Blank
5%	1.0	1.0	Clear	Clear
1%	.20	Clear	Clear	Clear
0.1%	Clear	Clear	Clear	Clear

Thus the 1% solution sensitises the plate slightly, but in the stronger concentration causes pronounced fogging

Sodium Nitrite. As before, 5%, 1% and 0.1% solutions were used. The densities obtained are given below

	Dipped Exposed	Dipped Only	Exposed Only	Blank
5%	1.2	Clear	0.35	Clear
1%	0.75	Clear	0.35	Clear
0.1%	Clear	Clear	Clear	Clear

The fact that the "exposed only" area of the thin plate shows no density indicates that the three results are not strictly comparable. The other plates show clearly however that in the use of sodium nitrite as an acceptor we have a very effective means of increasing the speed of the plate. Some further experiments with sodium nitrite were therefore carried out.

The highest concentration of sodium nitrite in the above experiments having given the greatest speed increase, still stronger solutions were next tried. It was found that 10% solutions were satisfactory and gave still greater sensitivity. Plates dipped in 20% solution however did not dry readily and, even when apparently dry, tended to adhere to one another. A number of thallous iodo - bromide plates were therefore dipped for 2 minutes in 10% $NaNO_2$ solution and rinsed and dried as before. They were then exposed in turn to the standard blue light ($\lambda = 4360A$) for varying periods of time. After processing the densities obtained were as given in table IV. These values are again plotted in figure 15 as a standard H. & D. curve, which, as will be seen, is of the normal form.

Table IV.

Br-I- NO_2'(dipped). Exposure = t seconds $\lambda = 4360$ A.

t	2	4	8	16	32	1x60	4x60	16x60	48x60	340x60
log t	.301	.502	.903	1.204	1.505	1.778	2.380	2.982	3.459	4.310
D	.139	.171	.205	.246	.348	.474	.635	.925	1.424	1.698

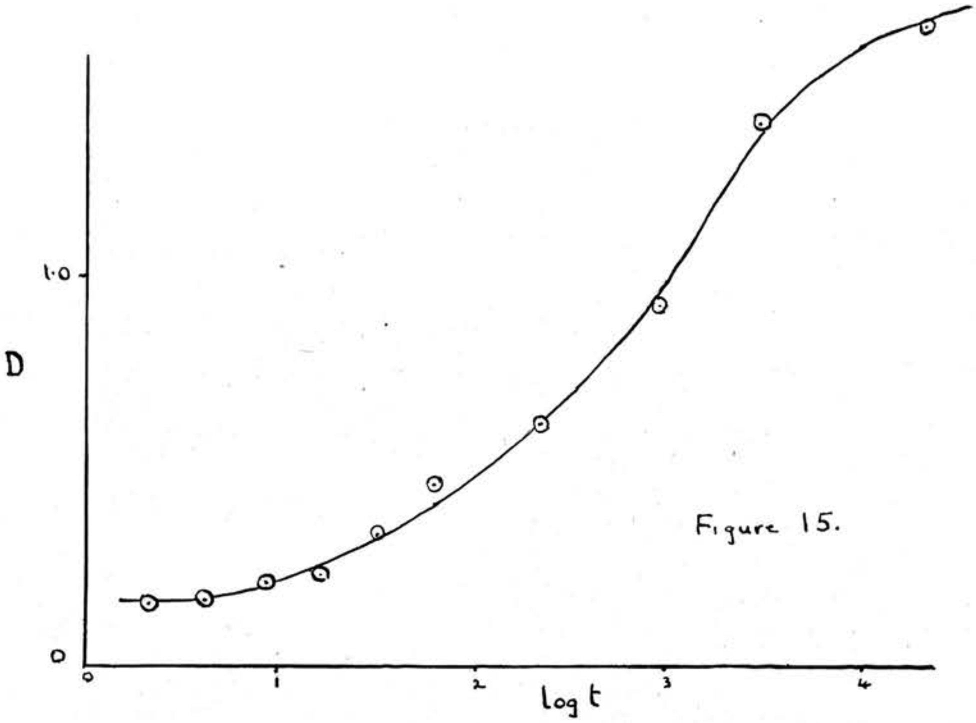


Figure 15.

It is thus seen that with sodium nitrite, a noticeable image is obtained for an exposure time of as little as 2 seconds. The particular plates employed in this experiment were incapable, when untreated, of forming a latent image even when exposed to the carbon arc. During the illumination of the dipped plates it was observed that distinct print-out densities were produced. Accordingly a further series was exposed for varying times and each plate, after silver nitrate treatment, was rinsed in distilled water and placed directly in the fixing solution, without previous development. The densities obtained are given in table V and are plotted in figure 16.

Table V.

Br-I- NO_2' Exposure = t minutes λ = 4360 A.

t	5	15	80	1,400
log t	0.699	1.176	1.903	3.146
Print-out density D.	0.338	0.427	1.164	2.067

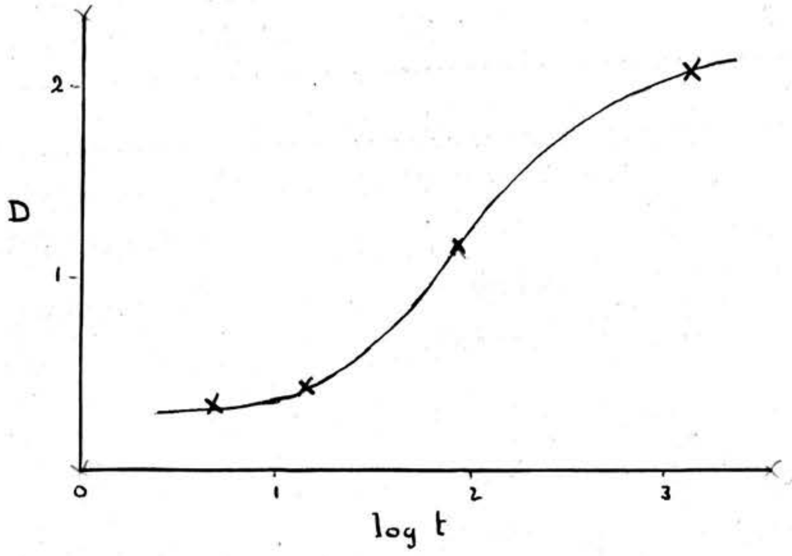


Figure 16.

(d) Different sources of Illumination.

Concurrently with the development of the above method of enhancing the plate sensitivity, indications had also been obtained that higher intensities of illumination were necessary. The first source of illumination employed was a 100 watt tungsten lamp at 17 inches from the plate. The very low densities obtained even after long exposures were increased slightly by reducing the lamp-to-plate distance to 6 inches. Sunlight was then found to produce still better densities, which were in turn increased by the use of an over-run half-watt ('Photoflood') lamp. The densities obtained, for the same batch of plates, for 2 minute exposures to this source were considerably greater than those obtained for 16 minute exposures to a 100 watt tungsten lamp at the same distance. Taking the effective wattage of the Photoflood lamp as 800 watts, these exposures should be equivalent and, if true reciprocity obtained, should yield the same densities on development. The results thus showing the desirability of high intensity, experiments were carried out with the most intense source of illumination available, a carbon-arc with half-inch carbons. With this source pronounced densities were obtained for very short exposures and the values obtained for a series of iodide-free thallous bromide plates (containing no nitrite) are given in table VI and are shown as an H. and D. (density-time) curve in figure 17.

Table VI.

TlBr plate Exposure = t seconds. Carbon arc 8" distance.

t	1	2	4	8	16	30	60	120	240	600	960	1920
log t	0	0.30	.60	.90	1.20	1.48	1.76	2.08	2.38	2.78	2.98	3.28
D	0.300	.051	.106	.146	.207	.252	.351	.436	.474	.592	.683	.757

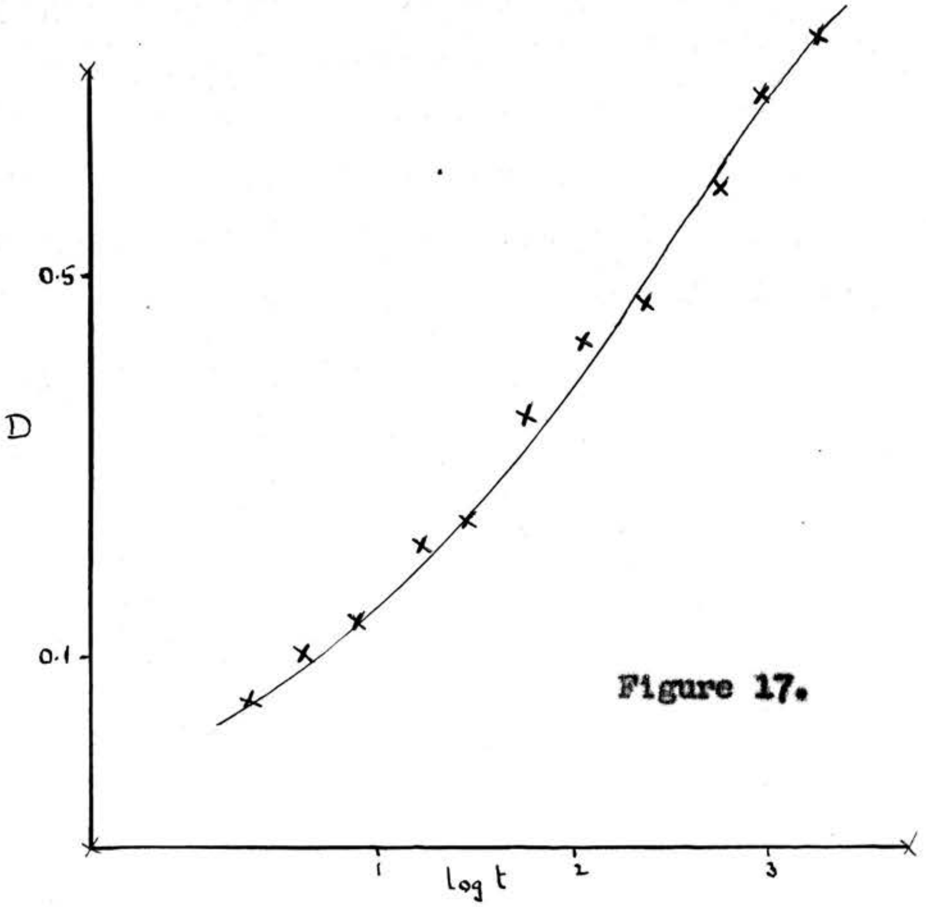


Figure 17.

Fading of Plates.

During these attempts to increase sensitivity a tendency was noted for both iodide-free and iodide-containing plates to lose even their slight initial sensitivity on storage. Plates which gave, immediately after preparation, slight but distinct densities when exposed to the standard blue source, became incapable after a few weeks' storage of producing a developable image even after prolonged exposures. In such cases higher sources of illumination such as the carbon arc, were capable of giving a density but the ability to do so also faded out with time. It was then found that these insensitive plates could be markedly sensitised by the use of sodium nitrite, as already reported, but this sensitivity was also found to be lost on long (1 year's) storage.

In view of the fact that gelatin when apparently dry still contains approximately 15% of moisture, it was considered possible that the loss of sensitivity might be due to the destruction of sensitivity specks by water. In this case any internal sensitivity specks would probably not be affected. Accordingly an insensitive "faded" plate was washed in running water for 10 minutes with the object of dissolving away the surface of the grain and thus revealing internal sensitivity specks. When dried and exposed, however, no density was obtainable.

Again, a batch of insensitive plates was kept in a thermostatic oven at 35°C and plates examined at intervals up to 3 weeks, but again no density was obtainable.

It has thus been shown generally by the above experimental results that, in agreement with Farrer's conclusions, thallous bromide plates showed a very low absolute sensitivity or speed to white light in comparison with silver bromide plates, although such speeds could be markedly increased by the presence of other substances commonly regarded as acceptors of bromine atoms. Farrer also found that the presence of iodide in small quantities (up to 7.5% of the bromide content) in the initial emulsion preparation resulted in a decided decrease in sensitivity, again in opposition to silver bromide practice. The effect of 5% iodide was therefore first examined in relation to spectral sensitivity and to absolute speed of the resultant emulsion.

Two emulsions were prepared, which differed only in that the second Br-I emulsion contained potassium iodide in an amount equivalent to 5% of the potassium bromide. Strips of the plates were exposed in a spectrograph, under standard conditions, to the spectrum of (a) a 100 watt tungsten lamp and (b) an Osira mercury-vapour lamp.

In the bromide plate, even after 2 hours exposure, only a faint trace of deposit corresponding to the 3650.A. line was to be observed. The mercury green and yellow lines on the developed plate were, however, lighter than the background fog, showing that reversal was occurring at these wavelengths. With the tungsten lamp, the spectral sensitivity obviously reached a limit, under the above conditions, very close to the 4360.A. wavelength.

With the bromide-iodide plate, on the other hand, not only did the spectral sensitivity extend considerably beyond the 4360.A. wavelength to approximately 4530.A, but the developed density at 4360, 4080 and 3650.A. was quite distinct. The evidence thus indicated an increased spectral and absolute sensitivity in contrast to Farrer's findings. Further, the very slight ground fog was entirely removed by the mercury green and the mercury yellow wavelengths, the effect being more pronounced than in the case of the bromide plate. A decided Herschel effect was therefore in operation.

This bleaching aspect of the bromide-iodide plate was further examined as follows. A strip was pre-exposed to the direct mercury lamp for 10 minutes at 6 inches distance, and then exposed in the spectrograph as before. On processing it was found that not only was reversal produced by the mercury green and yellow but, also, reversal was produced by the entire tungsten spectrum. Even in the blue there was a decided lightening of the deposit. Reversal similarly extended far into the red. At the same time the blue 4360.A. line of the mercury spectrum showed a decided darkening of the density produced by the pre-exposure. It was thus obvious that two opposing tendencies were in operation with blue light. As the blue light intensity of the mercury lamp was much greater, as judged visually on the ground glass of the spectrograph, than that of the tungsten lamp, it seemed probable that intensity was the deciding factory. Re-examination of the iodide-free plate showed that this reversal effect for blue and shorter wavelengths was also present although to a much less degree.

That these reversal effects were of no little importance in ordinary white-light exposures was evident from the results of direct stripwise illumination of a bromide-iodide plate by a 100 watt tungsten lamp at 9 metres distance for varying periods of time. This plate showed on development a decided ground fog. The developed density produced by exposure showed, with increase in time, a continual decrease below this fog, thus:

t (min)	0	1	3	9	27	54
D	0.16	0.14	0.10	0.09	0.06	0.07

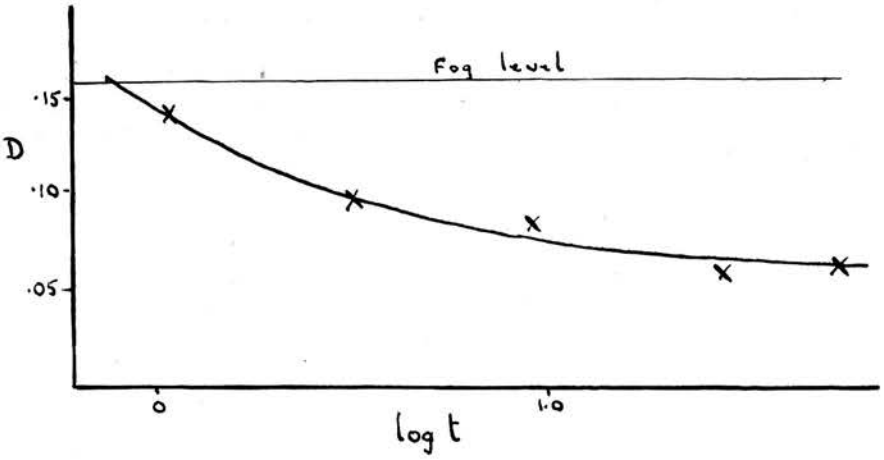


Figure 18.

In view of these observations it was decided that a more thorough investigation was required as to the relative speeds of bromide and bromide-iodide plates in relation to this reversal. For this purpose a steady high-intensity source was obviously required where distinction could be made between "actinic" and "non-actinic" spectral regions. The mercury vapour lamp was finally used as standard, with procedure and filters for blue and green light as already described.

As indicated, however, the decided "fading" or loss of speed in such plates made it essential that for accurate comparison of plates even in the same series, the rates and conditions of such fading should be determined. Experiments based on this point of view are therefore first described.

<u>Stability of the Latent Image after Exposure.</u>

Since the normal period of time between exposure and the first stage of processing was approximately 1 minute in duration, it was decided first to find if any appreciable difference in developed density arose from variation of this time factor. Accordingly a series of thallous bromide plates with no iodide or acceptor was exposed under constant conditions (at 6 inches from a carbon arc) for a fixed period of time. One of these plates was then processed immediately as usual, with the normal developer A, while the others were kept at room temperature in darkness for various times before development. Other series were similarly [illegible] out except that the time of initial exposure was varied to give different initial densities. The results are given in Table VII.

Table VII.

TlBr plate. Carbon arc Exposure = t (seconds)
Time elapsing between exposure and processing = T (minutes)

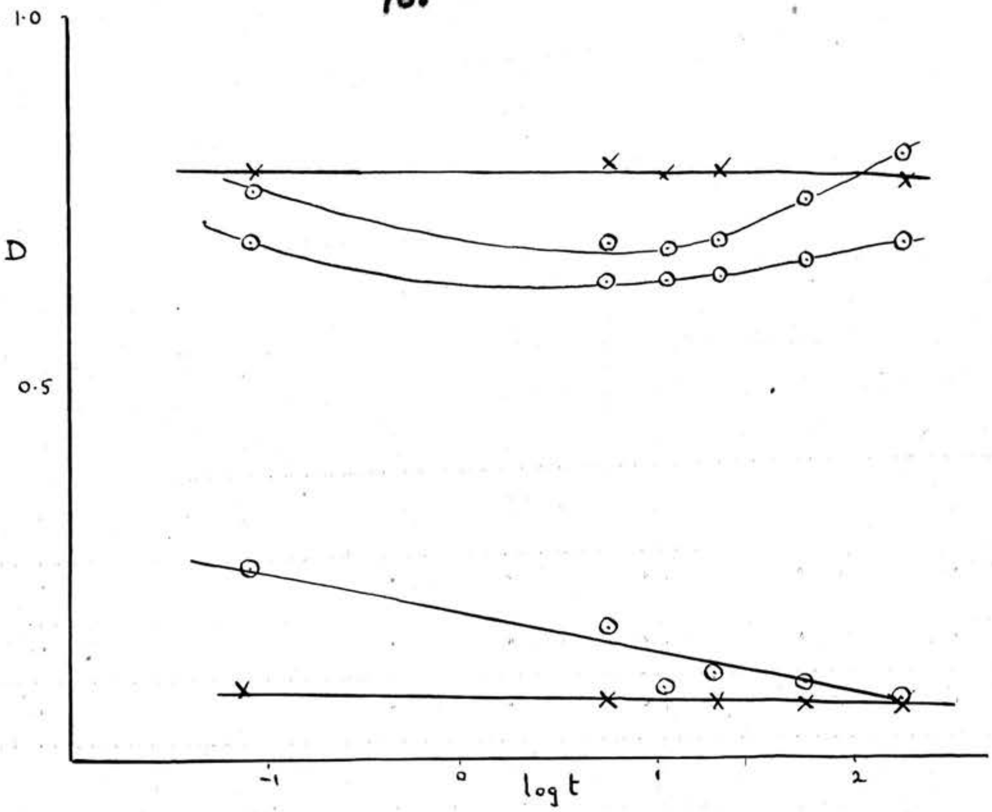
		Series	1	2	3	4	5
T	log T	t	0	10	120	300	540
5	0.699	D	0.05	.42	.78	.97	1.00
30	1.477	D	0.05	.43	.78	.96	1.01
60	1.778	D	0.05	.42	.78	.97	0.01

From these values it is seen that there is no measurable latent image regression in periods up to 1 hour. A further series of experiments was carried out on the same lines but with very much longer intervals (up to 1 week) between exposure and processing. The densities obtained in this set of experiments are given in Table VIII and shown graphically in figure 19.

Table VIII.

TlBr plate. Carbon arc Exposure = t (seconds)
Time elapsing between exposure and processing = T (hours)

		Series	1	2	3	4	5
T	log T	t	0	10	60	120	600
0	0.72	D	0.09	0.25	0.68	0.75	0.78
5.2	0.72	D	0.09	0.17	0.61	0.68	0.77
10.5	1.02	D	0.08	0.09	0.58	0.65	0.74
20	1.30	D	0.08	0.11	0.59	0.66	0.74
61.5	1.79	D	0.08	0.09	0.63	0.71	
171	2.23	D	0.07	0.07	0.65	0.76	0.73



It was thus observed that, generally, the densities tended to decrease with time, although in two cases the density appears to rise slightly after relatively long intervals. The changes however are so slow, being only appreciable after several hours, that it is obvious that small variations in the normal 1 minute period between exposure and processing must have only a negligible effect on the developed density.

Decrease in Sensitivity in Coated and Dried Plates.

For this purpose the wedge system was employed with the mercury lamp and blue (4360.A) light. In this and subsequent tables, I denotes the light intensity incident on the plate as measured in scale divisions by the photronic cell - galvanometer system, and D denotes the measured density. The density corresponding to I = o is that of the plate plus fog. The symbol Δ is used to denote density above fog, as given by simple subtraction. Unless otherwise stated, exposure was followed immediately by normal processing (Developer A). Table IX shows the densities obtained with comparable exposures made at different times after coating of the plates. These values are also plotted in figure 20.

Table IX.

Br - I plate. t = 30 min. λ = 4360

Time between coating of plate and exposure = T (hrs).

Expt.	T	I	0	12.9	73.7	38.3	21.5	16.7	10.6	4.87	1.91
		log I		2.11	1.87	1.58	1.33	1.22	1.025	0.69	0.28
1	0	D	.200	.395	.356	.312	.291	.275	.265	.236	.193
		Δ		.195	.156	.122	.091	.075	.065	.036	-.007
2	72	D	.200	.339	.302	.276	.190	.254	.237	.217	.223
		Δ		.139	.102	.076	-.01	.054	.037	.017	.023
3	216	D	.185	.316	.270	.253	.225	.212	.210	.196	.191
		Δ		.131	.085	.068	.040	.027	.025	.011	.006

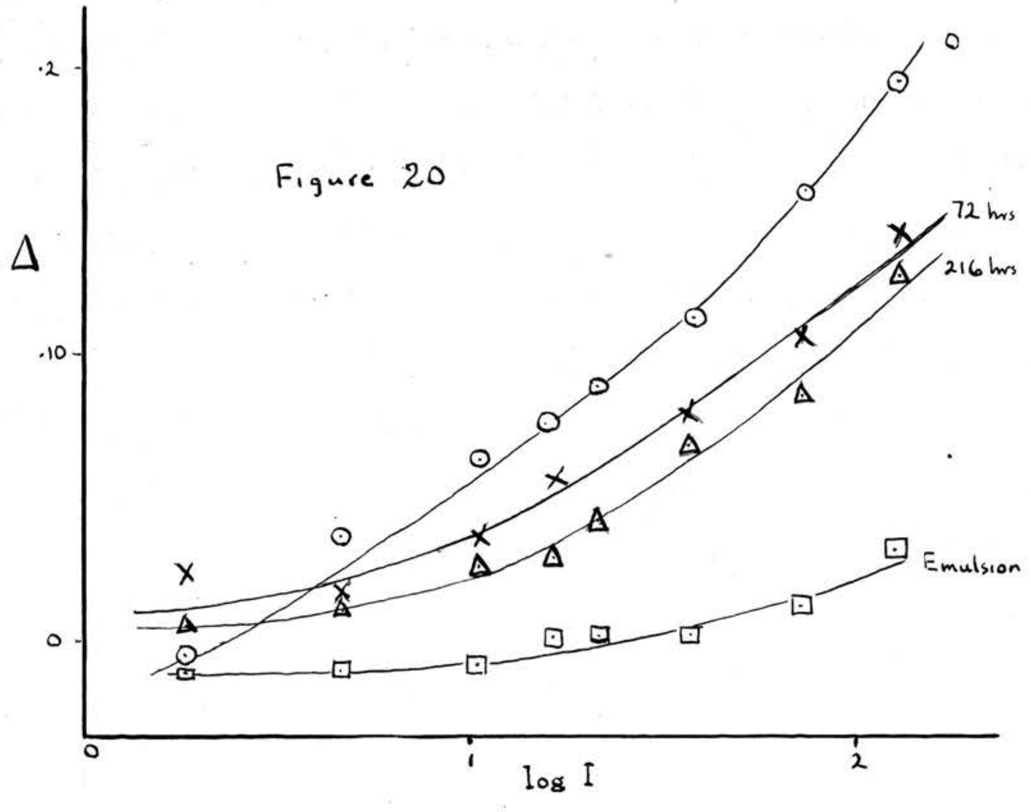


Figure 20

It is obvious that an appreciable fading occurs in 216 hours. For accurate comparison it was therefore necessary that comparable experiments should be done with as little intervening time as possible. Correction based on the table given above was found impracticable unless a "fading" curve was established for each plate. Even then this was not altogether satisfactory as different parts of the same (large) plate showed appreciable variations. This was regarded as due to the different rates of drying of parts of the same plate; the edge areas dried more quickly and gave higher densities. For this reason a fading "curve" for an emulsion was attempted as described in the next section.

Fading of Sensitivity of Emulsion.

One plate (1) was coated from a freshly prepared emulsion and the emulsion was then allowed to set and remain undisturbed in darkness for 15 days. A second plate (2) was coated as before. Both plates were allowed to dry under as far as possible identical conditions for 4 days, and were then cut and tested. Results are given in table X and are included in figure 20, where experiment 1 is represented by the highest density curve of the series.

Table X.

Br-I plate. t = min. λ= 4360.A.

	I	0	12~~.~~9.	73.7	38.3	21.5	16.7	10.6	4.87	1.91
	logI		2.11	1.87	1.58	1.33	1.22	1.025	0.69	0.28
1	D	.20	.395	.356	.312	.291	.275	.265	.236	.193
	Δ		.195	.156	.112	.191	.075	.065	.036	-.007
2	D	.09	.12	.10	.09	.09	.09	.08	.08	.08
	Δ		.03	.01	.00	.00	.00	-.01	-.01	-.01

It will be observed that practically no image was formed on plate 2. The undried emulsion lost its capacity for latent image formation much more rapidly than the dried plate. For this reason a practice was made of coating the emulsion as quickly as possible after preparation. During the drying of a plate, the more rapid drying of the edges was regarded as responsible for the greater densities obtained in such areas.

Fading of Plates containing Nitrite.

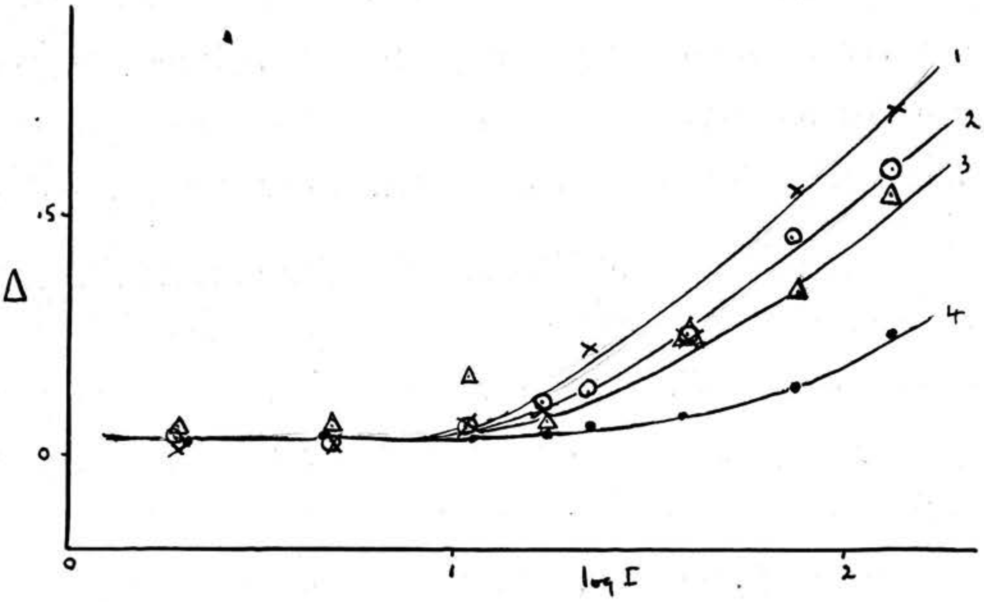
The effect of the presence of sodium nitrite on the fading of the plates was next examined. A bromide-iodide emulsion containing 40 ml of 1% $NaNO_2$ per ml (added dropwise to the finished emulsion over a period of 20 minutes with rapid stirring, stirring being continued for a further 10 minutes) was coated and the dried plates were examined at four intervals spaced over three weeks. Results are given in table XI and figure 21.

Table XI.

Br-I-NO_2 plate. $t = 30$ min. $\lambda = 4360$.A.

Time between coating of plate and explsure = T (hours)

		I	0	129	73.9	38.3	21.5	16.7	10.6	4.87	1.91
	T	logI		2.11	1.87	1.58	1.33	1.22	1.025	0.66	0.28
1	0	D	0.15	0.86	0.70	0.38	0.37	0.25	0.21	0.17	0.15
		Δ		0.71	0.55	0.23	0.22	2.10	0.06	0.02	0.00
2	72	D	0.12	0.71	0.57	0.36	0.25	0.225	0.18	0.14	0.15
		Δ		0.59	0.45	0.24	0.13	0.105	0.06	0.02	0.03
3	192	D	0.12	0.66	0.45	0.36		0.22	0.18	0.17	0.16
		Δ		0.54	0.33	0.24		0.10	0.16	0.05	0.04
4	504	D	0.13	0.385	0.26	0.21	0.19	0.18	0.17	0.16	0.15
		Δ		0.25	0.13	0.08	0.06	0.05	0.04	0.03	0.02



It will be observed that the rate of fading is relatively slower in these plates than in the previous nitrite-free plates. This is especially remarkable in the lower density ranges.

Having thus examined the "fading" properties of the above classes of plates, the required comparison of the relative speeds of bromide and bromide-iodide plates in relation to reversal was now carried out.

Comparison of Iodide-free and Iodide-containing Plates.

The two emulsions used differed only in the addition of potassium iodide in amount equal to exactly 5% by weight of the potassium bromide used. All other procedures were, as far as possible, identical. The dried plates were examined by exposure to blue light ($\lambda = 4360.A.$) as before. In table XII, Experiment 1 denotes the iodide-free plate and 2 the iodide-containing plate.

Table XII.

1. Br plate. 2. Br-I plate. $t = 30$ min $\lambda = 4360.A.$

	I	0	195	109	68.5	44.2	25.6	14.4	8.25	4.23
	log I	-	2.29	2.04	1.84	1.645	1.41	1.16	0.92	0.63
1	D	.0.95	.179	.159	-	.133	.115	-	-	-
	Δ	-	.084	.064	-	.038	.020	-	-	-
2	D	0.102	.367	.303	.265	-	.214	.195	.172	.162
	Δ	-	.265	.201	.162	-	.112	.093	.070	.060

As the results show, the iodide-free plate is definitely much less sensitive to light of wavelength 4360.A, measured as light incident on the plate surface.

Immediately after the coating of plates 1 and 2 above, 10 ml of .04% sodium nitrite solution were added drop by drop over a period of 20 minutes with rapid stirring, the stirring being contined for a further 10 minutes. Plates 3 and 4 were then coated, plate 3 representing the iodide-free emulsion. When dry these plates were exposed as before, all conditions apart from the addition of nitrite, being comparable. The results obtained are given in table XIII, and are shown graphically in figure 22, which also includes the results of table XII for comparison.

Table XIII.

Expt.	I	0	195	109	68.5	44.2	25.6	14.4	8.25	4.25
3	D	.085	.207	.187	.157	.135	.115	-	-	-
	Δ		.122	.102	.072	.050	.030	-	-	-
4	D	.094	.540	.445	.372	.313	.275	.229	.198	.180
	Δ		.446	.351	.278	.219	.181	.135	.104	.086

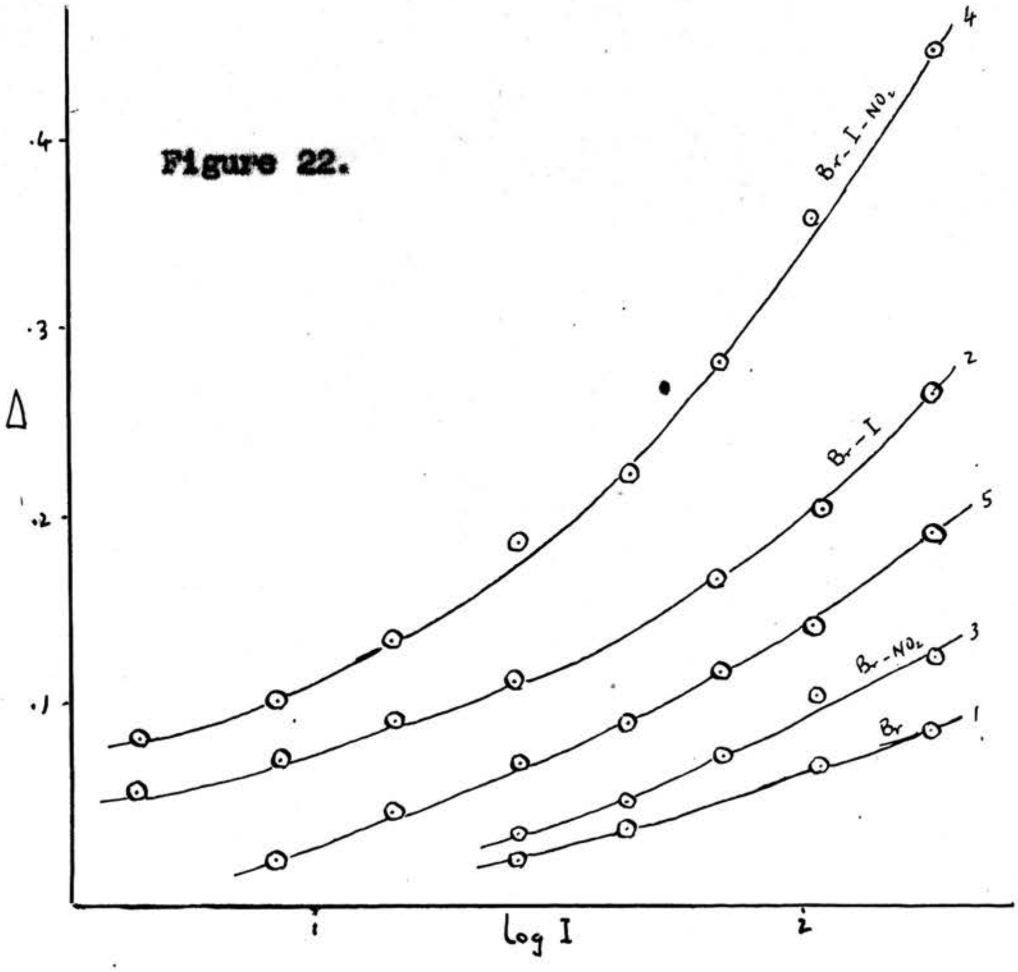


Figure 22.

In experiment 3, areas corresponding to the three lowest intensities were of uneven density, a phenomenon apt to occur when additions were made to emulsions as above. The above results show clearly however, that the effect of added nitrite in increasing the speed is less for iodide-free emulsions.

Two other experiments may be recorded here. To the iodide-free emulsion containing nitrite was added 0.02% sodium arsenite solution (in the proportion of 7.2 ml per 100 ml emulsion) which as previously noted, caused rapid visible blackening of a TlBr plate when exposed to light. A small increase in speed was then noted, as shown by results for plate 5, the exposure and other conditions remaining as before.

Table XIV.

Br-Nitrite - Arsenite.

Expt.	I	0	195	109	68.5	44.2	25.6	14.4	8.25	4.23
5	D	.10	.29	.24	.22	.19	.17	.15	.12	-
	Δ		.19	.14	.12	.09	.07	.05	.02	-

The quantity of nitrite in the bromide-iodide emulsion was doubled (plate 6). Results of exposure are given in table XV and figure 23. A decided large increase in density is again recorded.

Table XV.

Expt.	I	0	195	109	68.5	44.2	25.6	14.4	8.25	4.23
6	D	.142	1.42	1.59	1.10	0.97	0.70	0.55	0.45	0.336
	Δ		1.28	1.15	0.96	0.83	0.56	0.41	0.31	0.194

Finally, table XVI contains the results of addition of 0.5 gm $NaNO_2$/100 cc. emulsion, this being the largest quantity which can conveniently be incorporated in these emulsions. In this case, drying of the coated plates became very slow. Even when apparently dry a certain "tackiness" was experienced together with pronounced unevenness in the developed density. Exposure and processing conditions were as before.

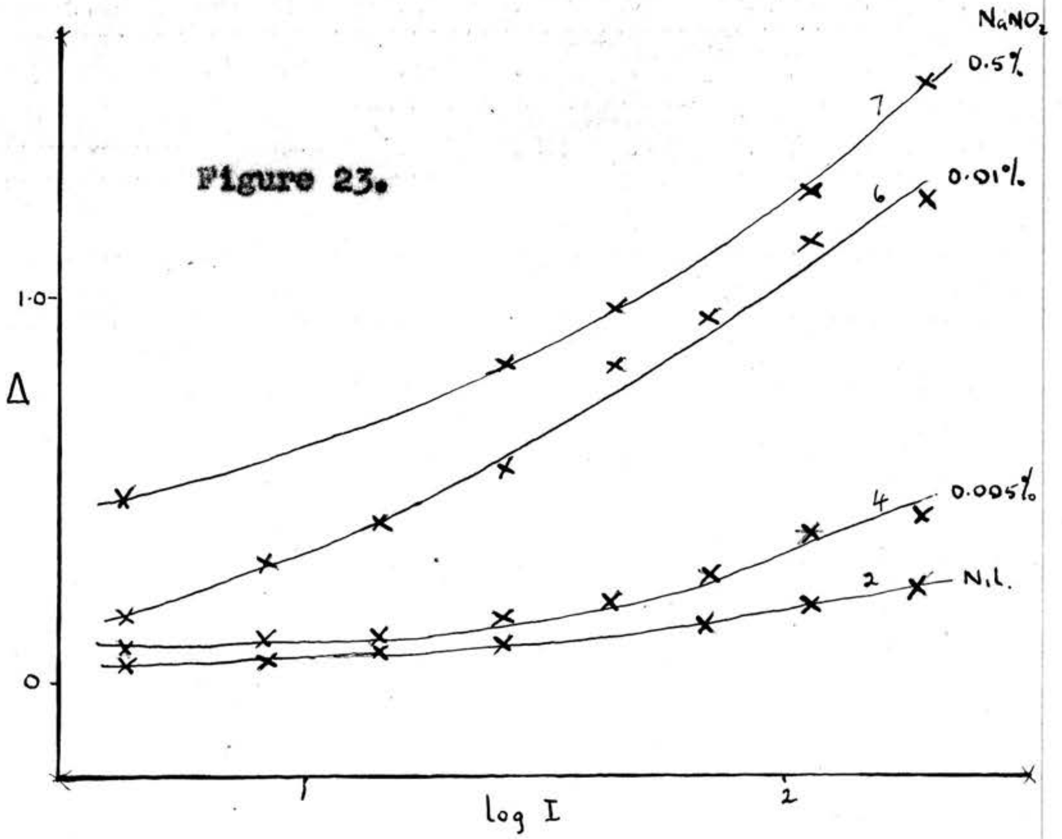
Table XVI.

$Br-I-NO_2'$

Expt.	I	0	195	109	68.5	44.2	25.6	14.4	8.25	4.23
7	D	.300	1.807	1.60	-	1.288	1.135	-	-	.800
	Δ		1.507	1.30	-	0.488	.835	-	-	.500

These densities are again plotted in figure 23 when it appears that the increase in sensitivity is by no means proportional to the amount of nitrite added.

Figure 23.



Reversal by Green Light.

In view of the preliminary results earlier described on the reversal by blue as well as by green light, it was decided to examine first the "normal" green light reversal, for comparison with the unexpected blue light reversal. Bromide-iodide plates were used, the iodide again being 5% of the bromide used in the emulsion preparation. Each plate was exposed for 30 minutes to blue light of a known intensity; the light was then cut off and the blue filters replaced by the $CuSO_4$ cell, the Chance green filter and the neutral filter N. The wedge was inserted in front of the plate as usual and the secondary "green" illumination then applied for various periods of time. The time between the end of the primary blue exposure and the beginning of the secondary green exposure was 2 minutes in each case. The results are given in the table XVII, where

t_1 = time of primary blue exposure (minutes)

t_2 = time of secondary green exposure (minutes)

As before, area 0 represents the plate plus fog density of the unexposed plate. Area 9, now gives the density arising from the primary exposure only.

Experiment 3 is not exactly comparable with experiments 1 and 2 in that the resultant density from the primary exposure was decidedly lower in experiment 3. The fourth experiment was therefore added in which the intensity of the primary blue illumination was reduced to 38 scale divisions, t_1 remaining at 30 minutes as before.

Table XVII.

Br-I plates $t_1 = 30$ $I_B = 190$ scale divs.

Expt.	t_2	Area	0	1	2	3	4	5	6	7	8	9
		I_g	-	21.0	12.0	6.25	3.51	2.73	1.73	0.795	0.31	
		log Ig	-	1.32	1.08	.80	.545	.44	.24	$\bar{1}$.90	$\bar{1}$.49	-
1	1	D	.102	.328	.334	.336	.340	.336	.340	.343	.336	.340
		Δ		.226	.232	.234	.238	.234	.238	.241	.234	.238
2	5	D	.100	.253	.287	.301	.320	.338	.348	.348	.339	.348
		Δ		.153	.187	.201	.220	.238	.248	.248	.239	.248
3	26	D	.097	.087	.095	.100	.130	.185	.243	.255	.270	.275
		Δ		-.01	-.002	.003	.043	.088	.146	.158	.173	.178
		$^{\Delta}$·240		-.013	-.003	.004	.058	.118	.197	.213	.233	.240

Table XVIII.

$I_b = 38$ scale divs.

Expt.	t_2	Area	0	1	2	3	4	5	6	7	8	9
4	5	D	.098	.158	.210	.238	.245	.260	.263	.263	.260	.263
		Δ		.060	.112	.140	.147	.162	.165	.165	.162	.165

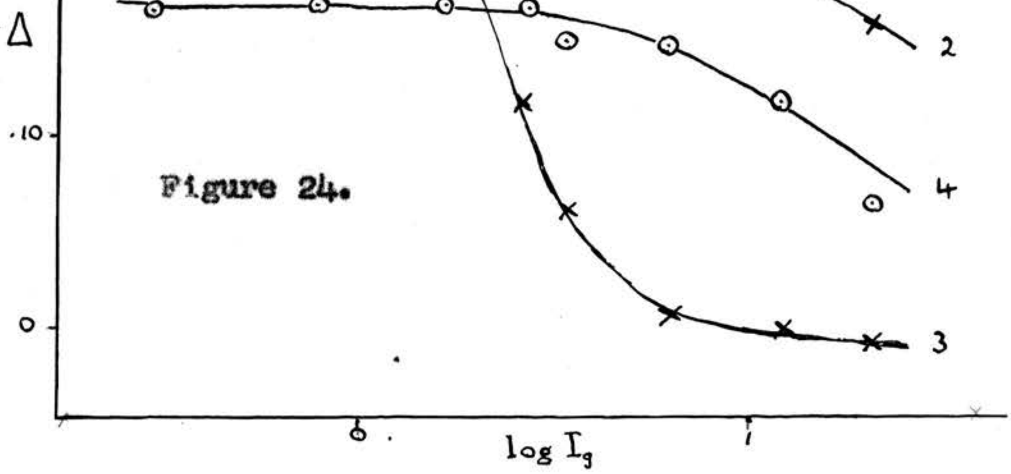


Figure 24.

The results of experiments 1, 2 and 4 are shown directly in figure 24. The similarity between experiment 2 and 4 shows that the shape of the bleaching curve does not markedly alter with the variation in initial density here concerned. For comparison, the observed densities Δ of experiment 3 were therefore increased by the factor $\frac{240}{178}$ and shown as Δ_{240}. The resultant values are also plotted in figure 24.

It will be observed that while a most pronounced bleaching is evident in 20 minutes (expt.3), little bleaching is apparent for 1 minutes exposure (expt.1) even at the highest green light intensity. For the 5 minute exposure (expt.2) no bleaching is to be observed below $\log I_g = 0$, i.e. below an intensity of 1 galvanometer scale division. This gives us a limit suitable for consideration when the bleaching by blue light is examined from the point of view of the amount of green light passed by the blue filters.

Reversal by Blue Light: Bromide-Iodide Emulsions.

A series of experiments is first reported, the results of which were not uniformly comparable throughout, by reason of fading of the speed of the plate but which gave the essential features of blue light secondary illumination. In each exposure of the series a bromide-iodide plate of the same batch as used in the green bleaching series was uniformly illuminated for 30 minutes by blue light of approximately 38 scale division (I_1). The plate was then covered by opaque black paper with the exception of a small aperture

7

(0.7 cm diam.) and a secondary illumination given of 5 minutes to blue light of varying intensity (I_2), blue glass filters being used to reduce the intensity to the necessary low values. As before, the dark interval between exposures was 2 minutes. Processing was carried out as usual; the developed densities are given in table XIX where D_1 = density due to primary illumination and D_2 = resultant density for both illuminations. The plate plus fog density of the unexposed plate is given by D_0; Δ_1 and Δ_2 represent the densities above fog. The experiments are given in the order in which they were carried out.

Table XIX.

t_1 = 30 min λ_1 = 4360.A. t_2 = 5 min λ_2 = 4360 ~~5480~~.A.

Expt.	I_1	D_0	D_1	Δ_1	I_2	$\log I_2$	D_2	Δ_2	$\Delta_2 - \Delta_1$
1	37.0	.090	.154	.064	2.95	.47	.230	.140	.076
2	2.95	.100	.108	.008	-	-	.108	.008	-
3	38.7	.086	.151	.065	1.50	.18	.120	.034	-.031
4	38.5	.075	.136	.061	0.12	$\bar{1}$.08	.072	-.003	-.064
5	38.0	.075	.130	.055	3.20	.51	.186	.111	.056
6	38.4	.084	.108	.024	38.4	1.58	.108	.024	.000
7	38.0	.087	.101	.014	88.0	1.94	.111	.024	.010

In wvery experiment, with the exception of experiment 2 which was included for comparison, the initial densities were approximately equal and may be taken as constant. The density Δ_1 resulting from this primary illumination shows a progressive decrease as a result of fall in plate sensitivity with time. For this reason, the changes in density as a result of the secondary illumination are given in the final column as $\Delta_2 - \Delta_1$. These are plotted against log I_2 in figure 25.

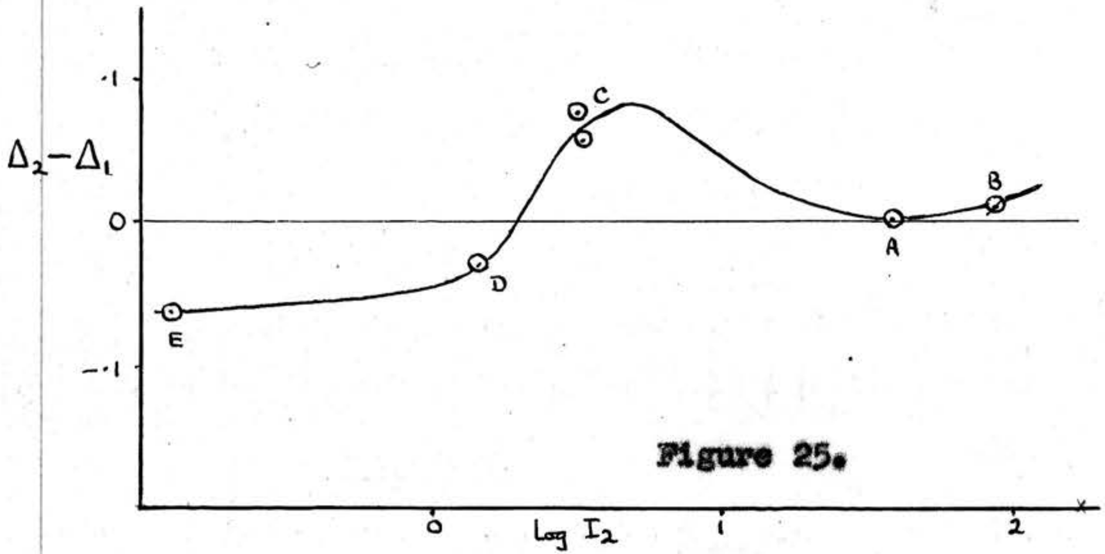


Figure 25.

In figure 25, point A represents 35 minutes illumination with I_1 = 38 divs., the resultant density being indistinguishable from 30 minutes illumination at the same intensity. The increase at point B corresponds to the normal increase in density produced by higher intensity. The increase at point C is however abnormal in that its magnitude is much greater than that produced in a previously unexposed plate by the intensity I_2 = 2.95 (expt.2). Finally at points D and E reversal is definitely observed, the resultant density at E being even lower than the fog density of the unexposed plate. It may be noted here that at the circumference of the image produced by the aperture in the superimposed black paper, a bleaching ring of width approximately 0.5 mm was always observed, this being attributed to light of small intensity scattered at the paper edge.

That the reversal at low intensities is not due to green light present in the blue by reason of imperfect light filters is obvious from consideration of the green reversal experiments recorded in the previous section. For 5 minutes secondary green illumination no bleaching was observed below an intensity of 1 division. The comparable blue light intensities as recorded for D and E are 1.5 and 0.12 divisions respectively. Since 190 scale divisions of blue light contained at most only 0.15 div. green light (from the data given in Experimental Procedures p. 47) it is obvious that the reversal observed must be due to blue light illumination. Since the standard blue glass filters were used to reduce the light intensity to the required values, the transmission for green light being always very small in comparison with the corresponding blue light transmission, the amount of green light finally incident on the plate must have been even less than that passed by B.G.I. and Cup.I.

A more complete series of experiments was therefore carried out in which a higher initial density was produced by illumination for 30 minutes to blue light of 190 scale divisions. The use of the standard wedge with blue light of this intensity gave a series of results over the intensity range 129 to 1.91 scale divisions. A second series identical with the first, except for a reduction in the blue secondary intensity

Table XX.

Br-I plates. t_1 = 30 min. I_1 = 190 scale divisions. λ = 4360.A.

Expt.	t_2 (mins)	D_1	$D_1^{.33}$	I_2	129	73.7	38.3	21.5	16.7	10.6	4.87	1.91	2.09	1.19	.62	.35	.27	.17	.08	.03
				log I_2	2.11	1.87	1.58	1.33	1.22	1.03	.69	.28	.32	.08	$\bar{1}.79$	$\bar{1}.54$	$\bar{1}.43$	$\bar{1}.24$	$\bar{2}.90$	$\bar{2}.49$
1	25	.380	.330	D_2	.38	.38	.38	.38	.38	.38	.38	$.38_6$								
				$D_2^{.33}$	.33	.33	.33	.33	.33	.33	.33	$.33_7$								
2	25	.344	.330	D_2									.340	.333	.298	.282	.282	.248	.203	.172
				$D_2^{.33}$									.330	.320	.286	.271	.271	.238	.195	.165
3	1	.337	.330	D_2	.34	.34	.34	.34	.34	.34	.34	.34								
				$D_2^{.33}$	.33	.33	.33	.33	.33	.33	.33	.33								
4	1	.315	.330	D_2									.318	.308	.308	.301	.301	.292	.299	.300
				$D_2^{.33}$									.334	.323	.323	.315	.315	.306	.313	.314
5	5	.303	.330	D_2	.300	.303	.305	.303	.303	.303	.303	.295								
				$D_2^{.33}$	.327	.330	.332	.330	.330	.330	.330	.321								
6	5	.305	.330	D_2									.308	.295	.277	.261	.255	.228	.210	.215
				$D_2^{.33}$									.333	.319	.300	.282	.274	.246	.227	.232

by means of the standard blue glass filters, gave secondary exposures over the intensity range 2.09 to 0.03 scale divisions.

These two series were then repeated with alterations in the time t_2 of the secondary exposure. Developed densities were recorded for t_2 = 25 min, t_2 = 1 min and t_2 = 5 min in that order and are given in table XX.

In view of the slight decrease in sensitivity as shown by decreasing values of D_1, all densities have been corrected by the factor $\frac{.330}{D_1}$, where .330 is the average D_1 density. These are included in the table as $D^{\cdot 33}$ The resultant corrected densities are plotted against log I_2 in figure 26, for each period of secondary exposure. In the 25 minutes secondary exposure the corresponding fog level of the unexposed plate is also shown at D = .18.

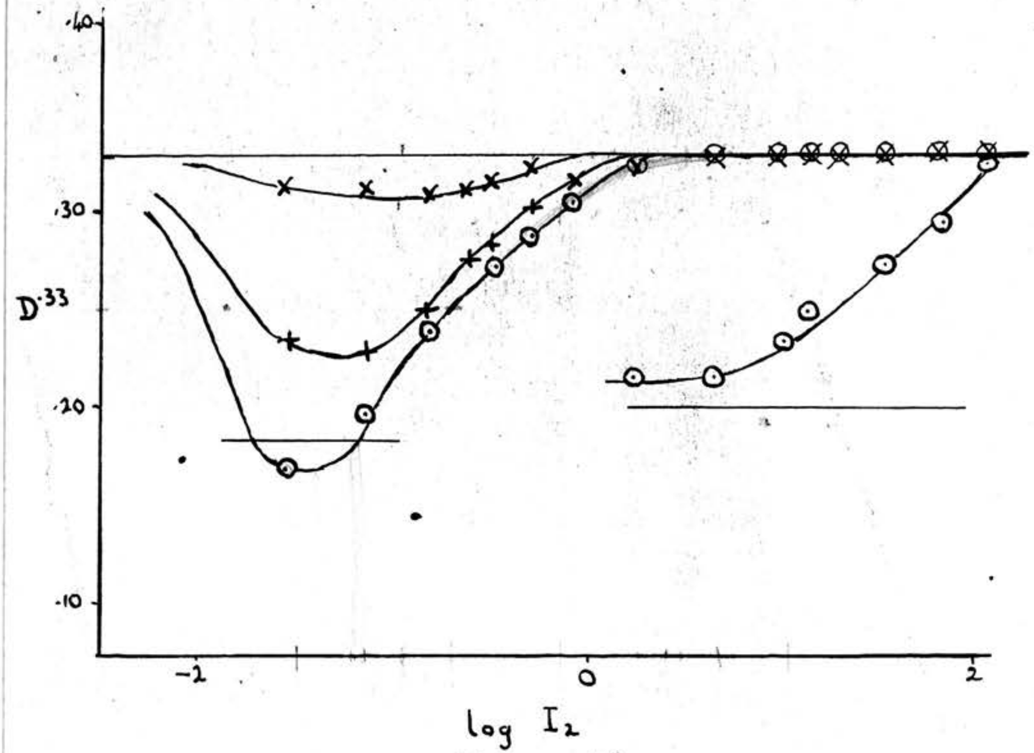


Figure 26.

It then appears that, for the relatively high initial density here concerned, no increase in density is to be observed at intensities slightly greater than the "bleaching limit". While the bleaching is relatively rapid at very low intensities, the fog of the plate being even removed by 25 minutes secondary exposure, it is obvious that for secondary intensities above 2 divs ($\log I = \cdot 3$) the rate of bleaching is very slow. The preliminary results on blue reversal had suggested the idea that an equilibrium was involved in the sense that bleaching would go on with increasing time until the normal H. and D. exposure curve was obtained; for comparison such a curve is included in figure 26, the experimental results being given in table XXI, with correction to $D^{\cdot 33}$ as before.

<u>Table XXI.</u>

Br-I plate. $t = 30$ $\lambda = 4360.$A.

Expt.										
	I_0	0	129	73.7	38.3	21.5	16.7	10.6	4.87	1.91
	$\log I_0$		2.11	1.87	1.58	1.33	1.22	1.02	0.68	0.28
7.	D_1	.20	.339	.302	.276	-	.254	.237	.217	.223
	$D_1^{\cdot 33}$		.330	.296	.271	-	.250	.233	.213	.219

It would appear therefore that if such an equilibrium is to be eventually established by bleaching the rate of approach to equilibrium must be exceedingly slow for the intensities here involved. The existence of the "hump" or increase in density at intensities just above that of the bleaching "limit" was however confirmed by examination of a plate with which the initial blue light exposure gave a much lower density.

This plate was made from a bromide-iodide emulsion as before and the results were as follows (Table XXII).

Table XXII.

Br.-I plate. t_1= 30 min. I_1= 268 Scale divs. λ= 4360.A.
t_2= 2 min. Fog density = .090

I_2	2.15	1.20	.755	.487	.282	.159	.091	.046	0
log I_2	.33	.08	$\bar{1}.89$	$\bar{1}.69$	$\bar{1}.45$	$\bar{1}.20$	$\bar{2}.96$	$\bar{2}.66$	-
D	.158	.154	.148	.140	.123	.120	.120	.110	.140

These are plotted in figure 27; the density for 32 minutes primary illumination is also given for comparison.

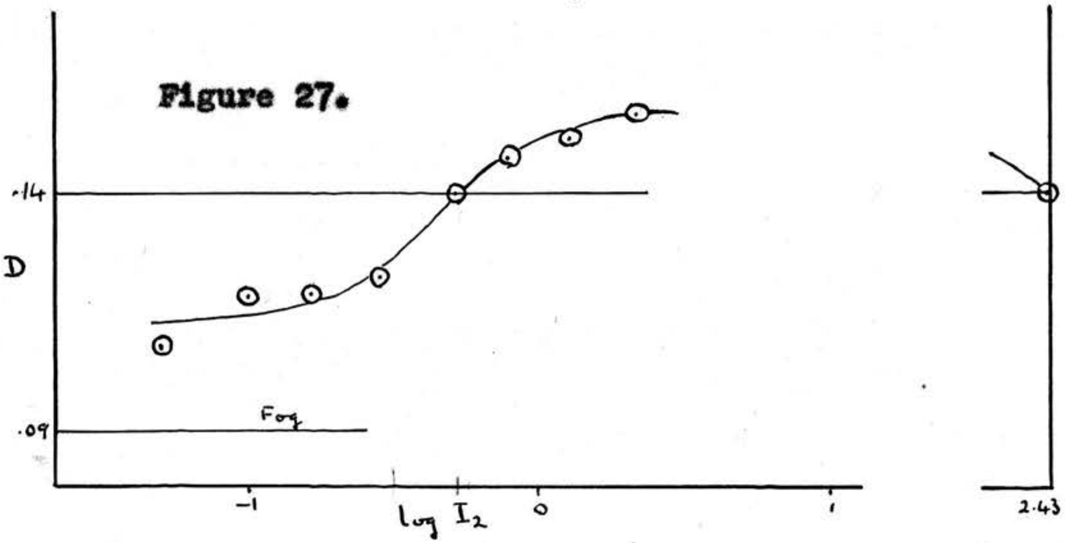


Figure 27.

It was therefore concluded that for the "hump" to be observed the initial primary density must be below a certain critical value.

A further set of results is here reported for the low primary density of .077 obtained with a bromide-iodide plate containing .005 gm $NaNO_2$ per 100 ml emulsion. The densities obtained are shown in table XXIII and are plotted in figure 28, from which the presence of the "hump" is again confirmed.

Table XXIII.

$t_1 = 2$ min. $I_1 = 268$ $t_2 = 2$ min $\lambda = 4360.$A.

I_2	0	2.09	1.19	.62	.35	.27	.17	.08	.03
log I_2		.320	.750	$\bar{1}.792$	$\bar{1}.544$	$\bar{1}.431$	$\bar{1}.230$	$\bar{2}.903$	$\bar{2}.477$
D_2	.077	.144	.146	.127	.104	.08	.077	.077	.077

In this plate practically no image was in fact visible as a result of the primary exposure.

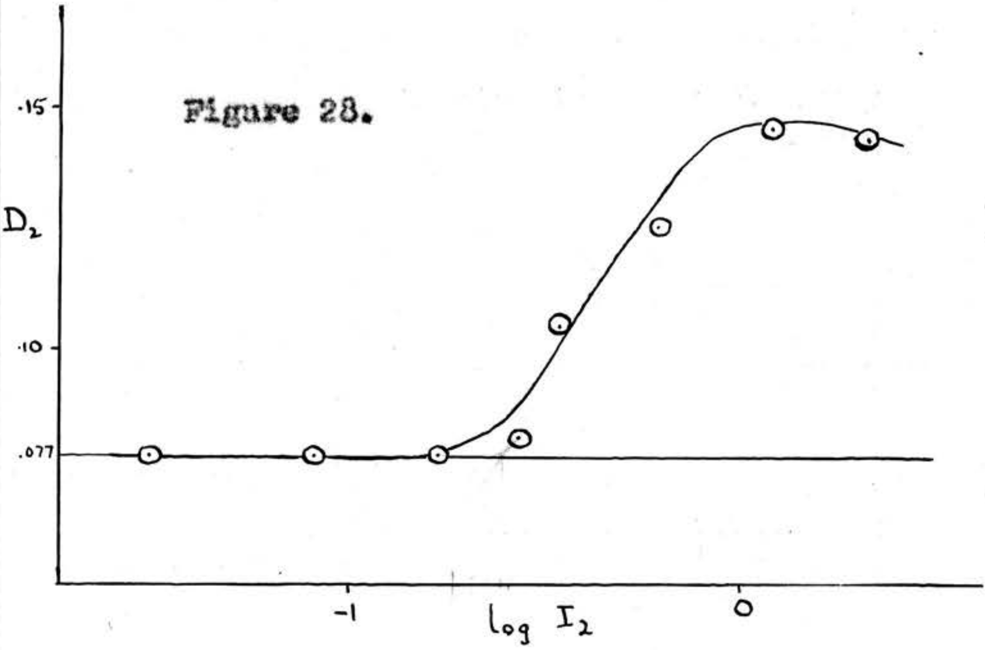


Figure 28.

Variation of Bleaching Limit with Initial Density and with added Nitrite.

The effect of added nitrite, on the basis of acceptor action on bromine atoms, would appear a priori to be always to raise the final developed density. For equal primary densities, we might expect the addition of nitrite thus to lower the bleaching limit, or intensity below which reversal appears. The effect of the initial primary density, for equal acceptor action, is however more complex. Development takes place when the latent image speck reaches a certain critical size; the greater the developed density the greater the average size of the specks. If bleaching increases with the size of the speck, we might expect a higher bleaching limit at higher densities, with a consequent flattening or removal of the intermediate hump.

The first experiments on density variations were carried out by reducing the primary exposure density by reducing t_1 from the 30 minutes value of tables XX, XXI AND XXII to 6 min. and 1 min. The secondary exposure was as before 5 min. Results were as given in table XXIV.

Table XXIV.

Br. I plate. $I_1 = 190$ $\lambda = 4360.A.$ $t_2 = 5$ min.

	t_1 (min)	I_2	25.8	14.7	7.66	4.30	3.34	2.12	.974	.382	0
		$\log I_2$	1.41	1.17	.88	.63	.52	.33	$\bar{1}.99$	$\bar{1}.58$	
8	6	D_2	.270	.271	.270	.273	.265	.260	.260	.265	.270
9	1	D_2	.245	.245	.250	.245	.247	.245	.245	.246	.245

No hump is to be observed in these experiments in agreement with the results for initial density 0.33 (table XX), with which these experiments are comparable. For initial density of 0.33, the bleaching limit is at approximately $\log I_2 = .3$; for experiment 8 above, little bleaching is observed except for a very small but apparently definite decrease at $\log I_2 = .3$ and at $\bar{1}.99$; for experiment 9, no bleaching was visible. Reduction of density by reducing t_1 as above does not therefore yield any definite information in respect of the relation between primary density and the bleaching limit.

From preliminary experiments at low densities it appeared that the density factor was more important than the nitrite. Because of the difficulty of exactly reproducing such densities on different plates, the experimental approach to these questions was as follows. Three sets of bromide-iodide plates were used, the first with no added nitrite, the second with a small amount of nitrite and the third with a larger amount of nitrite. The effect of density was then ascertained with the second series. It was hoped that, by comparison of the results so obtained with the results of experiments with the first and third series, information would be obtained on the effect of the added nitrite for a certain fixed density. The results are given in table XXV.

Table XXV.

Br-I plate containing .005% $NaNO_2$

Expt.	D_1	I_2	2.15	1.20	.755	.487	.282	.159	.091	.046
		$\log I_2$	.33	.08	$\bar{1}.89$	$\bar{1}.69$	$\bar{1}.45$	$\bar{1}.20$	$\bar{2}.96$	$\bar{2}.66$
1	.100	D_2	.150	.129	.115	.105	.100	.100	.100	.100
2	.142	D_2	.150	.145	.147	.142	.140	.122	.122	.110
3	.254	D_2	.244	.218	.195	.185	.185	.187	.185	.185

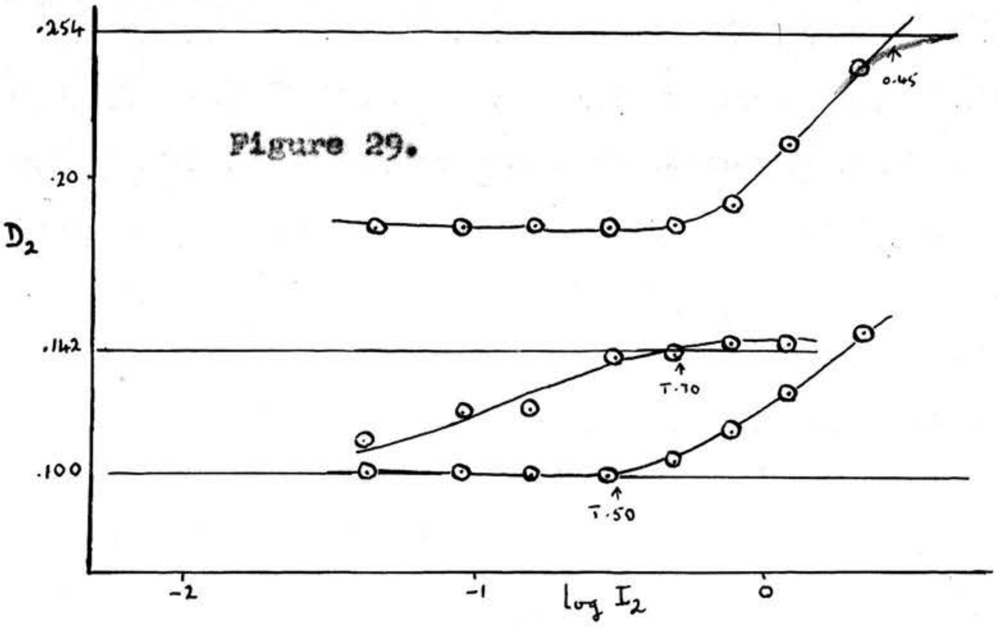


Figure 29.

When these density values were plotted against log I_2 (figure 29) it was found that the log I_2 values for which there is no change from the initial density D_1 are as follows:

D.	Log I_2
.100	$\bar{1}.50$
.142	$\bar{1}.70$
.254	0.45

It was therefore concluded that the intensity limit at which bleaching begins increases with the primary density. Further attempts were made to obtain a more complete series but unevenness in the plates available made accurate measurements impossible. In one of these experiments, however, with a plate of the same series, which was exposed soon after the preparation of the emulsion and which therefore gave a relatively high density of 0.235 for 30 minutes primary exposure to 24.0 divisions (in place of the 190 divs. necessary above) the bleaching limit was at log $I_2 = \bar{1}.20$ which is not in agreement with the above series. Since the conditions of primary exposure were thus not exactly comparable, other factors depending on these illumination conditions appear to be concerned.

The results of table XXII refer to a bromide-iodide plate containing no added nitrite and may therefore be now considered in relation to the above. The relevant figure 27 shows that the bleaching limit for the density 0.140 is at log $I_2 = \bar{1}.69$. In this case therefore the absence of nitrite does not affect the bleaching limit.

The bromide-iodide emulsion containing .05 gm sodium nitrite per 100 ml liquid emulsion, previously referred to in table XI was then considered.

The initial exposure intensity I_1 was now reduced to 3.15 divs. for t_1 = 30 min, this giving a D_1 value of 0.698, much larger than that previously investigated. No bleaching limit for such a primary density is available for direct comparison. Bleaching did however occur when the primary exposure producing such a density on this particular plate was succeeded by a secondary exposure of an intensity below 2.15 scale divisions, as is shown by the following data (table XXVI).

Table XXVI.

Br-I plate containing .05 gm $NaNO_2$/100 ml emulsion.

t_1 = 30 min. t_2 = 2 min. I_1 = 3.15 div. λ= 4360.A.

I_2	0	2.15	1.20	.755	.487	.282	.159	.091	.046
log I_2		.33	.08	$\bar{1}.89$	$\bar{1}.69$	$\bar{1}.45$	$\bar{1}.20$	$\bar{2}.96$	$\bar{2}.66$
D	.698	.707		.682	.659	.639	.635	.624	.624

The effect of nitrite on the bleaching limit for high density is therefore not further elucidated by this experiment. It is however to be noted that the primary exposure intensity is close to the upper limit of the secondary intensity. It would appear that the bleaching effect in this case represents an approach to the normal H. and D. curve for the primary exposure conditions. The normal H. and D. curve obtained for intensities up to 2.15 divs is given for comparison in table XXVII. On account of fading, the maximum density obtained (.510) is lower than that of table XXVI (0.707). The values obtained after correction by the factor $\frac{.707}{.510}$ are also given in table XXVII as $D^{.707}$.

Table XXVII.

Br-I plate. $t = 30$ min. $\lambda = 4360$.

I	2.15	1.20	.755	.487	.282	.159	.091	.046
log I	.33	.08	$\bar{1}.89$	$\bar{1}.69$	$\bar{1}.45$	$\bar{1}.20$	$\bar{2}.96$	$\bar{2}.66$
D	.510	.498	.484	.439		.378	.350	.318
$D^{.707}$	.707	.690	.670	.608		.523	.485	.449

The data of table XXVI and XXVII are shown in figure 30 from which it is apparent that at the higher intensities the two curves do tend to coincide.

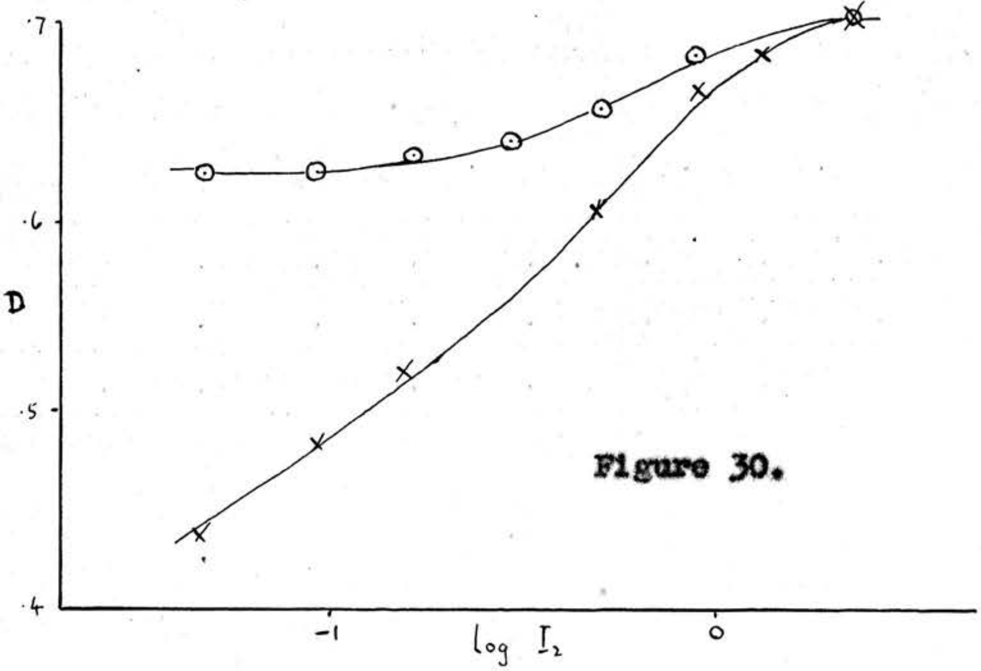


Figure 30.

The Effect of Secondary Illumination at very high Densities.

On illumination of the above bromide-iodide plate of high nitrite content for 2 minutes with an intensity of blue light corresponding to 268 scale divisions, the high density of 1.24 was obtained on development. When this primary illumination was succeeded in the usual way by a secondary blue illumination of the usual low intensity (I_2 from 2.15 to 0.05 divs) for 2 minutes no bleaching could be observed; the density remained unaltered. The same result was obtained for secondary exposures of 22 minutes and 135 minutes.

That this unexpected effect was not due to the alteration in the time factor of primary illumination from 30 minutes to 2 minutes was shown by exposing a similar plate for 2 minutes to a primary intensity of 3.15 scale divisions, corresponding to a density of 0.58, when the secondary exposure of 2 minutes to intensities from 2.11 to 0.05 divs. gave bleaching at the lower intensities as before. It was therefore concluded (see Discussion later) that above a certain critical density no comparable bleaching on secondary illumination is to be observed.

If this conclusion is correct, green light should similarly have no appreciable bleaching effect on this particular high density. A plate was exposed for 2 minutes to blue light of 268 divs. intensity as before and given a 25 minutes secondary exposure to green light of intensity range 38.4 to 0.85 scale divisions. No decrease in the primary density of 1.42 was observed.

It may be added here that in these plates of high density, the image in the silver bromide plate produced by the silver nitrate double decomposition was visible, in red light, before development. On immersion in developer the usual induction period was not observed, the black of the image appearing almost immediately.

Effect of Secondary Illumination on Iodide-free Systems.

A bromide plate containing no iodide or acceptor was exposed to blue light of intensity 268 divs., and a secondary exposure of 2 minutes to the usual range of blue intensities below I_2 = 2.11 div. On development no bleaching was observed in the primary density of 0.239. The experiment was repeated with a secondary exposure of 20 minutes: again no bleaching was observed. This is in sharp contrast to the previously reported bleaching of a nitrite-free bromide-iodide plate under the same conditions (P. 94) The experiment was repeated, green light being employed for the secondary illumination. Again 24 minutes secondary exposure of intensity 38.5 divs showed no decrease in the primary density.

While these experiments thus gave no evidence of reversal, it is to be noted that in one exposure in which the wedge system was used to determine the ordinary density-intensity curve for 30 minutes exposure to blue light, the edges of the secondarily exposed areas showed a slight reversal border, opposed to the slight fog of the unexposed plate, as already observed in the blue light reversal (p. 89). This was attributed to scattered light of low intensity. Since the fog density may be taken to correspond to latent image of just the critical size for development, such bleaching is relatively more evident than at high latent image speck sizes. It would appear generally therefore, that in iodide-free plates some bleaching does in fact occur, but at a rate which is very small when compared

8

with bromide-iodide systems. The bromide and bromide-iodide emulsions used above were prepared in an exactly similar way, apart from the presence of iodide, and the exposures were performed at the same time after preparation of the emulsions and the coating of the plates. There is thus no doubt that the reversals due to green light and to low intensity blue light are here closely connected with the iodide content.

In view of certain observations on bleaching by red light in silver bromide systems, whereby it appears that such bleaching is related to the relative amounts of latent image on the surface as opposed to the interior of the grains, certain experiments were carried out here on thallous bromide plates with different developers. Stevens[68] recommended as a total developer, whereby internal and surface latent image were both made use of, a metol-hydroquinone developer containing a relatively large amount of sodium sulphite, the solvent action of the sulphite being increased by various amounts of added sodium thiosulphate. (Appendix I, developer G) The action is then governed by the relative rates of development and solution of the grain. When this developer, with the proportions of hypo recommended, was applied to an unexposed thallous iodo-bromide plate which had been processed in the usual way, a high "density" of 0.88 was produced. It was at first thought that this was due to incomplete removal by washing of silver nitrate introduced by the double decomposition reaction; extended periods of washing did not however reduce the developed density. The modified method of processing with potassium bromide (p.57) gave also no improvement in this respect. It was therefore concluded that the silver bromide produced by the double decomposition is in a decidedly different physical state from that of the commercial silver bromide plate to which the total developer of Stevens applied. Omission of the added hypo reduced the developed density in the unexposed plate to 0.63, this being attributed to the solvent action of the high sulphite content of the developer.

The normal developer A contains 37.5 gm sulphite per litre as opposed to the 90 gm sulphite of the total developer. The experiments were repeated with the normal developer A with the addition of various amounts of hypo. A resultant plate density of 0.246 was obtained with developer A, to which was added 1 ml of 10% hypo per 25 ml of developer. With only 0.2 ml of 1% hypo the resultant density (.15) then approached that normally obtained (.10) with the developer A alone. Further work on this is necessary before definite conclusions can be drawn regarding the relative amounts of surface and internal image produced by illumination.

Reciprocity.

In as much as illumination by blue light at low intensities does not produce any latent image which can be made evident by the development process, but rather removed any latent image which may be present, even below the fog level of the plate, it is obvious that reciprocity failure must exist in the lower intensity ranges, in the same sense as already observed for silver bromide plates. Normal low intensity reciprocity failure can be expressed by saying that equal-energy exposures (i.e. It = constant) do not produce the same density for low intensities as for high intensities. In thallous bromide plates, especially in those containing iodide, even very long exposures at very low intensities will apparently produce no developable density.

The reciprocity relationship was therefore examined for the intensity ranges in which an appreciable density was apparent.

A series of bromide-iodide plates containing 0.1 gm sodium nitrite per 100 ml emulsion were exposed for a range of exposure times to blue light of a fixed intensity and the usual H. & D. curve drawn. The intensity of the light was then reduced to a quarter of the original value and a second series of plates exposed, the exposure times throughout the range now being each increased to four times the original value. That is, for each corresponding exposure, the product It remained constant. A third series was exposed at $\frac{1}{20}$ intensity, the exposure times being each 20 times the original value. The density values obtained are given in table XXVIII and are plotted against log exposure (i.e. log It) in figure 31. The inefficienty of latent image formation at the lower intensities is clearly seen by the relative positions of the three H. and D. curves so obtained

Table XXVIII.

Series	I	t (mins)	It	Log It	D
1	39.7	½	19.9	1.30	.538
	41.6	1	41.6	1.62	.626
	39.4	4	157.6	2.20	.822
	42.2	8	337.6	2.53	.985
2	10.3	2	20.6	1.31	.508
	10.4	4	41.6	1.62	.594
	10.6	16	169.8	2.23	.728
	10.1	32	323.2	2.51	.826
3	2.3	8.7	20.0	1.30	.447
	2.3	18	41.5	1.62	.509
	2.3	80	184	1.26	.549
	2.3	145	333	2.52	.580

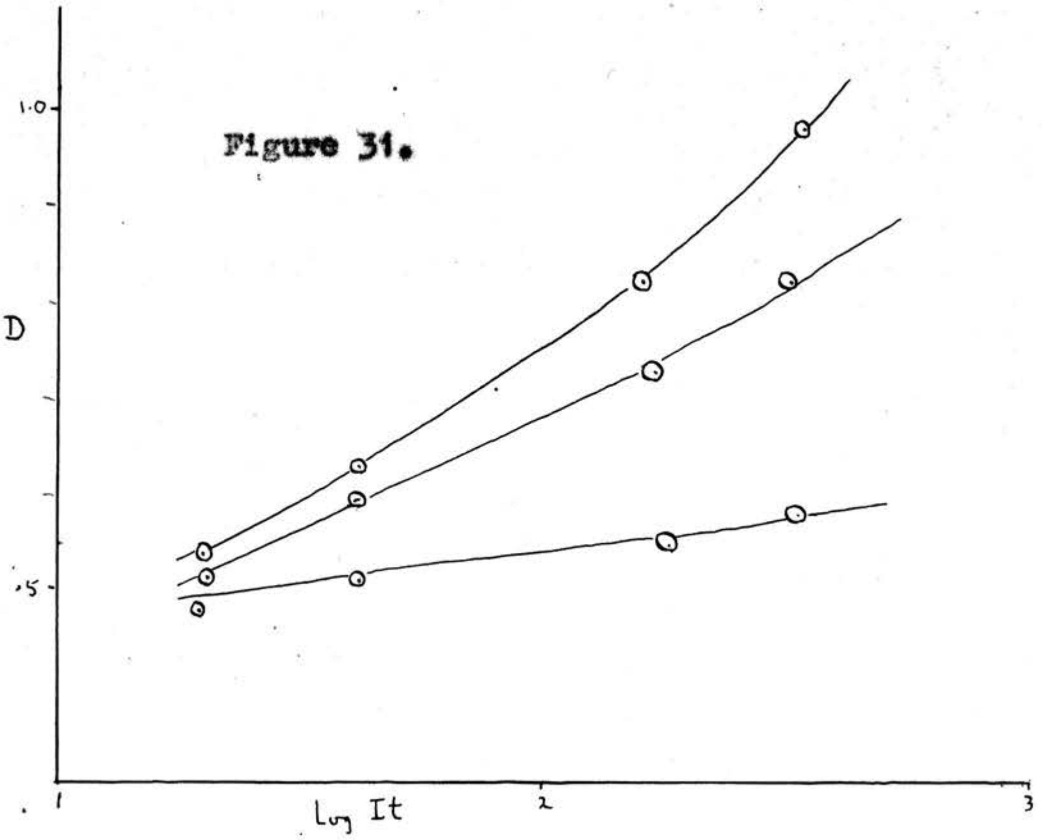


Figure 31.

Another set of experiments was carried out in which the wedge system was employed with a constant incident intensity of blue light. A bromide-iodide plate containing no added nitrite was used and four experiments were carried out in which the exposure times were 1 min, 6 min, 30 min and 150 min. The densities obtained are given in table XXIX.

Table XXIX.

Br-I plate.

	t min	I	190	129	73.7	38.3	21.5	16.7	10.6	4.87	1.91	0
		log I	2.28	2.11	1.87	1.58	1.33	1.22	1.025	.69	.28	
1	1	D	.266	.260	.252	.248	.235	.231	.225	.220	.215	.216
		Δ	.050	.046	.036	.032	.019	.015	.009	.009	-.001	
2	6	D	-	.441	.425	.405	.391	.382	.373	.362	.345	.360
		Δ	-	.081	.065	.045	.031	.022	..013	.002	-.015	
3	30	D	-	.339	.312	.274	.267	.257	.246	.217	.217	.220
		Δ	-	.119	.092	.054	.047	.037	.016	-.003	-.003	
4	150	D	-	.427	.367	.312	.273	.249	.221	.193	.145	.163
		Δ	-	.264	.204	.149	.112	.086	.058	.030	-.015	

The fog level in experiment 2 is unfortunately much greater than in the others and the actual measured density at 129 divisions is greater for 6 minutes exposure than for 30 minutes. The densities above fog are therefore considered and are plotted in figure 32.

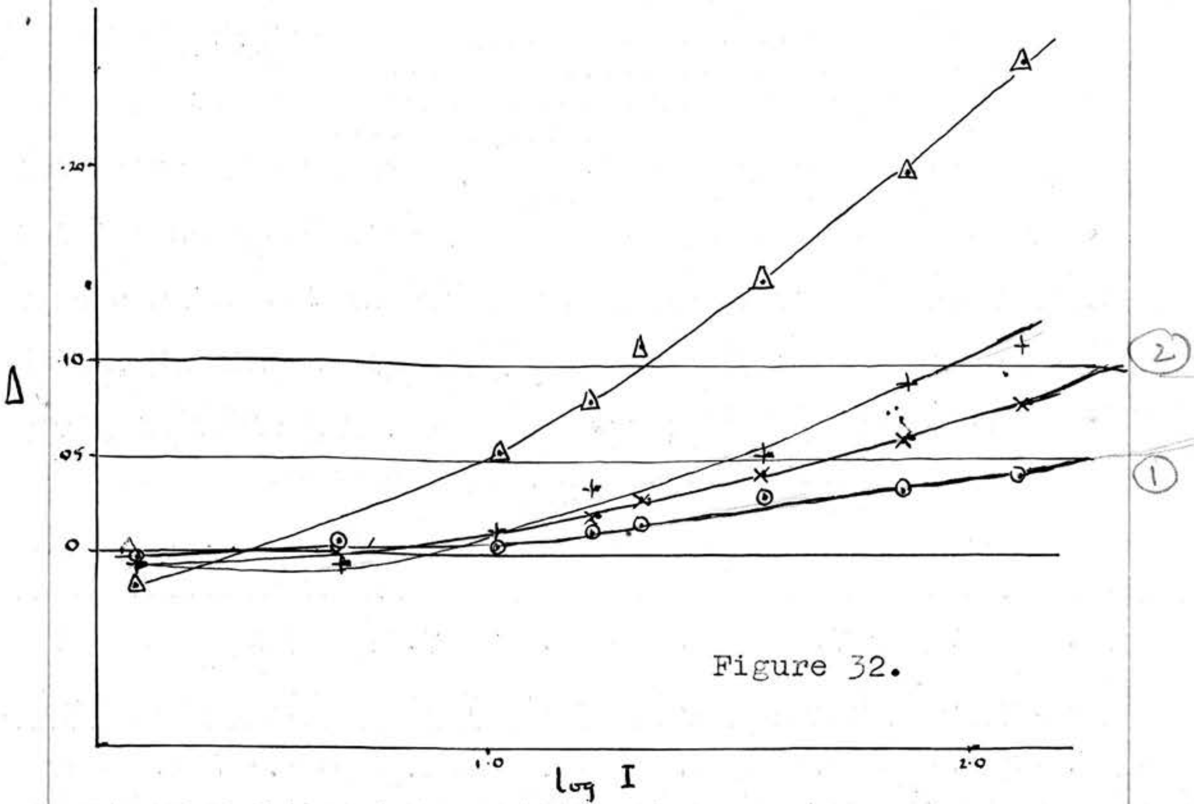


Figure 32.

To obtain a density above fog of 0.05 the required times of exposure are then

Δ = 0.05

t =	1	6	30	150
log t =	.000	.778	1.477	2.176
log I =	2.28	1.68	1.40	.93
log It =	2.28	2.458	2.877	3.106

Since log It is not constant the reciprocity law again is not obeyed; further, since log It is higher at low intensities, low intensity is relatively less efficient than high intensity. In comparison with silver bromide we are apparently dealing with the state of affairs corresponding to low intensity reciprocity failure.

Accurate measurements of log I at a density lower than 0.05 for each of the above exposure times is difficult but comparable figures are here given for the higher density of 0.10.

<u>Δ= 0.10</u>

t	=	1	6	30	150
log t	=	.000	.778	1.477	2.176
log I	=	3. -	2.35	1.95	1.30
log It	=	3.20	3.128	3.457	3.476

At the higher density true reciprocity appears more nearly to be observed, as seen by the nearer approach to the horizontal, in the upper curve in figure 33. The points A and B in this figure represent the two "high density" 6 minute exposures and as such may be considered doubtful.

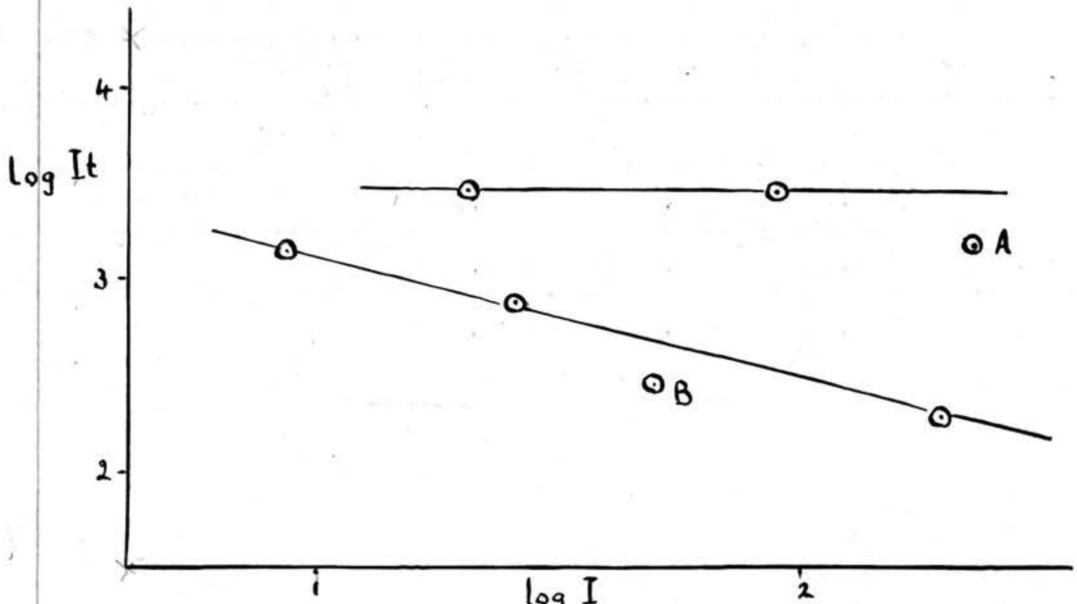


Figure 33

A similar set of experiments was carried out with a bromide-iodide emulsion of very high sodium nitrite content, in this case six different exposure times being exployed, and the results obtained are given in table XXX, the corresponding density-intensity curves being shown in figure 34.

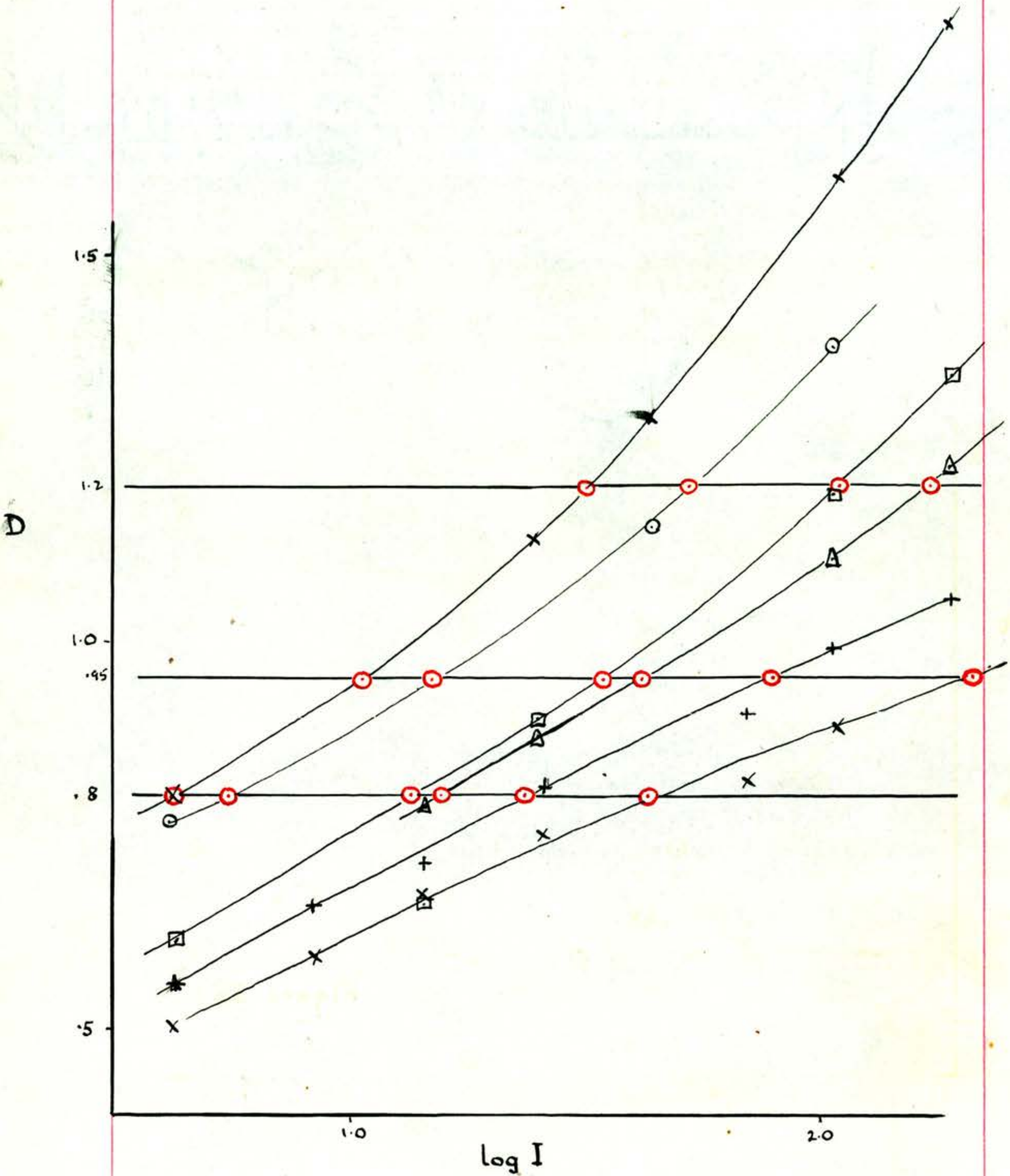


Figure 34.

Table XXX.

Br-I-NO_2'plate.

t	I	195	109	68.5	44.2	25.6	14.4	8.25	4.23
(min)	log I	2.29	2.04	1.84	1.64	1.41	1.16	0.92	.626
.25	D		.898	.822	.788	.754	.674	.594	.507
1	D	1.052	.983	.907		.824	.710	.666	.544
2	D	1.222	1.100			.875	.782		
4	D	1.35	1.180			.899	.652		.611
16	D		1.375		1.150				.766
32	D	1.807	1.60		1.288	1.135			.800

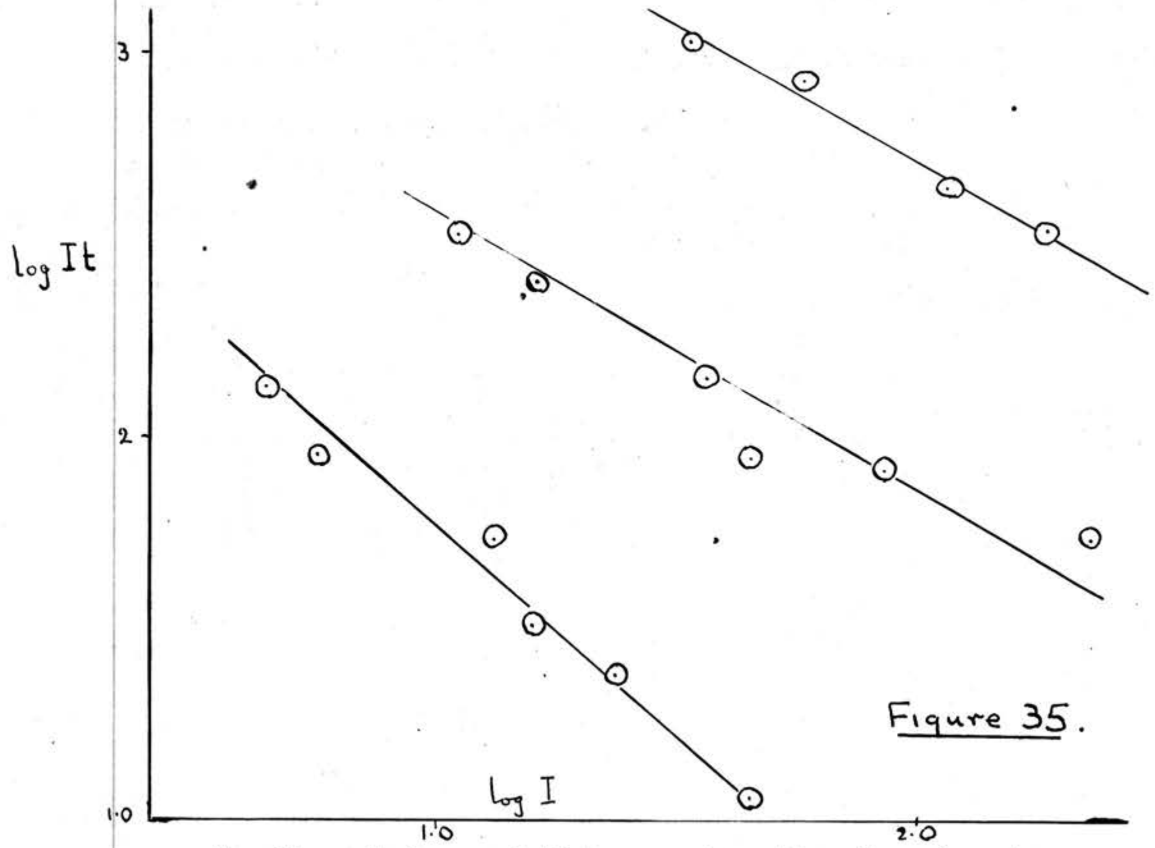


Figure 35.

In the plates of this series the fog level was constant at .30; the density values plotted in figure 34 are uncorrected for fog. The log I values corresponding to certain arbitrarily chosen density values are given in table XXXI.

Table XXXI.

D	t	.25	1	2	4	16	32
	log t	$\bar{1}.398$	.000	.301	.602	1.204	1.505
.80	log I	1.65	1.38	1.20	1.14	.75	.63
	log It	1.048	1.380	1.501	1.74	1.954	2.135
.95	log I	2.33	1.91	1.64	1.55	1.18	1.04
	log It	1.728	1.91	1.941	2.152	2.384	2.545
1.20	log I	-	-	2.25	2.05	1.73	1.52
	log It	-	-	2.551	2.652	2.934	3.025

These log It values, i.e. exposures required to gove a certain fixed density, are plotted against log I in figure 35. Again low intensity reciprocity failure is present as shown by the decreasing value of log It for increasing log I. In each curve there is no evidence of alteration in the reciprocity failure law for variation in intensity, but at the higher density, there is some evidence of an approach to true reciprocity as shown by the decreasing gradients. In both figures 33 and 35, there is no evidence of "high intensity" reciprocity failure, where increasing I would give an <u>increase</u> of log It (see figure 8).

In these experiments therefore the type of reciprocity failure encountered has been low intensity failure, the indications being that with these emulsions continued illumination at a constant high intensity produced continually increasing density.

That prolonged exposure at relatively high intensities does, in fact, lead to reciprocity breakdown is evident from the curve of figure 15 which shows a tendency to bend over at long exposure times. Further, the following values may be quoted, which were obtained, for an emulsion similar to that of table XXX, by continued exposure at approximately constant intensity of 36 scale divisions blue light.

Table XXXII.

I	0	36.1	38.5	40.7	35.6	35.4
t (mins)	0	8	15	30	60	140
log t	-	.90	1.18	1.48	1.78	2.15
D	.090	.143	.186	.226	.222	.223

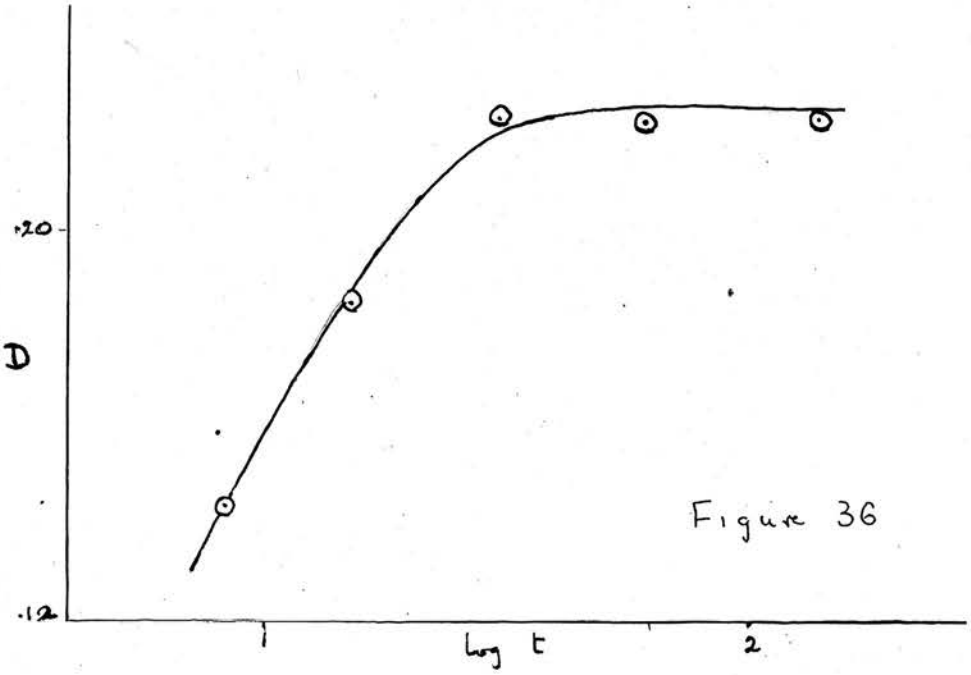


Figure 36

Here again no further increase in density appears after 30 minutes illumination; reciprocity failure is therefore present. Two further experiments may be quoted, which were obtained with a bromide-iodide plate containing .005 gm of nitrite per 100 ml. The density for 30 minutes illumination at a blue intensity of 268 divisions, was less than for the same period of illumination at 177 divisions. The density figures were 0.143 and 0.301 respectively.

Evacuation Experiments.

The removal of bromine atoms from the grain, as usually achieved by acceptor action, necessitates the addition of the bromine acceptor to the emulsion and consequently renders impossible any control of the acceptor during the course of a given exposure. The idea suggested itself of exposing plates in a closed system in the presence of various gaseous substances at various pressures. In this manner, by the choice of suitable gaseous acceptors, control could possibly be exercised over their action, and variation in pressure might thus be expected to yield information on the mechanisms involved. In this respect, reduction of pressure alone, by facilitating the diffusion of bromine atoms away from the grain would be expected to yield a greater density for equal exposures. Conversely, exposure in an atmosphere of bromine should have the opposite effect. Again, for a plate exposed at a very low pressure any observed increase in pressure during the exposure would indicate the formation of gaseous products (e.g. bromine) as a result of the illumination. To investigate these points the apparatus shown diagrammatically in figure 37 was constructed. With the exception of the reaction vessel and exposure system the entire apparatus was constructed of soda glass, and

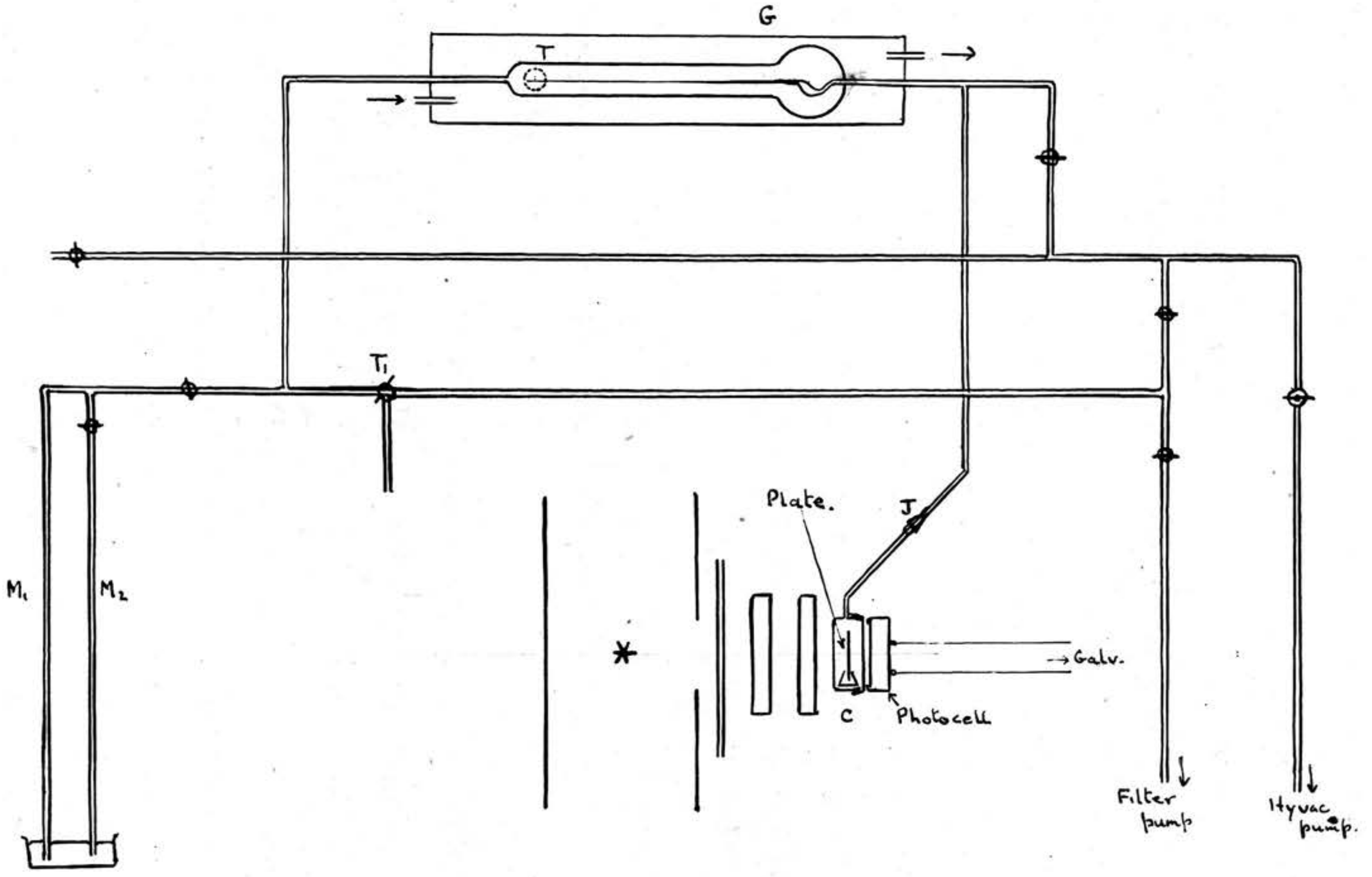


Figure 37.

all taps and ground joints lubricated with Apiezon L grease. The cylindrical quartz insolation cell C was capillary connected via the ground joint J, to the spring of the Bourdon gauge G, the pointer of which was observed against the eyepiece of the telescope T. Dry air could be admitted to the outer jacket of G by means of T_1 to balance the reaction gases in the cell C. In this manner the gauge was used as a null instrument, the pressure in C being indicated on the manometer M_1, which was read in conjunction with the standard manometer M_2. Water jackets, gravity fed from a thermostat, maintained the temperature of the closed system at 25°C ± 0.1°C. The quartz cell C, 2" in diameter and with two place faces 1" apart, was so situated as to fit into the exposure box carrying the standard filters. The plate was held vertically inside the cell in a glass support, and could thus be illuminated with blue or green light as desired. The transmitted intensities could, as before, be measured by the photronic cell. The quartz cell had to be specially made and delay in its manufacture curtailed the time available for the experiments planned. The following was however carried out.

Four bromide-iodide plates were exposed for 30 minutes to blue light of a fixed intensity; the pressure was varied in each experiment and the densities obtained on development are given in table XXXIII and are plotted against log p in figure 38.

Table XXXIII.

Br-I plate. t = 30 min. λ= 4360.A. Pressure = p min.

p	760	250	51	9
log p	2.88	2.40	1.71	0.95
D	1.08	1.30	1.53	1.64

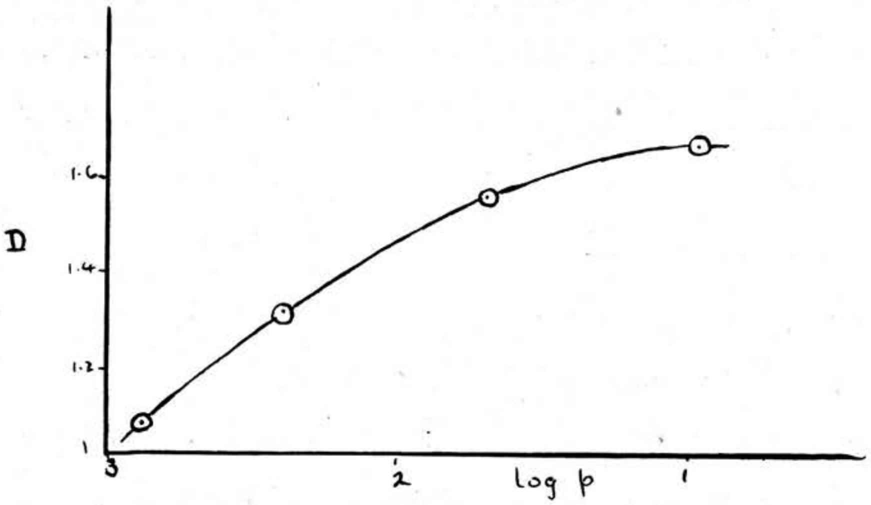


Figure 38.

From the figure it is seen that, as expected, the effect of reduction in pressure is to increase the final developed density. Further work along these lines is required.

Plate Transmissions to Blue and Green Light.

Finally are given the values obtained for the relative transmissions, to blue and green light, of iodide-free and iodide containing plates. The results were obtained by direct measurement of a comparable series of plates.

Table XXXIV.

Plate	Additions to Emulsion. (gms/100 ml)	Transmission for blue light $\lambda = 4360.A.$	Transmission for green light $\lambda = 5480.A.$
Iodide-free	-	0.09	0.16
	% $NaNO_2$	0.10	0.18
	% $NaNO_2$ % Na_3AsO_3	0.10	0.19
Iodide-containing.	-	0.01	0.14
	% $NaNO_2$	0.01	0.14
	% $NaNO_2$	0.01	0.14

On account of the scattering and reflection of light at the plate surface it is not possible to obtain from the above figures the actual amount of light absorbed, but it is clear that the presence of nitrite has very little effect on this. On the other hand the presence in the emulsion of 5% of iodide markedly increases the absorption of the plate to blue light, and also increases the absorption to green light although to a much less degree. This effect can be seen visually by the deepening, for addition of iodide, of the yellow colour of the emulsion, an effect analogous to the similar change observed in the silver bromide system.

GENERAL DISCUSSION.

It is a characteristic of the majority, if not all, of these reactions which are sensitive to light and which are normally classified under the general title of Photochemistry, that the changes brought about by light have been detected and measured through a resultant definite chemical change in the illuminated substance. The silver salt series have long been considered as somewhat outside this classification, in that a relatively small amount of light will bring about a change which cannot be detected by the most refined methods of chemical analysis. This change is of course commonly known as latent image formation which can be made evident only by suitable development, by means of chemical methods which produce no similar change in the non-illuminated substance.

General Properties of Thallous Bromide Emulsions.

Practically all the experimental results and conclusions which have been described and reached in the previous pages have been based on development of silver bromide grains produced by the double decomposition process. Here however the silver bromide operations have in every case been the same and any changes finally observed can only be ascribed to changes caused by illumination of the original thallous bromide. The double decomposition process is therefore only an additional step in these chemical processes which may render a possible latent image visible. In one series of experiments, however, the development process was not involved: the use of a sufficiently high light intensity gave a visible print-out effect with a characteristic H. and D. curve (figure 16, page 68) of generally similar shape to the H. & D. curve obtained by development. Here the development process may be regarded as simply extending, for lower and more conveniently obtainable intensity ranges, the changes in rate of image growth produced by illumination.

It seems inevitable that the result of illumination of thallous bromide should then be considered as an aggregation of metallic particles, which can be replaced by the silver aggregates long recognised as necessary for development of silver bromide grains. If isolated thallium atoms were produced and replaced by silver atoms it is difficult to understand how isolated silver atoms can produce developability of the silver bromide grain. There is no evidence that such neutral atoms are in fact mobile. We are indeed faced with the fundamental question of latent image formation which the Gurney-Mott theory seeks to answer.

The existence of the latent image speck of the silver bromide system then presupposes the existence of latent image specks in the thallous bromide system, and raises immediately the question of transfer of atoms or ions through the crystal on illumination. It is most improbable that the light action is concerned only with a number of immediately adjacent ion pairs, illumination of which produces thallium atoms which can cohere without any appreciable movement; further, the size of the resultant silver speck must be above a certain critical value, unlikely to be obtained, even by intense illumination, in the presupposed restricted area. If we are then obliged to postulate the movement of thallous ions through the crystal we are in effect bound to consider the possible application of the Gurney-Mott theory to this system.

As has been shown experimentally the presence in small quantities of other substances commonly regarded as halogen acceptors increases the speed of the plate as judged by the resultant developed density. The similarity of the normal spectral sensitivity of silver and thallous bromide systems can only be interpreted by regarding the primary light action as the removal of an electron from the bromine ion, with production of a neutral atom; this atom must have a certain mobility whereby the acceptor action can operate. At the same time thallium has a much greater tendency to resume the ionic state than silver, as is exemplified by the replacement of metallic thallium by silver from silver nitrate solution. In addition to the mobility factors in producing a latent image there must in relation to these be considered the possible reproduction of thallous and bromine ions by a reversal process. How much this differs from the ordinary silver bromide system will be reflected in the relative densities to be obtained in each system.

Processing and Development.

One of the main points of importance in this respect is the observation of low speed, or efficiency of latent image formation, in thallous bromide systems. Since the latent image has normally been detected by the silver nitrate double decomposition process, it is first necessary to inquire if such a process results in the loss of any previously produced thallium latent image. The original thallium image must be in close contact with the thallous bromide crystal. If the silver nitrate double decomposition produced an entirely new set of crystals the contact between the latent image and the original crystal might be largely lost, resulting in only a small fraction of the original latent image specks being finally in the necessary close contact with the silver bromide. Farrer[4], however, from photomicrographic comparison of the same set of grains before and after the silver nitrate treatment, observed that very little change in crystal shape took place. The normal crystal lattice forms of thallous bromide and silver bromide are not identical the former being a body-centred cubic lattice and the latter a face-centred cubic lattice. Farrer indeed observed in larger crystals an increase in opacity which led him to suggest the presence of aggregates of submicroscopic particles. It may here be remarked however that the density of precipitated thallous bromide is given by Mellor as 7.54 and that of silver bromide as 6.2; a gram molecule of thallous bromide would thus occupy $^{284}/7.54 = 3.76$ c.c. and a gram molecule of silver bromide $^{188}/6.2 = 3.03$ c.c., a decrease of approximately 20%. There should thus be no tendency for compression to occur in the gelatin framework, with a consequent possible loss in the number of developable "particles" produced by the double decomposition. The question of developability in adjacent grains of silver bromide has, however, previously received some considerable attention. Normally developability is not transferable from one separate grain to another,[55] but small silver bromide grains in a clump do tend to adhere together and, if one of these grains is affected by light, the whole aggregate becomes developable.[56]

The size relationships between the bromide and the resultent developed silver grain have also been the subject of considerable investigation and it has been shown that this is frequently dependent upon the developer used. Wightman and Trivelli[57] found that with hydroquinone developer the silver grains had roughly the same contour as the silver bromide crystals from which they were produced; a metol developer gave some distortion while a metol-hydroquinone developer of one-tenth the normal concentration gave a very porous deposit. Recent motion-picture photomicrography has shown that during development threadlike streamers or filaments were thrown out from the grain,[58] an aspect further confirmed by more recent and more definite work achieved by the electron microscope.[59] These filaments were observed to be in rapid movement. Finally a spongy mass of silver fibres was produced, with a degree of compression determined by the rigidity of the surrounding gelatin of the emulsion. From the present viewpoint, the ejection of such silver filaments and the compression of the system must be such as to counteract the possible 20% volume decrease resulting from the silver nitrate treatment. If the initial thallium latent image is on the original grain surface, there is then every probability that development of the entire clump of grains will finally result, with little or no loss of efficiency.

Plate Sensitivity.

For development to occur with a normal developer, the latent image specks must be available to the developer by virtue of their position on the grain surface. In the case of thallium it is well known that thallium metal is attacked by water containing oxygen and it is at the surface of the grain that such effects will be at a maximum. "Dried" gelatin retains a certain amount of water, the amount present at equilibrium being dependent on the relative humidity of the surrounding atmosphere; for a percentage relative humidity of 50, the gelatin may contain as much as 20% moisture. If then the latent image or the sensitivity speck from which the latent image is derived, consists of thallium atom aggregates, deterioration of both the latent image and the sensitivity of the plate must be expected to occur. Since the latent image must be above a certain critical size, decrease in a definite latent image speck, once formed, will not be so rapid as in the case of the critically small sensitivity speck or the small - and -specks (page 22). The experiments reported are in agreement with these conclusions; once formed the latent image speck is relatively stable (table VIII, figure 19), but the decrease in sensitivity of the plates is very marked (table IX, figure 20) a decrease considerably accentuated for conditions where the amount of available water is considerable, as in the uncoated emulsion (table X figure 20). It is perhaps of interest in this connection that an emulsion uncoated but hardened by chrome alum to such an extent that a temperature of over 60°C was required to melt it, preserved its latent image formation capacity for a period of several months; this may be due to the restriction on the movement of water imposed by the increased "solidity" of the emulsion. In the procedure under discussion, however, the thallium latent image can only be subject to attack by the water of the silver nitrate solution for a very short time before complete conversion to the silver latent image takes place, and since this silver image is relatively unaffected by water, it would appear that the general slowness of the thallous bromide system is not to be attributed to the development processes.

Although Farrer does not give details of the intensities of light used in his experiments the emulsions prepared by him were apparently decidedly faster than those used here, as judged by the daylight exposures. In Farrer's method the plates were coated with the unwashed emulsion, the washing then following; in the present procedure extensive washing of the shredded emulsion preceded the coating. Microscopic examination of the resultant washed shreds showed usually an appreciable decrease in the thallous bromide content, due to the appreciable solubility of the bromide in water. Altogether the operations of shredding, remelting and coating involved a considerable time of contact of the grains with water. It is therefore believed that the relative slowness of the present plates is partly due to some removal of thallium specks by such action. For the plates as finally prepared, however, a high density could be obtained by suitable illumination, indicating no lack of centres for the purpose; the rate at which such densities could be reached can only be explained in terms of the mechanism following illumination of the crystal.

In addition to the question of the relative mobilities of thallous ions and bromine atoms, consideration must be given to the absolute numbers of these species for the given conditions. On the Gurney-Mott theory as applied to the silver bromide grain, the rate of growth of a speck is more dependent on the number of interstitial silver ions available, this number being dependent on the temperature and the energy required to raise a lattice ion to an interstitial position. Information on such a point appears to be lacking for thallous bromide, but the experiments in which high densities were obtained rapidly in the presence of bromine acceptor (p.67) may be taken to indicate an essential sufficiency of thallous ions for the purpose. For developed densities less than this high value, and obtained for the same conditions of exposure, the capacity for the production of such ions must be present as before but be obscured by the presence of bromine atoms not removed by acceptors.

Reversal Effects.

So far the mobility of the thallous ion has been considered solely in relation to the "forward" process of latent image "building". Similar considerations must however apply to the reverse process, the reversal or bleaching of the image by exposure to illumination suitable for the purpose. As already pointed out, the Herschel Effect in the silver latent image is regarded as a decrease in latent image size, the silver atoms losing an electron by a photoelectric effect due to the red or other "non-actinic" light illumination, and returning to the grain as silver ions. If these ions were relatively immobile and did not move appreciably from the remaining latent image, the developing solution with its readily available supply of electrons would rapidly restore the original situation and give a developed density much as before. On this basis we would always expect a parallelism between the rate of increase of a speck and the rate of decrease in reversal. Thallium however tends to revert to the ionic state much more readily than silver; Although the parallelism must still exist reversal phenomen~~i~~a may be expected to be much more marked than in the case of silver.

Normally the reversal effects in the case of silver are only considered in relation to the effect of longer-wavelength non-actinic radiation. If, however, the action is a photoelectric one acting on the metallic aggregates of the latent image, there seems no reason why actinic radiation should not have a similar effect, although in the case of the silver system one would expect the effect to be marked by the rapidity of the image-forming processes than in action. S In the thallous system with its slow latent image formation one would expect such reversal by actinic light to be perhaps more accessible.

The experiments previously reported have indeed shown that, in thallous bromide plates containing iodide, reversal is easily accomplished not only by green light (page 85) but also by blue light of relatively low intensity (page 87 et seq.) Reasons have already been given for the conclusion that blue light alone does definitely cause reversal and that this is not due to green light passed by the blue filters. On the other hand with bromide plates containing no iodide reversal by both green and blue light is inappreciable for the same conditions although there is evidence that it does take place to a certain extent (page 73). At the same time these plates containing no iodide were found to be relatively insensitive in respect of ordinary blue illumination (see comparable density curves, figure 22).

It might be urged that since the presence of iodide increases the spectral sensitivity range to which thallous bromide plates are sensitive (page 72), an increased absorption coefficient for blue light (see page 116) might be responsible, conditions otherwise remaining as before; since, however, reversal, by green as well as by blue light, may be taken as an even better indication of metallic ion mobility than latent image formation, which may be complicated by other factors, it would appear that the presence of iodide in the thallous bromide system does definitely increase the mobility of the thallous ion through the lattice. Even when added acceptor is present to remove any bromine which may be available, relatively little increase in density is found in iodide-free as compared with iodide-containing plates (figure 22, tables XII and XIII). Either the bromine atom mobility is similarly less or the "excess" electrons not neutralised by thallium ions moving up to the sensitivity speck, are removed by combination with bromine atoms before acceptor action at the surface can be completed.

In one respect these findings are in disagreement with the results of Farrer, who found the progressive addition of iodide to be accompanied by a progressive decrease in the speed of the plate, as judged by exposure to white light. In the present experiments with the spectrograph, the densities, for the wavelengths producing a deposit, were throughout greater for iodide-containing plates. Farrer however prepared his emulsions and plates in a yellow light. It is here suggested that the inherently faster iodide plates were reduced in sensitivity by the bleaching action of such light on the thallium aggregates acting as latent image centres (of p. 72) The greater the iodide content the greater would be such bleaching action. It is true that the subsequent image formation should also be faster provided the latent image centres are not reduced beyond a certain critical value; but bleaching action at relatively low intensities has been shown to be much more efficient than image formation (figure 25, page 89), and for the low densities normally obtained it is possible that the developable image size was not reached for the illumination conditions in question. Other results previously reported are in general agreement with Farrer's conclusion that the sensitivity of thallous bromide plates is not appreciably increased by application of standard silver plate production technique. For example introduction of small amounts of sulphur-containing substances does not result in much change in sensitivity. This last indeed may be quoted as an example of the general confirmation of certain aspects of the silver system theory, in that such a difference is to be ascribed to the replacement of silver by thallium. The fact that such differences exist, in those cases where the original effect in the silver system is to be ascribed to the silver present, is an indirect confirmation of the correctness of the general theory.

In discussing the features which arise as a result of secondary illumination, at various intensities, superimposed on a uniform primary exposure it is to be remembered that these results are made evident by the development process, in which a speck is regarded as developable if it reaches a certain critical size. Since any one grain which possesses such a latent image develops completely the final density is a measure of the number of grains in which the latent image has reached the critical size. If all grains were alike in the number and size of the original sensitivity centres, the result of development would be either maximum density or no density at all. The density obtained however does give an indication as to the rate of growth of a latent image speck. In particular, if the result of the secondary illumination produces a decrease in density, then obviously the average size of the latent image is decreasing. If no effect is produced, the rate of growth is zero; if the density increases the rate of growth is positive. This of course refers to such latent image specks as are affected by the developer; distinction may require to be made, for example, between surface and internal latent images.

The main features which are then evident as a result of secondary illumination by blue light are three in number, as indicated by figure 25 (page 89). Of these, the increase produced by secondary illumination of intensity higher than that of the primary illumination would appear to call for no special comment, being the normal increase which is to be expected. When the secondary intensity is equal to the primary, the relatively small time of secondary exposure for the above experimental conditions is such as to produce no appreciable change. This again is not abnormal in view of the long time of exposure normally required to produce appreciable density changes in such emulsions.

When, however, the intensity of the secondary illumination is lower, by a factor of 10, a marked increase is to be observed for low primary densities (figure 26, page 92) this however not being apparent at higher primary densities. At low densities, the number of grains which are developable is relatively small, because the latent image centres as a whole are not above the developable critical value. If the majority of such latent image centres are just below the critical size value, a relatively small intensity may thus suffice to raise the size above this critical value, the resultant density being then naturally in excess of the value produced by primary illumination of this intensity alone for comparable periods of time. The resultant intensity is however greater than that produced by secondary illumination ten times greater in intensity. At this higher intensity some retarding effect must be in operation. Since in general the addition of bromine acceptors removes this retarding effect, it is to be concluded that bromine atoms are in some way responsible, the normal rate of bromine atom removal being insufficient at the higher intensity, i.e. at higher bromine atom concentrations. In silver bromide systems a similar general effect of an increase due to a low-intensity post-exposure has been recognised for some time, and

explained on similar lines. The data obtained have been further of value in tracing the rate of growth of sub-image specks, from the point of view of low intensity reciprocity failure,[60, 61, 62, 63].
According to Berg however the picture of low intensity failure is not here complete in that a mechanism of recombination or trapping of electrons is required which so far has not been studied or understood. It may be that the bromine atom behaviour, as above, will provide the clue.

Perhaps the most striking feature of the present experiments in thallous bromide systems is the rapid decrease in density at very low secondary exposure intensities, where the primary latent image and the general fog of the plate is entirely removed. A decrease in effective latent image size is obviously in operation. In figure 26, 1 minutes' exposure to a secondary illumination of an intensity 1,000 times less intense than the primary intensity, produced an appreciable lightening of a density which required 30 minutes high intensity illumination to produce. There are two methods of approach to this problem. In the first the effect of the secondary illumination is to be considered as entirely in relation to light absorbed by the grain, i.e. by the bromine ions, this being the normal mechanism tending to produce a latent image. This is however the mechanism which is put forward to explain the "hump" or rapid increase in density at intermediate intensities and it would seem impossible to deduce the noted decrease at still lower intensities on such a basis. A new opposing tendency is required which is in effect independent in itself of the "normal" processes taking place in the grain as the result of light absorption. Since the bleaching limit, or point of balance between the two opposing actions, has been shown experimentally to depend, first, on the primary density or size of the latent image already present, and, second, on the intensity of the secondary illumination, the second of the above alternatives must be considered, namely that the reversal is due to absorption of light by the latent image itself. Reversal by blue and green light must then be considered on a common basis.

The general parallelism between blue and green light has already been noted and discussed in connection with ionic mobility in different emulsions. In the present instance, attention is to be drawn to the high efficiency of blue light reversal, the more unexpected because the normal opposing image-building processes must still be in operation. If reversal is due to the expulsion of electrons from the thallium latent image by a photoelectric effect, then the size of the speck becomes of importance in relation to its absorption. For latent image specks of size approaching metallic thallium, application of the usual laws of the photoelectric effect would indicate an efficiency of electron expulsion which would be the same, on a quantum basis, for both green and blue light, these being expressed as incident intensity. Consideration of figures 24 and 26, however shows that approximately the same decrease (viz 0.15) in density is produced by an incident green intensity of 3.2 galvanometer scale divisions for 20 minutes, as is produced by an incident blue intensity of 0.063 scale divisions for 25 minutes. If we convert galvanometer scale divisions to incident quanta, as given by the data of pages 51 and 54, we find the blue quanta to be 26.4 times more efficient than the green quanta, contrary to expectation. If the hypothesis of photoelectric dispersal of the latent image is to be retained the absorption of the speck must, in relation to wavelength, be a function of the size of the speck.

This conclusion is then in agreement with parallel results obtained for silver bromide systems. Hilsch and Pohl[64] attributed the coloration produced by illumination of large single crystals to an induced absorption band, with a maximum at 7,000 A, due to the presence of the latent image. The great width of this induced absorption band was interpreted to mean that it arises from colloidal particles of silver of a variety of sizes, each particular size having its own absorption band. From other results of Gorokhovskii and Shestakoff,[65] it may be concluded that the wavelength of the reversing radiation varies inversely with the size of the latent image nuclei.

Although no experiments have been carried out on the relative efficiencies of blue and green light for different latent image sizes in thallous bromide, it would appear that the marked efficiency of blue light reversal is to be interpreted in terms of a similar absorption band, with a maximum lying much closer to the shorter wavelength end of the spectrum. On the basis of equal blue and green quantum efficiencies of electron and thallous ion expulsion from the grain, for the grain sizes here involved, the respective absorption coefficients would then be in the ratio of 26.4:1.

Examination of the normal absorption band for silver bromide and of the induced band dur to absorption by the silver latent image shows that some overlapping occurs even at 4,000 A. The relative coefficients are of course very different, the latent image absorption being roughly a million times less than the normal bromide absorption at 3650 A. Nevertheless, under certain extreme conditions, reversal by actinic light in the same sense as noted above for thallous bromide has been observed. Thus reversal has been obtained in all wavelengths of visible radiation in plates desensitised by dyes, with a strong reversal band in the blue region at about 4200 A.(see Mees, Theory of Photographic Process, 1942, p.281). No correlation between the spectral sensitivity of reversal and the spectral absorption of the desensitiser was observed; apparently the forward action of further latent image formation was arrested to an extent which made reversal visible.

Finally, reference may be made to a series of experiments reported by Volmer,[66] in which latent images corresponding to various developed densities were produced by exposures to X-rays, secondary exposures to white light then being applied on a time scale basis to each pre-exposure. The action of such secondary exposure may then increase, decrease, or leave unchanged the action of the primary exposure. At high primary densities a pronounced decrease was obtained, but at low densities an increase was observed. At intermediate densities both effects were recorded, a slight increase being succeeded by a decrease with increasing time of the secondary illumination. It will be observed that there is a general parallelism between these results and those here recorded for thallous bromide, in that at high initial densities a decrease is initially recorded but at lower densities an increase may be obtained. In silver bromide systems these effects are generally regarded as related to the Clayden effect as a special case of the general phenomena shown by the addition of high and low intensity exposure, although the Clayden effect does not require that the effect produced by the original exposure be reduced by the second exposure. As usually observed the density resulting from the two exposures is less than that of the single exposure to low intensity light, with therefore an apparent reversal.

While the present experiments indicate a removal of developable thallium latent image on exposure to low intensity light, there seems no indication of the final state.in the grain when such removal has been accomplished. Return to the initial conditions cannot be possible unless a sufficiency of bromine atoms remain available in the grain. Even if bromine atoms did remain in sufficient number to reduce the latent image below the developable critical size, the mobility of such atoms might rather be regarded as causing spontaneous and rapid disappearance of latent image without the necessity for secondary illumination, whereas the latent image has been shown to be relatively stable. Berg, Marriage and Stevens[67] investigated the surface and internal image formation in silver systems exposed to high and subsequent low intensity radiation. A strong Clayden effect was observed for the surface image but the reverse effect was obtained for the internal image. It was therefore concluded that the initial exposure forms a large number of internal latent image nuclei which act as traps for the product of the secondary exposure to weak light, the result being a transference of the latent image. As reported in the experimental results a few preliminary experiments only were carried out in this respect with reference to thallous bromide images. The silver bromide produced by the silver nitrate double decomposition process was apparently of a different nature in its behaviour to the internal developer recommended by Stevens for ordinary silver bromide emulsions. Further work on this aspect is therefore necessary. It may be noted however that certain departures from the normal "bleaching limits" have been recorded for conditions where the initial pre-exposure conditions have been altered in time and intensity (page 98); and since these alterations are those which, in silver bromide systems, are theoretically connected with the relative distributions of surface and internal latent images, it is not improbable that here also similar effects are in operation.

The above considerations have all been applied to these experiments in which bleaching etc. was actually observed. It is a point of considerable interest that such phenomena are limited to a certain range of primary densities. At certain higher densities, as shown by results of page 101, no bleaching either by blue of by green light was recorded. Such failure to observe reversal might be ascribed to the interpretation of developed densities in terms of latent image formation rates, in that latent image specks of size greatly in excess of that required for development would not be reduced quickly enough for the reversal effects to become evident. Thus, the grain might develop as before if the critical size is not reached. The experiments show however that, at a primary latent image size corresponding to developed density 0.3, reversal is evident in 1 minute, but even 135 minutes similar secondary exposure shows no trace of reversal at speck sizes corresponding to the high density 1.24. It therefore is concluded that an entirely different state of affairs is here concerned. The tendency to reversal must be present as before, in even greater degree by reason of the increased average size of the image specks. It would thus appear that the thallous ions produced by secondary illumination of the speck must be unable to move away from the speck neighbourhood. The mobility characteristics of the grain must then be absent; the postulation is thus made that the grain structure is entirely altered. It will be recalled from the Introduction that Berg attributed the induction period in silver bromide development to the mobility of the relatively small number of interstitial metallic ions, the end of the induction period being characterised by the bodily removal of normal ions from the lattice. In the present instance the non-occurrence of reversal is accompanied by disappearance of the induction period, visible blackening taking place immediately the plate is placed in the developing solution (page 101). It would therefore appear that in thallous bromide such a state of affairs can be brought about by light action, a conclusion which supports the general parallelism between light action and development (p.16). In both cases the latent image speck is increased by the supply of electrons, although the source of these electrons is different in the two cases.

Reciprocity Failure.

There remains for consideration these experiments designed to investigate the application of the reciprocity law. Since the reversal by blue light indicates a removal of developable latent image specks already present, reciprocity failure at low intensities must exist quite apart from any reciprocity failure inherent in the normal formation as in the case of silver. It is convenient to consider the results in relation to the time factor as follows. If the reciprocity law is obeyed, log It is constant for any given density, and the graph of log I against log t should be represented by a straight line of slope -1.

In figure 39 log I is plotted against log t for the various densities already recorded for a bromide-iodide emulsion containing 0·5 gms $NaNO_2$ per 100 cc. of emulsion.

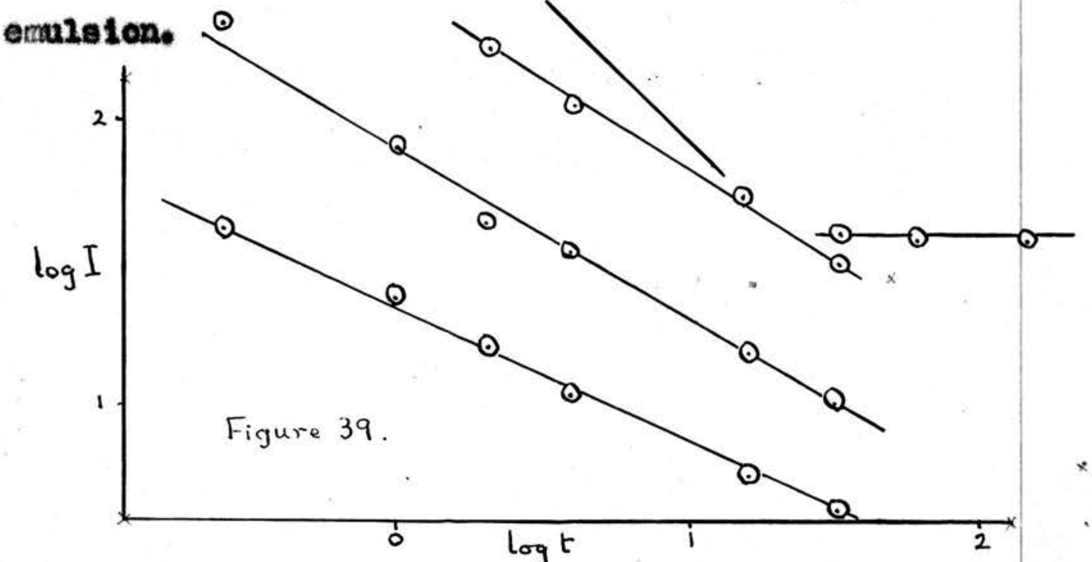


Figure 39.

In agreement with the previous calculations these curves show the characteristic "low intensity reciprocity failure" as decreasing at the higher densities, the slopes of the lines tending then to approach the ideal -1.

For comparison the results of figure 36 and table XXXII may be here included. In this case the emulsion contained no added nitrite and a constant density was obtained which did not increase for longer periods of illumination. For this maximum density the slope of the line showing variation of log t against log I is zero, corresponding to "normal" high intensity failure. It is to be noted that addition of nitrite tends therefore to remove high intensity failure; again the mechanism of bromine atom removal is important. Exposure of such nitrite-free plates under reduced pressure again increases the developed density. Although no further experiments on this aspect were carried out, it seems probable that removal of bromine is again the predominant feature.

Low intensity reciprocity failure in the silver system is normally regarded as due to disintegration of the latent image speck in its initial stages of formation. This regression is usually considered as due to thermal ejection of electrons, since it tends to decrease at lower temperatures. As pointed out by Mees, however, such a decrease does not necessarily limit the action to such thermal electronic regression, since any chemically induced action effect would be likewise expected to decrease with temperature. In the present instance of thallous bromide, three effects may be in action, viz. thermal, photoelectric and chemical, this last being due to attack by the mobile bromine atoms present as a result of illumination and not removed sufficiently quickly by acceptor action.

In the Gurney-Mott theory, high intensity reciprocity failure is attributed to the relative slowness of migration of silver ions through the grain to the latent image speck. Immediate neutralisation of electrons on the speck does not then occur; the negative charge repels further electrons and limits the subsequent rate of trapping of electrons to that at which silver ions can reach the speck. The evidence of Berg, Marriage and Stevens[67] indicates that the majority of these electrons contribute to the internal latent image formation inside the grain. In thallous bromide as already stated evidence on this point is lacking but the effect of acceptor in removing high intensity failure would seem to indicate that bromine-atom acceptance of electrons is here more in evidence.

In reviewing as a whole the conclusions reached as a result of this study of latent image formation in thallous bromide- gelatin systems it seems evident that the general Gurney-Mott mechanism must be taken to apply. Substitution of thallium for silver accentuates certain aspects in a manner everywhere to be ascribed to the nature of the metallic ion. In particular it would appear that, in comparison, these features are emphasised which involve the behaviour of the bromine atoms set free by the illumination, corresponding to a decreased relative mobility of the thallous ion.

Since latent image formation in silver and in thallous bromide emulsions thus is regarded as taking place by the same general mechanism, it is of interest to consider the results of illumination of a system which contains both halides at the same time. The essential difference between the two systems would appear to relate to the greater mobility of the bromine atoms produced by illumination. In silver bromide the bromine atom is generally regarded as relatively immobile, whereas in thallous bromide allowance must be made for the pronounced retarding effect when bromine atoms are not removed by acceptors. In a mixed system the predominant feature will then be the lattice structure present; for small amounts of thallium the silver bromide lattice will be largely preserved. If a centre is established by suitable illumination both silver and thallous ions will tend to move to the centre and be neutralised.

Since development is regarded as an extension of the light illumination process in that both involve the supply of electrons, a similar double decomposition of silver and thallium may be expected to occur if thallium ions are not initially present in the grain but are introduced with the developing solution, provided that such thallous ions are adsorbed at the grain surface. In this position they would in effect become part of the lattice structure.

In both instances, whether thallous ions are originally present or added with the developer, the effect on the rate of image formation and on development would then be expected to be in the same direction. If, for example, the latent image is found more readily in the first case, then development would be more rapid in the second.

The question of whether the rate of formation of "silver" image would be increased or decreased by the presence of thallous ions is however more difficult to answer. It is to be noted that thallous bromide is not reduced by a normal developer, even when thallium latent image is present. When, however, the electronic actions of light and developer are applied together, as in the preliminary experiments noted on page 63, a rapid darkening does occur. That this is not due simply to acceptor action of the alkali of the developer is indicated by the relative inefficiency of hydroxide alone as an acceptor. Developer is, however, able to reduce silver bromide when silver image is present; if the action of developer, in the case of the silver image, is similar to that of light action in the case of the thallium image, in that both supply the same activation, the simultaneous addition of thallium to the complex would increase the size of the speck above that attained in the case of silver alone. That is the availability of positive mobile thallium ions will tend to increase the image size, assuming that the thallium does not displace the silver but is additional thereto, as for example in interstitial ion positions. Therefore we would expect, in the presence of thallium ions, that the "silver" image would be of greater size than in the case of the thallium-free system, and be thus nearer the critical limit for development. Also, in the development of silver bromide plates by a developing solution containing thallous ions we should expect a greater rate of development since again the image is more rapidly increasing.

This should then hold for small additions of thallous ions; at higher concentrations, where the lattice structure tends to approach that of the thallous bromide, latent image aggregation will be slow, and a reduction in sensitivity and in the rate of development should be observed.

No reports of detailed investigation of these points seem to be available, although the evidence quoted in the Introduction (page 25) is in fact in agreement with these speculations.

In the conceptions which have been put forward in explanation of the various effects observed, the number of varying factors present complicate considerably appreciation of all the aspects involved. An attempt to contain all such factors in one expression whereby the effect of alteration in any one parameter may be more easily visualised is given in the following sections. It is to be strongly emphasised that certain influences are here presented in rate equation forms for which there is no strict numerical justification, but it is believed that such expression of the various tendencies will show at least the relative effects of the various factors. In general, derivation of an equation for the final developed densities must include recognition of (1) the actual rate of growth of any one centre in a grain, (2) the distribution and relative sizes of latent image centres in a grain and (3) the varying sizes of the emulsion grains. It is with the first of these that the following is concerned. Correlation of this rate of increase with the final developed density will in general only be possible for certain restricted densities, a matter to which reference has already been made (page 137).

The Rate of Growth of Latent Image on Illumination.

The latent image at all stages of its growth is here assumed to consist of aggregates of thallium atoms, i.e. $(Tl)_n$. Let the number of such latent image specks or centres in a grain be s, and the concentration of electrons in the conductivity layer as a result of illumination be e.

Electrons. In general, the electrons in the conductivity level may be

(a) produced from Br ions by initial light absorption.

(b) produced from the thallium aggregates by reversal.

(c) removed by combination with the bromine atoms produced in (a).

(d) removed by other means, e.g. any other electron traps in the grain.

In (a) we have

$$\text{rate} = k_1 I.$$

where I is the incident light intensity and k_1 is the absorption coefficient for the grain.

In (b) the rate will depend on the light intensity, the absorption coefficient k_2 for thallium atom aggregates, and the "area" of the complex exposed to the light. If it is assumed that only the outer surface of thallium atoms is concerned, then, for a reasonably large complex the number of surface atoms will be proportional to r^2; where r is the radius of the spherical complex. Thus we have

$$\text{rate} = k_2\ s\ I\ r^2$$

In (c) we have

$$\text{rate} = k_3\ e\ Br$$

where Br represents the available concentrations of bromine atoms.

In (d) we have

$$\text{rate} = k_4\ e\ L$$

where L represents the number of other electron traps, not directly concerned with latent image formation as made evident by development.

Combining these four rates we have, for the rate of increase of electrons in the conductivity level

$$\frac{de}{dt} = k_1 I + k_2 s\, I\, r^2 - e(k_3 Br + k_4 L) \ldots\ldots\ldots (1)$$

Bromine atoms. Within the grain bromine atoms may be

(a) produced by the initial absorption.

(b) removed by acceptor A.

(c) removed as bromine ions by the addition of electrons.

(d) removed by mutual recombination, probably at the grain surface as bromine molecules.

(e) removed by action on latent image speck. The size of the speck is here considered as of negligible effect.

The rates of these five processes are

(a) Rate = $k_1 I$

(b) Rate = $k_5 A\, Br$

(c) Rate = $k_3\, e\, Br$

(d) Rate = $k_6\, Br^2$

(e) Rate = $k_7\, s\, Br$

Thus, overall,

$$\frac{d\,Br}{dt} = k_1 I - k_5 A\, Br - k_3 e\, Br - k_6 Br^2 - k_7 s\, Br \ldots\ldots\ldots (2)$$

Bromine molecules. Bromine molecules may be

(a) formed from bromine atoms.

(b) removed by action on latent image.

(c) removed by diffusion, evaporation, etc.

The rates of these three processes are

(a) Rate = $k_6 Br^2$

(b) Rate = $k_8 s\, Br_2$

(c) Rate = $k_9 Br_2$.

In (c) the action of acceptors should be included as a separate term depending on the concentration A; in view of the complexity of the expression finally obtained this is for the present included in k_9.

Hence, overall,

$$\frac{d\,Br_2}{dt} = k_6 Br^2 - k_8\, s\, Br_2 - k_9 Br_2 \;\ldots\ldots\ldots\ldots (3)$$

The rate of formation of latent image, i.e. the rate of addition of thallium atoms to the aggregates already present will be then given by

$$\frac{dx}{dt} = k\, s\, e - k_2\, s\, I\, r^2 - k_7\, s\, Br - k_8\, s\, Br_2 \;\ldots\ldots (4)$$

In equation 4, it is assumed that each electron added to the latent image speck is neutralised by one thallium ion from an interstitial position.

To evaluate equation 4, e, Br and Br_2 must be eliminated. The normal stationary state condition is then assumed, viz.

$$\frac{de}{dt} = 0 = \frac{d\,Br}{dt} = \frac{d\,Br_2}{dt}$$

From equation 3,

$$Br_2 = \frac{k_6\, Br^2}{k_9 + k_8\, s}$$

and from equation 1,

$$e = \frac{(k_1 I + k_2\, s\, I\, r^2)}{(k_3\, Br + k_4 L)}$$

Substituting in equation 2, we find

$$\begin{aligned} k_3 k_6 Br^3 &+ Br^2(k_4 k_6 L + k_3 k_7 s + k_3 k_5\, A) \\ &+ Br(k_4 k_7 s\, L + k_4 k_5 A\, L + k_3 k_2\, s\, I\, r^2) \\ &- k_1 k_4\, I\, L = 0 \;\ldots\ldots\ldots\ldots\ldots\ldots (5) \end{aligned}$$

This equation, being cubic, cannot readily be solved for Br. The cubic term can be eliminated if $L = 0$, a possibility which however it seems unjustifiable to assume in the light of experimental evidence. The cubic term will also disappear if $k_6 = 0$; this however would neglect the experimental fact that evacuation markedly increases latent image formation, this being attributed to the removal of bromine. Thus it has been judged best to obtain an approximate value of Br from equation 5 by dropping here the cubic term, while still retaining in the other terms all the reactions concerned.

Solving then the resulting quadratic in the usual way, and remembering that Br cannot be negative, we find from equation 5

$$Br = \frac{\sqrt{(b^2 - 4ac)} - b}{2a} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(5a)}$$

and from equation 1,

$$e = \frac{k_1 I + k_2 s I r^2}{k_3 \frac{\sqrt{(b^2 - 4ac)} - b}{2a} + k_4 L}$$

where

$$a = k_4 k_6 L + k_3 k_7 s + k_3 k_5 A$$

$$b = k_4 k_7 sL + k_4 k_5 AL + k_3 k_2 s I r^2$$

$$c = k_1 k_4 I L$$

Substituting for $k_6 Br^2$ from equation 2, and applying these results to equation 4, we find the rate of addition of thallium atoms to the latent image speck to be

$$
\begin{aligned}
\frac{dx}{dt} = {} & \frac{k\,s\,I\,(k_1 + k_2\,s\,r^2)\,2\,a.}{k_3\,(\sqrt{[b^2 - 4\,ac]} - b) + 2\,a\,k_4\,L} \\
& - k_2\,s\,I\,r^2 \\
& - \frac{k_7 s}{2a}\,(\sqrt{[b^2 - 4\,ac]} - b) \\
& - \frac{k_8\,s\,I}{(k_9 + k_8\,s)}\left[k_1 - \frac{k_3(k_1 + k_2\,s\,r^2)(\sqrt{[b^2 - 4\,ac]} - b)}{k_3(\sqrt{[b^2 - 4\,ac]} - b) + 2\,a\,k_4\,L}\right. \\
& \qquad \left. - \frac{k_5\,A + k_7\,s}{2\,a\,I}\,(\sqrt{[b^2 - 4\,ac]} - b)\right] \qquad \ldots\ldots\ldots\ldots\ldots (6)
\end{aligned}
$$

As already emphasised, the relationship between rate of growth of latent image and developed density is perhaps most apparent in the experiments on secondary illumination by blue and green light, in that no change in density corresponds to zero $\frac{dx}{dt}$, while increase and decrease in density correspond to positive and negative values of $\frac{dx}{dt.}$ respectively.

The results of secondary blue illumination may therefore be first examined in relation to the above general equation. If r, s, A and L be then taken as constant, equation 6 may be written as

$$
\begin{aligned}
\frac{dx}{dt} = {} & P\,\frac{I}{\sqrt{[(m + I)^2 + n\,I]} - (m + I) + d} \\
& - Q\,I \\
& - R\left[\sqrt{[(m + I)^2 + n\,I]} - (m + I)\right] \\
& - S\,I\left[1 - \frac{p\,\sqrt{(m + I)^2 + n\,I} - (m + I)}{\sqrt{\{(m + I)^2 + n\,I\}} - (m + I) + d}\right. \\
& \qquad \left. - \frac{q}{I}\left\{\sqrt{(m + I)^2 + n\,I} - (m + I)\right\}\right] \qquad \ldots\ldots\ldots\ldots\ldots (7)
\end{aligned}
$$

where P, Q, R, S, d, m, n, p, q are all constant

The curve showing variation of dx/dt with variation in I, thus depends on the value of

$$y = \sqrt{(m + I)^2 + n I} - (m + I)$$

It can easily be shown by a series expansion that y increases with I up to a maximum (=.5) independent of the value of I; to take a numerical example, for $m = n = 1$ and $I = .1, 1, 10, 100, 1000$, the values of y are as follows

I = .1 , 1.0 , 10 , 100 , 1000.

y = .045, .24, .45, .5, .5.

With suitable constants, the effect of secondary blue illumination may then be illustrated as follows

Table XXXV

P = 1 Q = 1 R = 1·3 S = .835 d = 1

I	0	.1	1	10	100	1000	
P term	0	+.096	.80	6.9	66.6	666	
Q term	0	-.01	-.1	-1.0	-10	-100	
R term	0	-.045	-.24	-.45	-.5	-.5	× 1·30
S term	0	-.036	-.40	-4.5	-5.6	-569	
$\frac{dx}{dt}$	0	+.005 -.32 -.01	+.06 -.01	+.95 .92	+.1 .05	5.5 5.4	

These rates then correspond to the general features indicated by experiment (figure 25 , page 89), a decrease at low intensities, a hump at intermediate intensities, and an increase at high intensities.

In the case of secondary green light reversal, k_1 is normally regarded as zero, since no image is produced by green light illumination. In equation 6, the term c then becomes zero, and with it, Br. The R and S terms thus vanish while the Q term remains as $- k_2 s I r^2$

and the P term becomes

$$\frac{k\,s I\,k_2\,S\,r^2}{k_4 L}$$

Thus, summing, we have

$$\frac{dx}{dt} = \frac{k\,s I\,k_2\,S\,r^2}{k_4 L} - k_2\,s I\,r^2$$

$$= k_2\,s I\,r^2\left(\frac{k\,s}{k_4 L} - 1\right)$$

For bleaching to occur, the term $\frac{k\,s}{k_4 L} - 1$ must thus be negative. The ratio ks/k_4L represents the removal of electrons from the conductivity level by the developable latent image, relative to the removal by other traps. In the present instance $ks/k_4L - 1$ must obviously be negative and bleaching by green light takes place for all intensity values at a rate here indicated as proportional to I and to the "area" of the image speck.

The position of the bleaching limit for blue light with respect to the primary density level will be determined by the relative values of those terms which include r. The higher the density the higher the value of r. Both P and Q terms will tend to increase, but in the former the effect of increasing r^2 will only be of secondary importance compared with the increase in the Q term. The bromine atom concentration, also, will decrease. The general effect will be to remove the "hump" and raise the bleaching limit to higher I values, which conclusions are again in agreement with the experimental results.

If the concentration A of acceptor increases, the bromine atom concentration will decrease (cf. equation 5a); the Q term remains as before, but the P, R and S terms all increase. The exact effect of such alterations is obscure in the general formula by reason of its complexity and the unknown value of the various constants, but small variations in A, by reason of the square root relationship, will have only a negligible effect in the intensity ranges with which the bleaching limit is concerned. At higher intensities the effect of the P term may be expected to predominate; here the effect of added acceptor will not be proportional to A for large values of A, because the "a" term of equation 6 occurs in both numberator and denominator. These again are conclusions in agreement with the results of experiment.

There remains for consideration the ordinary H. and D. curve as produced by plotting incident light intensity (or log I) against the developed density. The general equation above indicates that the rate of growth of an image centre on the above model will not be exactly proportional to I, unless in certain circumstances where an apparent proportionality may arise as a result of compensating influences. The situation is further complicated by the fact that at a given time the value of r will be different for the different intensities. At high intensities and high r values, the rate of growth of latent image will tend to decrease, both because of the increased bleaching action as represented by the Q term and by the effect of bromine atom and bromine molecule attack, as represented by the S term. These conditions would tend to indicate "high intensity" reciprocity failure. On the other hand, at low intensities, the rate of increase of latent image will be relatively small, as evidenced by the removal of image of size above a certain critical value. These conditions correspond to "low intensity" reciprocity failure.

Complex as are the conditions under which latent image formation takes place, it does appear that the above expression, derived on the most simplified of assumptions, yet gives a certain picture of the latent image process which is more or less in agreement with the experimental results here obtained. It would seem that the Gurney-Mott theory gives, in the thallous bromide system, an adequate representation of the processes taking place on suitable light absorption. Where extensions to the silver bromide scheme have been necessary, these have always been related to the substitution of silver by thallium and, although in many aspects further work is necessary, it may be claimed that the results so far obtained do support and extend the present view of latent image formation.

APPENDIX 1.

Developer A. Normal MQ developer.

Metol	5 gm.
Hydroquinone.	15 gm.
Sodium sulphite (cryst.)	150 gm.
Sodium carbonate(cryst.)	150 gm.
Potassium bromide.	2 gm.
Distilled water to	2,000 ml.

For use this solution was diluted with an equal volume of distilled water.

Developer B. Ferrous oxalate.

A.	Potassium oxalate.	120 gm.
	Distilled water (70°C)	500 ml.

When cool, the clear liquid was decanted.

B.	Distilled water (70°C)	500 ml.
	Sulphuric acid (conc.)	1.5 ml.
	Ferrous sulphate (cryst.)	120 gm.

For use, 1 part of B was added to 3 parts of A.

Developer C. Physical development.

A stock solution was prepared as follows:-

To 50 gm. of anhydrous sodium sulphite dissolved in 250 ml. of water was added 200 ml. of a 4% solution of silver nitrate. This was stirred until the white precipitate was completely dissolved and then was added 80 gm. of sodium thiosulphate. The developing solution had the following composition:-

Stock solution.	5 ml.
Distilled water.	25 ml.
2:4 diaminophenol ("amidol")	.0375 gm.

Before development the exposed plate was placed for 5 minutes in a forebath of the following composition:

Potassium iodide	5 gm.
Sodium thiosulphate.	12.5 gm.
Distilled water.	500 ml.

The plate was then rinsed and immersed in the above developing solution for 30 minutes at 18.5°C.

Developer D. Restrained M.Q. developer.

Metol.	2.5 gm.
Hydroquinone.	7.5 gm.
Sodium sulphite (cryst.)	75 gm.
Sodium carbonate (cryst.)	75 gm.
Potassium bromide.	20 gm.
Distilled water to.	1,000 ml.

For use this solution was diluted with an equal volume of water.

Developer E. Kodak D.76.

Metol	2 gm.
Hydroquinone.	5 gm.
Sodium sulphite (cryst.)	200 gm.
Borax.	2 gm.
Water to	1,000 ml.

Developer F. Kodak D.76d.

Metol	2 gm.
Hydroquinone.	5 gm.
Sodium sulphite (cryst.)	200 gm.
Borax.	8 gm.
Boric Acid.	8 gm.
Water to	1,000 ml.

Developer G. Steven's "Internal developer" (See Ref.68)

Metol	1.5 gm.
Sodium sulphite (cryst.)	45 gm.
Hydroquinone.	6 gm.
Sodium carbonate (cryst.)	75 gm.
Potassium bromide.	1 gm.
Distilled water.	500 ml.

For use, to 50 ml. of this solution was added 10% sodium thiosulphate solution in amounts varying from 2.5 ml. to 15 ml.

Developer H. Steven's "Surface developer."

Stock solution.

Sodium carbonate (cryst.)	120 gm.
Distilled water.	1,000 ml.

The water was boiled to remove dissolved oxygen and the sodium carbonate then dissolved. For use 1.2 gm of glycin (p-hydroxyphenyl-glycin) was added to 50 cc. of this stock solution.

Fixing Solution.

Sodium thiosulphate	500 gm.
Potassium metabisulphite.	65 gm.
Distilled water to	2,000 ml.

APPENDIX 2.

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The author desires to thank Professor Kendall and Dr. Mowbray Ritchie for the provision of the facilities which made this research possible, and for unfailing interest and kind advice during the course of the work.