LATENT IMAGE FORMATION IN THALLOUS BROMIDE-

GELATIN AND RELATED SYSTEMS.

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INTRODUCTION.

Certain solid chemical compounds darken on exposure to light. The marked effects of light on silver chloride and silver bromide have been used in photography for a considerable time. The darkening of such salts as thallous bromide (1), lead bromide, antimony oxybromide and bismuth oxybromide (2) has been reported, but in comparison to its effect on the silver halides, light effects these other salts to a much smaller degree.

In the case of photographic emulsions, i.e. silver chloride and silver bromide (3) and also thallous bromide (4)(5), besides the darkening which is visible to the eye (the print-out effect) obtained after comparatively long exposures, a brief exposure also produces an effect which is invisible and has been called the latent image. The latent image can be shown up in silver halides by either physical or chemical development.

In the case of silver bromide-gelatin emulsions although/

although a considerable amount of work had been done
on latent image formation (6) no adequate theory as
to the mechanism involved could be presented until
the general quantum theory had been enunciated in
1900 (7). However once the idea that radiation
energy was composed of discontinuous 'quanta' had
been suggested by Einstein in 1905 (8), a theory of
latent image formation in silver halides became
possible. The theory was produced by Gurney and
Mott (9)(10), and it explains very satisfactorily
the formation of latent images in silver bromide-
gelatin systems. Work done recently on thallous
bromide-gelatin systems by M. Ritchie and J.A. Thom
(11) shows that the theory can also be applied in the
case of thallous bromide emulsions. A brief account
of the theory as it was applied to silver bromide-
gelatin systems is given below.

It is known that in general photochemical reactions
do not always appear to obey the Einstein Law of
Photochemical Equivalence (1909) when the overall
chemical result of illumination is the criterion(7).
But the fact, that for a certain number of quanta of
radiation absorbed, an equal number of molecules can
react, can be applied to the initial stages of the
reaction. These considerations were applied too for
the/

the silver bromide-gelatin system.

Since a photographic emulsion consists essentially of small crystals 'grains' of silver bromide dispersed in a gelatinous medium, the effect of light on a photographic emulsion can be considered as the effect on a number of single crystals. There is, however, the important difference that whereas for a normal ionic crystal the absorption of light is shown as bands which occur at definite wavelengths, the absorption of a silver bromide-gelatin system falls off at longer wavelengths, thus giving an 'absorption tail' (12). The presence of the absorption tail is very important in photography because it means that the emulsion is sensitive to a range of wavelengths, all of which are capable of producing a latent image. The absorption tail is shown to be due to surface ions only (13) and the accepted explanation is the presence of impurities which have been adsorbed on the surface of the grain.

Before an adequate theory of latent image formation could be formed a study of the energy levels involved in an alternating series of silver and bromine ions as present in the three dimensional crystal lattice had to be undertaken.

If there is no thermal excitement of the silver bromide crystal the 5s level of the silver ion is vacant/

vacant, the valence electron which normally occupies
this level in the silver atom having been transferred
to the lower 4p level of the bromine atom, thus
forming the ionic compound silver bromide. A study of
the potential barriers existing in the crystal shows
that although the lower part of the 5s level has
slight potential barriers the upper part has none at
all. This means that electrons reaching the upper
half of the 5s level can travel unhindered through-
out the whole lattice of the crystal. The 5s level
of the silver ion is known for this reason as the
conductivity level of the crystal. The presence of
the conductivity level was shown very clearly by the
fact that at low temperatures silver bromide crystals
only conducted electricity if illuminated with light
of a wavelength included in the absorption bands (14)
(15). Thus the effect of a suitable wavelength of
radiation is to raise the electrons into the 5s
level whereupon they can travel through the crystal.
It has been shown that the conductivity of a crystal
of silver bromide at low temperatures is due to the
production of free electrons in the conductivity
level of the crystal.

Two outstanding facts arose from the mass of
experimental work already accomplished on the for-
mation of the latent image in silver bromide emulsions.
These/

These were: (a) that although a grain in the emulsion was uniformly illuminated over its whole area the resulting latent image was always found as a small speck on the grain (16) and (b) that the amount of bromine liberated by the action of light on the emulsion was approximately equal to the number of quanta of light absorbed by the emulsion (17). Any theory had to explain these two points and the Gurney-Mott theory achieved this.

The theory postulates (9)(10) that there are two processes involved when light acts on silver bromide. The first is the electronic process which occurs immediately light is allowed to fall on the silver bromide plate. The process consists of the ejection, by absorption of the quantum of the impinging radiation, of an electron from the bromine ion. The absorbed energy is transferred to the electron, thus enabling it to jump from the 4p level into the conductivity level of the crystal. It thus passes unhindered throughout the grain. After the ejection of the electron the bromine atom which is left is generally assumed to be absorbed by the gelatin. Gurney and Mott (9) assumed that the hole left in the lattice by the bromine atom would be relatively immobile, a condition which must be fulfilled if any latent image is to be formed. Incidentally it is seen at once that the second fact, that of the equivalence of quanta and the amount of halogen liberated has/

has been explained since for every quanta absorbed one electron is ejected from the bromine ion and consequently one bromine atom is produced.

The second process involved in latent image formation is one due to ionic motion. In the ordinary silver bromide lattice the silver and bromine ions are situated on the lattice points at the positions of minimum potential energy. It is possible for some of the ions, more especially the silver ones which are the smaller, to be displaced and occupy intermediate positions between the lattice points. These positions are called interstitial ones and the ions in them are termed interstitial ions. The movement of the interstitial ions is not dictated by ordinary lattice behaviour and in fact these ions are mobile, although at room temperature there are relatively few of them (18). The holes left in the lattice when ions go into interstitial positions can be filled up by other ions. The movement of the interstitial ions constitutes the second of the two processes involved. At normal temperatures both processes occur at rates which make it impossible to discern their individual effects separately although the electronic process is considered to be instantaneous as compared with the ionic process. Work has been/

been done on silver bromide at low temperatures (19)
(20) where a partial separation can be effected
because the ionic process is much reduced in rate as
compared with the electronic process, the rate of
which remains unchanged.

The sensitivity of a photographic emulsion to
light is considered to be due to small specks called
sensitivity specks which are present on the silver
halide grains. The specks are thought to consist
mainly of silver sulphide (21). They are produced
in the process of digestion of the emulsion from
various complexes of silver halide and sulphur-
containing compounds which are present in the gelatin
in minute quantities. The sensitivity specks act as
traps for electrons by virtue of the fact that they
have energy levels which are below that of the con-
ductivity level.

When light falls on a silver bromide plate electrons
from the bromine ions are set free in the conductivity
level, the resulting bromine atoms being absorbed by
the gelatin. The free electrons may be regarded as
trapped by the sensitivity specks which have the
lower energy levels. The electrons thus trapped
lose their mobile energy and charge up the speck
negatively. The second (ionic) process now comes
into play. The interstitial silver ions being
relatively/

relatively mobile are attracted first to the nega-
tively-charged speck. The ions neutralise the speck
and are changed into silver atoms. This aggregate
of silver atoms is the latent image. Several
electrons can be trapped successively on one sensi-
tivity speck and so the resulting silver latent image
can consist of several atoms of silver. It is also
known that before a latent image is developable it
must be above a critical size. It is also recognised
that it is possible for the latent image to be
situated inside as well as on the surface of the
grain (22)(23). The latent image has now to be
developed by some means and thus made visible. The
image is itself lost in the process, the final product
of development, as shown by microphotographs, being
twisted thread-like filaments of silver (24)(25).
Development. For an ordinary chemical developer the
essential feature is that the developer should be able
to supply electrons. The developing solution then
attacks the surface latent image. The emulsion grain
is considered to be surrounded by a double layer of
electric charges. This double layer consists of a
layer of bromine ions at the surface of the grain and
another of potassium ions just outside the first layer.
The double layer acts as an effective potential
barrier because any electron placed in the double
layer experiences a force repelling it away from the
grain/

grain. So normally grains are thus protected from the action of the developer. If, however, a grain has been exposed to light and a surface latent image of silver has been formed the double layer is broken at this point (according to Webb(26)). Electrons supplied by the developer can now reach the image and charge it up negatively. The process initiated by the action of light is then continued. More interstitial ions are attracted to the negatively charged speck and after neutralisation increase the size of the speck. The image grows by this process outwards in the form of a filament of silver. When the plate is being developed there is some little time in which nothing appears to happen. This is called the induction period. Then there follows a period in which the process of development becomes very rapid. According to Berg (27) the first stage is slow because it depends on the rate of formation of the interstitial silver ions. But the image can take up more and more electrons because of its increasing size until there comes a point at which the charge on the speck is so great that its attraction for the silver ions of the grain lattice exceeds the forces which keep the lattice in place. A resulting complete disruption of the grain occurs, the silver ions being dragged out of the lattice.

The other method of development is by a physical developer/

developer.   Here the silver ions are supplied by
the developer, the final silver deposit coming from
the ions contained in the developer and not as in the
case of chemical development from the grains them-
selves.   The latent image in the case of physical
development can be regarded as either (a) acting as a
centre of crystallisation or a nucleus for the
deposition of silver atoms from a supersaturated
solution of silver ions (28), or (b) catalysing the
reduction of silver ions in the developer (29)(30).
It is also a known fact (31) that the exposure of
light necessary to produce sufficient latent image to
be developable by a physical developer is consider-
ably greater than what would be required for chemical
development.

Such is the general theory applied to the
photolysis of silver bromide. Recent work done on
its application to the photolysis of thallous bromide
is to be considered but first it might be convenient
(a) to summarise and explain the terms which will be
used during the course of descriptions and (b) to
give, in view of results obtained later, a short
description and explanation of the sensitising power
of different gelatins used in emulsion manufacture.

Photographic/

Photographic Terms.

Density: The amount of silver produced by the
exposure and development of photographic material
can be measured by the amount of light it transmits.
If I_0 represents the original intensity of a beam of
light of unit area cross-section, and I, the reduced
intensity due to placing the plate with its developed
image in the beam, the opacity of the plate is given
by the ratio I_0/I and the relation $I_0/I = e^{kA}$
holds where e is the base of natural logarithms, k is
the coefficient of absorption of the image and A is
the number of atoms of silver in the path of the
light beam. The density of the photographic
negative is defined as the number of particles of
silver spread over the unit area and so Density D =kA.
Therefore Opacity = e^D or Density = $\log_e$ Opacity.
In practice Hurter and Driffield used the relation
Density = $\log_{10}$ Opacity. In all results obtained
here density is given by the $\log_{10} I_0/I$. Methods
used for measuring the density are described later.

proportional to

constant

Reciprocity. In the strict sense of the term
true reciprocity is observed when the product of the
intensity of light absorbed and the length of time
of the exposure produces a constant density. For
photographic emulsions the measurement of I_{abs} is
difficult/

difficult because of inevitable reflection and scattering. It is usual to define reciprocity as the product of the intensity of the incident light I and the time t of the exposure. If, when the product It is kept constant but I or t varied proportionally, the effect observed as given by the developed density is always the same true reciprocity is said to be present. If on the other hand the constant product It produces different effects when I or t is varied then 'reciprocity failure' is present. True reciprocity is present when on plotting log It against log I for a
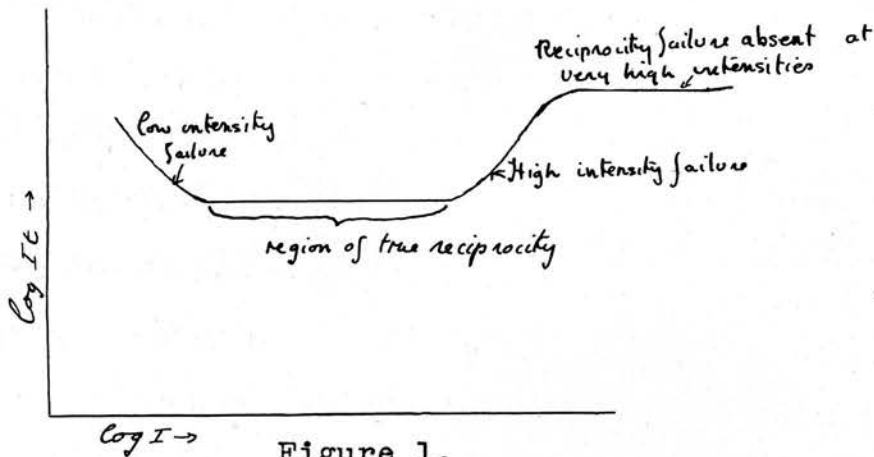

Figure 1.

definite given density, a straight line parallel to the axis is produced (see Fig. 1). Reciprocity failure of two types which occur at low and high intensities are shown by the variations from the straight line.

Low intensity reciprocity failure is attributed to inefficient latent image formation in the initial growth stages (32)(33). Either the growth process of the/

the latent image does not start until there is a
minimum concentration of electrons in the conductivity
level (9) or the latent images when formed are dis-
integrated by thermal agitation (33). In connection
with this it is known that if the temperature at
which the plate is illuminated is lowered, reciprocity
failure appears at lower intensities than it does at
ordinary temperatures.

The cause of reciprocity failure at high inten-
sities is usually regarded to be the great excess of
electrons produced by the high intensity of light.
These electrons may recombine with bromine atoms or
may fall into other electron traps so forming specks
which compete with the main speck for development.
In both cases the result is a reduction in the density
which would be expected if all the electrons had been
used up in the normal way to produce latent images.
Again the effect of lowering the temperature of
exposure is to lower the intensity at which high
intensity reciprocity failure becomes present.

Solarisation.   Solarisation is the name given to the
experimentally known fact that continued increasing
times of exposure lead to decreases in the developed
density. The effect only occurs at latent image
specks which are on the surface of the grain and is
regarded as due to the free bromine atoms destroying
the latent image. The exposure sets free bromine atoms
which unless they are taken up by an added bromine
acceptor/

acceptor, will attack the latent image. Added
bromine acceptors are known to minimise solarisation
effects. If the theory of rebromination of the sur-
face latent image is correct and that the surface
latent image becomes coated with silver halide thus
preventing the action of the developer, treatment of
the plate before development with a silver halide
solvent should minimise solarisation. This was shown
by Nafe and Jauncey (34). Luppo-Cramer (35) had
shown that if exposed silver halide grains were
treated with potassium iodide solution solarisation
effects were eliminated. He attributed this to the
fact that the potassium iodide disrupted the silver
halide grains in forming silver iodide and thus
exposed any subsurface latent image to the developer.
Thus although the surface latent image was solarised,
the existence of normal latent image specks situated
inside the grain was shown possible. In their work
on internal and surface developers Berg, Marriage and
Stevens (36) showed the presence of an internal
latent image, which could be developed up by an
internal developer, i.e. a developer containing
silver halide solvent, in presence of a solarised
surface latent image or even if the surface image
had been destroyed first by a dichromate bleacher.
Reversal/

Reversal Effects. Besides solarisation there are a number of other reversal effects. Among these are the Herschel and Albert effects.

Herschel Effect.   The Herschel effect is the reversal of the latent image caused by post-exposures to red or infrared light. The effect of red light is to eject electrons from the latent image. The silver atoms are then transformed back into silver ions which wander into the crystal taking up interstitial positions again. Complete reversal of the image can be effected so that the whole image is bleached out. Two facts: (a) that red light which would produce a forward action on/a suitable plate already suitably exposed to give a low density, yet could produce reversal of a higher density present on a plate and (b) that as the density increased so the wavelength of the maximum activity of red light decreased, lead to the postulations that there are two processes in operation when/a plate is illuminated with red light. One process is a forward process of latent image formation and the second is a destruction process. When there is a Herschel effect present the forward process is not predominant (37)(38). The actual regression of the latent image is found to proceed faster if the blue and infrared exposures are given simultaneously (39) and so it is thought/

thought that the silver nuclei of the latent image
can be broken up more readily when they are forming
and are not stabilised. The fact that as the density
produced by the primary exposure increases the wave-
length at which the maximum activity of red light in
disrupting the image decreases, can be explained by
the fact that the energy required to eject the
electrons might be smaller the smaller the number of
atoms in the silver speck.

Experiments which support the theory of the
destruction of the latent image were carried out by
Berg (20) and Webb and Evans (40) who worked on the
effects of temperature on the Herschel Effect. If
the primary exposure was given at -186°C., the plates
warmed up to 20°C. and then the infra-red exposure
given at -186°C. no Herschel effect was observed. If
on the other hand the plate was not warmed up between
the exposures the Herschel effect was observed. If
the assumption is made that at -186°C. the silver ion
migration ceases, then the primary exposure at this
temperature does not produce a true latent image but
only the electronic part of the process occurs. If
the red light exposure is given without warming the
plate to room temperature, the potential latent image
is readily destroyed by ejection of electrons. If,
however, the plate is brought to room temperature after
the/

the primary exposure, the ionic movement of the
interstitial ions completes the normal latent image.
Now if the plate is cooled to -186°C. and the infra-
red exposure given, the regression of the latent
image does not occur. This is because although the
infra-red light does, as normally, eject electrons
from the image, the positively-charged image which
results cannot lose the silver ions because of their
immobility at low temperatures. Consequently as the
temperature is finally increased the positively
charged silver speck attracts the electrons from the
conductivity level, thus giving a neutral latent image
of the original size. So that in this case no
regression can be detected.

Albert Effect.   The Albert Effect is observed if a
plate has been given a primary exposure with a step-
wedge in position and after treatment with chromic
acid or some other mild oxidising agent, is given a
second exposure to diffuse light. The image after
development is found to be reversed. Stevens (41)
proposed the mechanism of the Albert Effect to be as
follows. The first exposure produces internal latent
image specks in addition to those on the surface of
the grain. The surface nuclei are readily destroyed
when the film is immersed in a solution of a suitable
oxidising agent which also produces a partial
desensitisation of the whole film. The sub-surface
nuclei/

nuclei are not affected by the immersion although
the grains containing these nuclei are desensitised.
The cause of the desensitisation is uncertain unless
it is that the internal nuclei cause any deposition
of silver produced by the second exposure to be
situated inside the grain where it does not act as a
normal latent image. However any internal developer
will show it up and thus the correlation between the
Albert Effect and the 'residual latent image', i.e.
the latent image remaining after chromic acid
treatment is explained.

Sensitising Power of Gelatins.

In view of the fact that in contrast to thallous
bromide emulsions prepared by Farrer and J.A.Thom,
great increases in speed were obtained in emulsions
prepared for the present work, it is interesting to
investigate the question of why some gelatins give
'fast' and others 'slow' emulsions.

For photographic use, gelatin has to be prepared
from specially selected material. The chief function
of gelatin in a photographic emulsion is to keep a
uniform suspension of silver bromide particles when
the emulsion is in the liquid form and to act as a
support for the grains when the emulsion has been
coated and dried. Although collodion has been used
for/

for this purpose gelatin appears to be more
satisfactory. Gelatin too has the property of a
protective colloid on the grain dispersion and protects
unexposed grains from the action of the developer.
The bromine atoms when released by the action of the
light are absorbed in the gelatin which thus has
another important function. But more marked than
these which appear in all gelatins, there is the
fact already mentioned that different gelatins
appeared to have very widely differing effects on the
speed of the photographic materials produced. Some
gelatins gave fast plates while others for some reason
only relatively slow plates.

A series of investigations were undertaken by
Sheppard in 1925 (42) to find the substances
responsible for 'sensitisation effects' in gelatin.
From gelatin which was known to have good sensitising
power there was isolated an active material which
was termed 'Gelatin X'. It was found that photo-
graphic material made from a 'slow' gelatin to which
an addition of 'Gelatin X' had been made, possessed a
greater speed than material made with the original
'slow' gelatin. At first 'Gelatin X' was thought
to be cholesterol but pure cholesterol was found to
possess no sensitising power. Finally it was
discovered that an extract made from black mustard
seed/

seed was very effective in increasing the sensitisation
of the gelatin. The active sensitiser then was
reasonably identified as either allyl mustard oil or
some compound closely related. Further work showed
that the sensitising power was the property of the
grouping

$$C \overset{NH-}{\underset{N}{=}} S$$
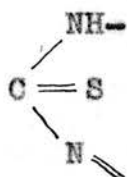
and that sulphur alone had
very little effect. Eventually the sensitising com-
pound present in various amounts in the different
gelatins was shown to be similar to allyl isothio-
cyanate or allyl thiocarbimide. In addition gelatin
contains anti-fogging or desensitising materials in
the nature of imidazoles or azines and the final
sensitivity of the gelatin is due to a balance of the
sensitising and desensitising compounds present.

Sheppard, Trivelli and Wightman (43) postulated a
mechanism whereby silver sulphide sensitivity specks
were produced in the emulsion from the action of allyl
thiocarbimide present in the gelatin. The allyl thio-
carbimide contained in the gelatin is regarded as
being adsorbed on to the grain surface and there
forms a molecular compound with the silver halide.
Degradation of the molecular compound to silver
sulphide is accomplished by the alkali present and the
silver sulphide is formed as a speck where the
molecular/

molecular compound had been originally situated. The
pre-existence of such sensitivity specks in the grain
had been already suggested by Clark (44) who reported
that the fogging action of sodium arsenite solution
on silver halide emulsions was due to a reducing
action similar to that of light itself.

It has been shown by Kornfeld (45) that the
majority of the sensitivity specks must lie on the
surface of the grain since with ordinary exposures
the bulk of the latent image formed is on the surface.
But it has been found as stated above, that, by
dissolving off the outside of exposed grains a resid-
ual latent image could be developed up by a total
developer. This points to the presence of sensitivity
specks situated inside the grain surface. This
capacity for internal latent image formation becomes
very important, as shown above, in certain reversal
effects, notably the Albert Reversal. Internal
sensitivity specks if composed of silver sulphide
could be formed by the same mechanism as stated
above for the surface specks. If the speck was formed
when the grain was in the growth process it would be
enclosed within the boundaries of the grain as it
grew further. It is also to be remembered that any
internal flaws in the crystal would also act as
electron traps if the energy levels are lower than
that of the conductivity level and thus internal
images/

images could be formed.

When it became so clear that the presence of sulphur-containing compounds in the gelatin could influence the resulting plate speeds so much, methods of estimating the sulphur present were investigated. The amount of labile sulphur present in gelatin samples was estimated by Sheppard and Hudson (46) using the method of decomposing the sulphur-containing substance with an ammoniacal solution of silver chloride, thus giving silver sulphide. The silver sulphide was decomposed quantitatively with concentrated hydrochloric acid and the hydrogen sulphide so formed was absorbed in p-aminodimethylaniline solution to form methylene blue, which was estimated colorimetrically. Excess labile sulphur tends to produce black or normal chemical fog and a relation (47) between the total labile sulphur and the tendency to produce fog if the films were developed without bromide was found. In 1942 A. Steigmann published a paper (48) in which a new test for restrainers in photographic gelatins was described. Restraining impurities occur naturally in gelatin or they can be added to naturally unrestrained gelatins. The action of restrainers is to inhibit the growth of the grains and the sensitising silver or silver sulphide nuclei during the digestion of the emulsion. This new test shows the effect of restrained and unrestrained gelatins/

gelatins on the growth of silver nuclei in a boiling solution of gelatin, ammoniacal silver nitrate and ammonium sulphite. The rate of production of silver is proportional to the restrainer in the gelatin, the more restrained the gelatin the slower the production of silver nuclei. Full details of the test are given later but although it is not recommended as an independent test it does serve as a means of comparing the different gelatins used in the preparation of the emulsions.

Very recently (49) attempts were made to use the polarograph to get an estimation of the sulphur bodies present in gelatin. But, in particular, allyl isothiocyanate was detectable by the polarograph only in amounts which greatly exceeded those existing in photographic gelatins.

Review of Previous Work done on Thallous Bromide
    Emulsions.

Although the darkening of thallous salts exposed to light had been observed, the first reports on the use of thallous salts was in connection with silver bromide plates. Luppo-Cramer (50) showed that thallium halides appeared to sensitise silver bromide and silver iodide emulsions. Additions of thallous halides increases the spectral sensitivity and speed of silver iodide to a great extent. The sensitisation of silver iodo-bromide plates by using erythosin in conjunction/

conjunction with small amounts of thallous nitrate
was reported by Haidrich (51). In addition thallous
salts were reported to be capable of speeding up
hydroquinone development and this increase was thought
to be due to the increased absorption of hydroqui-
none (52)(53)(50). The first investigation on the
possibility of emulsions made of thallous bromide
exhibiting latent image formation was carried out by
Farrer (4)(5). Farrer found that thallous bromide-
gelatin emulsions were capable of latent image for-
mation but that direct chemical development of the
image was not possible. However a weak image was
obtained when a physical developer was used. The
most important fact that when the thallous bromide
plate was immersed in a 10% silver nitrate solution
a double decomposition took place and the identical
silver bromide system was formed with no loss of the
latent image in the process was the starting point
for all subsequent work. Farrer showed by photo-
micrographs that in this exchange the crystal shape
and position remained unaltered. Recent confirmation
of this comes in work done on the growth of silver
halide on thallous halides(54). Silver bromide
grows as an orientated layer on thallous bromide,
the (110) planes of the silver bromide and thallous
bromide lattices growing parallel. Incidentally it
is/

is noted in connection with emulsions containing
thallous iodide in addition to thallous bromide,
that thallous bromide is completely miscible in all
proportions with thallous iodide. Once the exchange
has been effected and after excess silver nitrate had
been removed from the plate, development and fixation
of the image could be carried out using normal chemi-
cal developers and fixers employed for silver
bromide plates.

Farrer prepared thallous bromide emulsions by
adding thallous nitrate to a gelatin solution which
contained excess potassium bromide, in yellow light.
This general method with some alterations was adopted
by subsequent workers and full details of the final
procedure which was obtained after much preliminary
work by J.A.Thom are described later. As to the
spectral sensitivity of the plates Farrer found that
thallous bromide plates were normally sensitive to
blue light but that certain dyes had the effect of
increasing the sensitivity in a similar way to the
increases found in silver bromide emulsions.
Increases in the speed of the thallous bromide plates
could be effected by using certain 'bromine acceptors'.
Sodium nitrite was one of the most effective although
use of these substances enhanced fogging. Farrer
found too that small amounts of iodide which were
known to increase the speed of silver bromide plates
apparently/

apparently had the opposite effect for thallous
bromide plates.   With reference to the use of
samples of 'fast' and 'slow' photographic gelatins
in making his emulsions, Farrer reported that contrary
to expectation 'while the differences between the two
emulsions prepared were not great the faster and
foggier emulsion was that prepared from the 'slow'
gelatin'.   The experiment was repeated and the
result confirmed.

Work was continued by M. Ritchie and J.A.Thom(11)
on the lines Farrer had indicated and the general
results obtained are summarised below.

The plates prepared by J.A. Thom showed prominent
fading properties.   That is, during the course of
time the effect produced by a known intensity of blue
light became less and less as measured by the
developed density. Fading took place more rapidly
in the liquid emulsion than in the dried coated
plates.   The characteristic curve (H $\curlyvee$ D) obtained
on an exposed and developed thallous bromide plate
was similar in shape to that obtained from a silver
bromide plate, the middle region of the curve being
approximately a straight line and the regions of the
curve at low and high intensity showing reciprocity
failure.

In the examination of the spectrograph
obtained/

obtained by exposing a thallous bromide-iodide plate
to a tungsten lamp it was found that (a) the yellow
and green regionsof the spectrum were always bleached
out and (b) that if the plate had been fogged by a
previous exposure, the blue region was also bleached
out.   On the other hand an unexposed/gave a building
plate
up effect in this region. When a mercury lamp was
used instead of the tungsten it was found again that
the green and yellow lines were always bleached out
but that the blue lines showed whether a pre-exposure
had been given or not. This was attributed to an
intensity factor.

The speed of the plates in comparison with
silver bromide plates was very slow but increases
in plate speeds could be effected by use of 'bromine
acceptors' and sodium nitrite proved the most suitable.
Methods of introducing the acceptors were first by
dipping but later the solution of the acceptor was
added slowly to the liquid emulsion with vigorous
stirring.

The reversal effects of green and low intensity
blue light secondary exposures on a thallous bromide
plate which had been suitably pre-exposed were
investigated. It was found that the secondary green
exposure always produced reversal of the primary
density/

density and that the extent of the reversal effect
depended on the time of the green light illumination.
When low intensity blue light was used as a secondary
instead of green the curve obtained was of the shape
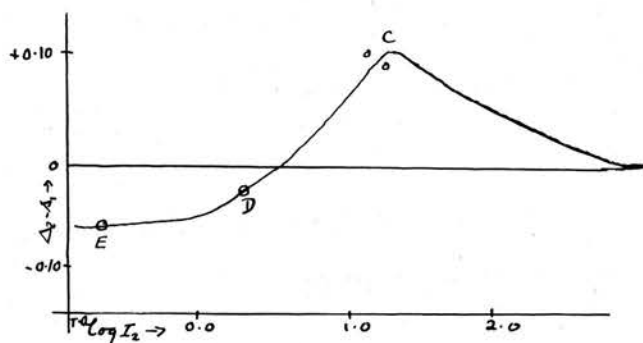shown in Figure 2.

Figure 2.

The density at the point C was confirmed and is
abnormal being greater than the density produced by
the same intensity in a previously unexposed plate.
The points D and E show that there is a reversal in
progress and the reversal was proved to be due to
blue light alone because the maximum green light
which could have passed by the blue filters produced
no effect at all.   Incidentally it was noted that if
the primary density was very high neither green nor
blue light even with long exposures could produce any
reversal and it was concluded that no reversal could
be obtained if the primary density was above a criti-
cal limit.   It was thought that the high intensities
of light which produced these high primary densities,
altered/

altered the grain structure of the thallous bromide.

In experiments on the variation of the bleaching limit (i.e. where reversal just appears) with the primary density the conclusions obtained were: (a) the bleaching limit increases towards higher intensities as the primary density gets greater; (b) No increase in density above the primary density after secondary illumination (hump at C) can occur unless the primary density is below a certain critical value c). The reversal at intensities below the bleaching limit gets less and less depending on the time of illumination and a stationary curve is postulated. Although the presence of added sodium nitrite affected the general speed of a thallous bromide-iodide plate in that there was an increase, the effect of low concentrations of nitrite in the emulsion on the bleaching limit seemed to be negligible. With emulsions containing larger amounts of nitrite the bleaching limit is displaced towards the lower intensity region.

When a thallous bromide emulsion which contained 5% iodide was prepared an increase in plate speed was found in comparison to the plain bromide plates. This was contrary to what Farrer had reported. This variation was attributed to the fact that Farrer had used yellow light when preparing his emulsions whereas J.A.Thom used a very dim red light where there would have been much less possibility of desensitising the emulsion/

emulsion.

The effect of adding nitrite to a thallous bromide plate containing iodide was much greater than the effect of adding the same quantity of nitrite to an iodide-free plate. Iodide-free plates only gave deposits up to $\lambda 4440$ in the spectrograms but deposits up to $\lambda 4530$ could be obtained from plates containing iodide. Reversal could be obtained by both green and low intensity blue light in plates free of iodide, but the rates were much smaller than for iodide-containing plates, this being due to a decrease in image reversal with an accompanying decrease in the rate of latent image formation,

Finally on the question of reciprocity, thallous bromide-iodide plates with or without added sodium nitrite show reciprocity failure of the low intensity type.

The latent image mechanism as visualised by Gurney and Mott is essentially a lattice phenomenon which should be apparent in other suitable crystal systems, where however the replacement of silver and bromine ions will accentuate certain aspects of the processes following light absorption. In recent years more emphasis has come to be laid on the viewpoint that in latent image formation two opposing tendencies/

tendencies are in operation, the normally rapid image
forming process being to some extent retarded by an
image disintegration. Evidence in thallous bromide
systems shows (11) that here even a very low intensity
of blue light will remove rapidly an image which
required some considerable time to produce. Accord-
ingly this aspect has been further examined particu-
larly from the point of view of the relative size of
the latent image, the effect of desensitisers, the
dispersal of an image already formed by pre-illumin-
ation, and the 'photographic' nature of the gelatin
used in the emulsion manufacture.

A report is also given of investigations on
possible latent image formations in lead bromide
antimony oxybromide and bismuth oxybromide-gelatin
systems.

EXPERIMENTAL PROCEDURE.

EXPERIMENTAL PROCEDURE.

Two kinds of gelatin were made use of in
emulsion manufacture, neither of which was of the
same stock or source as used by J.A.Thom in his
experiments.   The first type of gelatin intended
in the first instance for preliminary experiments
only, gave such a 'rapid' thallous bromide plate
that investigation was further continued as described
below.   The second type of gelatin was standard
'photographic' gelatin obtained from Nelson Dale Ltd.

Preparation of the Thallous Bromide Emulsion.

For the most part the procedure adopted here
follows the method advocated by M. Ritchie and J.A.
Thom (11). Changes in the quantities of substances
used were made because of the different properties
of the gelatin employed. The method finally chosen
was as follows.

7 g. gelatin were added to 33 ml. distilled
water in a beaker. The mixture of gelatin and
water was warmed in a small thermostat at 35°C. with
a temperature control of ± 0.1 degree. When the
mixture was homogeneous, a condition reached by use
of a mechanically driven glass stirrer, 1.33 g.
potassium bromide and 0.067 g. potassium iodide were
added, stirred and dissolved in the mixture. In dim
red/

red light 33 ml. of a solution of thallous nitrate
(4 g. per 50 ml. water) were slowly added. The
thallous nitrate solution was almost at saturation
point and it was necessary to leave the solution in a
stoppered bottle in the thermostat until the thallous
nitrate was completely dissolved. The solution was
poured into a burette so that addition could be done
drop by drop. Constant vigorous stirring was used
throughout the addition. The thallous bromide
emulsion was thus prepared in presence of 13% excess
potassium bromide. Stirring of the emulsion was then
continued for a further twenty minutes. After this
the emulsion was allowed to stand in the thermostat
at 35°C. for varying periods of time. In the case
of most emulsions the digestion period was chosen
as one and a half hours, this time appearing to give
the best results as far as the sensitivity of the
emulsion was concerned. At the end of the digestion
time the emulsion was chilled by holding the beaker
under cold running water. The emulsion was then
left overnight in a lightproof box.

The washing process which is necessary to
eliminate excess bromine and potassium ions from the
emulsion, was carried out the next day. The most
satisfactory method of washing the emulsion was found
to be that of squeezing it through muslin which was
boiled in distilled water before use. After
squeezing/

squeezing through the muslin the emulsion is in the
form of threads. The threads were washed by decan-
tation eight times with about 200 ml. of distilled
water to each wash, the threads being gently stirred
during the washing. Each wash was of five minutes'
duration, and it was noted that during the washing
process the gelatin swelled up until finally about
100 ml. of emulsion were obtained. The threads were
drained thoroughly by leaving them on a piece of
muslin stretched taut over the mouth of a beaker.
They were then transferred to special wide-necked
bottle for remelting. The bottle was heated to 35°C.
in the thermostat and the emulsion remelted and
stirred thoroughly. Additions of sensitisers were
made at this stage. Slow additions from a burette
and vigorous stirring were employed again to ensure
thorough mixing. The emulsion was then ready for
coating on to glass plates.

. The glass plates which were used were obtained
by cutting old thin glass spectrographic plates to
the size 13 x 8.3 cm. (i.e. the size of the frame
used). The plates were first left in concentrated
nitric acid until all the old gelatin had been
removed and then left for a few days in a 50:50
mixture of sodium hydroxide and ammonium hydroxide
solutions. Then the plates were scrubbed with
cotton/

cotton wool soaked in the above alkaline solution,
placed in a glass-rod holder and rinsed with tap
water, dilute nitric acid, tap water and finally
distilled water.   The plates were then set up edge-
wise to dry in a clean dust-free cupboard.   This
procedure was adopted because in previous work it was
noticed that when the plates were wet, touching even
the edges of the glass by hand, spread a film of
grease over the glass and made subsequent emulsion
coating difficult.

When the emulsion was to be coated, one of the
clean plates was placed in a printing frame (13 x 8.3
cm.) and the back of the frame adjusted to hold the
plate steady.   The frame was placed on a small glass
table and levelled by screws until a sensitive spirit
level indicated that the frame and the plate it con-
tained were horizontal.   The melted emulsion was
transferred from the bottle to the centre of the
printing frame by means of a glass pipette having a
wide nozzle.   The pipette held about 8 ml. of
emulsion.   The printing frame was tilted so that a
uniform layer of emulsion coated the entire plate.
It was then left in a level position for 10 minutes
covered by a glass sheet to prevent irregularities in
the plate caused by dust.   After this time the
gelatin had set and the back of the printing frame
was/

was removed, the plate taken out and left on glass
rod supports to dry in a small lightproof cupboard.
Dishes of phosphorus pentoxide and calcium chloride
were left in the foot of the cupboard to facilitate
drying which was usually accomplished in four to five
days.   During this time the plates were left un-
disturbed.   After drying the plates were stored in
boxes in a drawer in the darkroom and were cut when
required for exposures.

The plates as prepared above contain 0.0015 g.
thallous bromide per sq. cm., i.e. 0.385 g. thallium
metal per whole plate.   The corresponding figures
given by J.A.Thom were 0.0023 Tl.Br per sq.cm. and
0.59 g. thallium metal per whole plate. Farrer's
plates contained 0.50 g. thallium metal for a whole
plate.

Normal Plate Exposure and Development Procedure.

The thallous bromide plates when dried were
usually cut into small squares 1" x $1\frac{1}{2}$ " which were
used for exposures. The edges of the large plates
were cut off first and rejected because of uneven-
ness.   For exposures, a small 1" x $1\frac{1}{2}$ " square was
held in a plate holder which was placed at right
angles to the source of light. For many of the
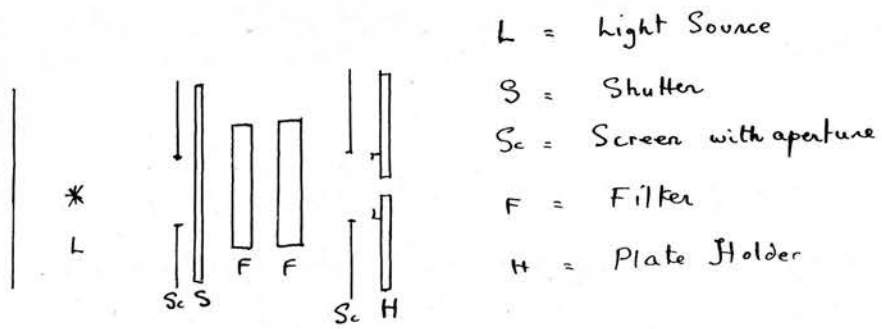exposures a step-wedge was held lightly but firmly
against/

L = Light Source
S = Shutter
Sc = Screen with aperture
F = Filter
H = Plate Holder

Figure 3.

against the plate by means of a spring, a strip of
thin cellophane separating the wedge from the sensi-
tive surface. The source of light used throughout
was a mercury vapour lamp, suitable filters being
inserted for isolating monochromatic light and cutting
down the intensity of the light. The description of the
step-wedge, its calibration, the calibrations of the
blue and green light and the factors for the filters
are dealt with in the next section. When the expos-
ure had been given the lamp was switched off. The
plate was removed from the holder, immersed in 25 ml.
of a 10% aqueous solution of silver nitrate in a
small evaporating basin which was covered with a
black bakelite screen. This operation was done in
darkness but after two minutes in the silver nitrate
solution the red darkroom light was switched on. The
total time of immersion in the silver nitrate solution
was five minutes. Then the plate was rinsed three
times in distilled water by dipping it for a minute
at/

at a time in three small evaporating basins contain-
ing 25 ml. of distilled water.   To prevent silver
nitrate stains on the developed plate the nickel
tongs used for lifting the plate out of the silver
nitrate solution were kept for this operation alone.
A second pair of nickel tongs were used for lifting
the plate into and out of the developer.

After the exchange, final traces of unused
silver nitrate were eliminated in two ways.   In
general the first method was used for small squares
but for larger strips of plate the second method was
found to be the most satisfactory.

The first method was to support the plate after
immersion in the distilled water, inclined at an
angle to a perforated porcelain disc.   The disc was
placed on a glass tripod which rested inside a glass
bowl.   A constant head of water arrangement was
devised so that water continually flowed through the
bowl which was itself enclosed in a lightproof cup-
board.   Thus water flowed over the plate continuously.
The time allowed for this washing was usually 45
minutes which sufficed to remove all unwanted silver
nitrate from the plate without damaging the gelatin
surface.   Any traces of silver nitrate which remained
after too short a washing period became evident
immediately/

immediately the plate was placed in the developer since blackening took place at once.

The second method of processing which is used later was shorter. After the silver nitrate treatment the plate was washed in the usual way with distilled water. A brief period of immersion in running tap water was given, the length of the washing (10-30 min.) depending on the size of the plate. The plate was then taken out and immersed for three minutes in 2% potassium bromide to remove the last traces of un-washed silver nitrate from the plate. After a second short period of washing in running water, given to eliminate potassium bromide traces, the plate was ready for development.

Development.

For all the developers used the temperature of development was kept at $17^{\circ}C. \pm 0.1$. This was done by supporting the developer dish (another small evaporating basin) on a copper stand placed inside a small thermostat. Bottles containing the developer were suspended inside the thermostat so that they were immersed up to the neck. These arrangements ensured that the temperature remained constant during the development. The time allowed for development was usually three minutes but for some developers (see later under experimental results) five minutes was/

was given.

Unless otherwise stated all the plates which were exposed were processed and developed as above. Any variations which were necessary in particular cases are mentioned in the appropriate places.

A list of the developing solutions used is given below.

Normal MQ developer.

Metol	5 g.
Hydroquinone	15 g.
Sodium Sulphite (cryst.)	150 g.
Sodium Carbonate(")	150 g.
Potassium Bromide	2 g.

Distilled water to 2,000 ml.

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

'Surface Developer'

Stock Solution.

Sodium Carbonate (cryst.)	120 g.
Distilled Water	1,000 ml.

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

'Internal Developer'

Metol	1.5 g.
Sodium Sulphite (cryst.)	45 g.
Hydroquinone	6 g.
Sodium Carbonate (cryst.)	75 g.
Potassium Bromide	1 g.
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.

Physical/

Physical Developer (Odell's)

A stock solution was prepared as follows:-

To 50 g. 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 80 g. of sodium thiosulphate was added. The developing solution had the following composition:-

Stock Solution	5 ml.
Distilled Water	25 ml.
2:4 diaminophenol ('amidol')	0.0375 g.

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

Potassium Iodide	5 g.
Sodium thiosulphate	12.5 g.
Distilled Water	500 ml.

The plate was then rinsed and immersed in the above developing solution for 30 minutes at 17°C.

Fixing Solution.

Sodium thiosulphate	500 g.
Potassium metabisulphite	65 g.
Distilled water to	2000 ml.

Calibrations/

Calibrations.

The measurement of Developed Densities

The density of the plate is given by $\log_{10}\dfrac{I_o}{I}$

where I_o is the initial intensity of light and I is the intensity of light transmitted by the plate.

A diagram (Fig. 4) of the arrangement used to measure the densities is given. The light source used in the apparatus was an ordinary 60 watt lamp. The voltage supplied to the lamp was stabilised by means of a Solus stabiliser placed in series with the mains. The galvanometer used was of the moving mirror type, the light spot being reflected back on to a scale. The initial and transmitted light intensities were measured by the deflections of the galvanometer which was connected in series with a photoelectric cell whose position in the apparatus was rigidly fixed. The hole in the bakelite screen was of a suitable size such that for plates in which the wedge had been used each of the various/
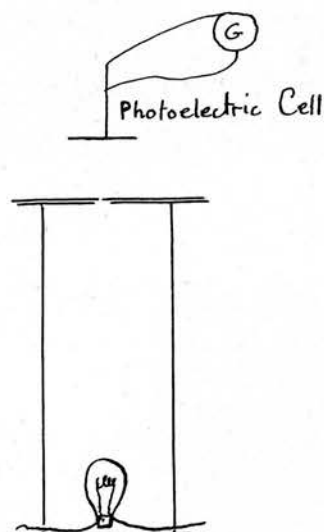
Photoelectric Cell

Figure 4.

various densities caused by the wedge squares could
be measured easily.   The measurements of I_O and I
are in terms of the galvanometer deflections in scale
divisions.

Description and Measurement of Wedge.

The step-wedge used for these plates consisted
of a strip of silver bromide photographic plate
which had been suitably exposed and developed so
that a wedge pattern of eight $\frac{1}{4}$" squares had been
formed. The squares were such that there was a fifty-
fold variation of the light intensity over the
squares. The whole wedge was covered with black
paper with the exception of the eight squares and the
whole of the gelatin side of the wedge was covered
with cellophane. When in use the wedge was placed
cellophane-side towards the emulsion of the plate to
be exposed. The densities of the various wedge
squares were determined simply by measuring the
initial intensity and the intensity of light in scale
divisions transmitted by the various squares. These
figures gave the transmission factors for every wedge
square. The factors for each wedge square were
sensibly the same for red, green and blue light.

The results of the wedge measurements are given
below.

Table 1 /

Table 1.

Area	1	2	3	4	5	6	7	8
$\frac{I_o}{I}$	1.47	2.73	4.33	7.07	12.5	21.2	35.3	70.7
$D = \log_{10} \frac{I_o}{I}$	0.17	0.43	0.63	0.85	1.10	1.33	1.55	1.85

Light Sources and Filters

Blue Light $\lambda 4360$.

A single blue glass was used with a 1 cm. parallel-sided glass cell containing 2% cuprammonium sulphate with a little added ammonium hydroxide.

Green Light $\lambda 5460$.

The filters used for green light are recommended by Bowen (55). 20 ml. of a solution of 1000 g. $CuCl_2 2H_2O$ per litre was added to 80 ml. of a solution of 333 g. anhydrous $CaCl_2$ per litre. A 1 cm. glass filter of this mixed solution was used in conjunction with a 3 cm. glass cell containing neodynium nitrate (100 g. $Nd(NO_3)_2 6H_2O$ per litre). The green Chance glass No. 5 was also used for some experiments.

Transmission Factors for Glass Filters.

The filters used were:-

a) a packet of 5 blue glasses bound together.

b) three neutral filters of factors about 0.5, 0.25, 0.001 (see actual figures in Table 2). In Table 2 these filters are designated $\frac{1}{2}$ Neutral, $\frac{1}{4}$ Neutral, and Dark Neutral.

c) The green Chance glass which was also used to cut down the intensity of blue light since its transmission for $\lambda 4360$ is so small.

In/

In the same way some of the blue filters were used to cut down the intensity of green light.

The measurements of the transmission factors for these filters for blue and green light are given below in Table 2. The factor is given by $\frac{I_o}{I}$ where I_o is the intensity of the monochromatic light and I is the intensity transmitted by the filter.

The measurement of the factors was achieved by fixing a position for the photoelectric cell in the path of the light coming from the lamp, and then assembling different groups of filters in front, with a view to ascertaining the reduction effect caused by each individual filter.

Table 2.

Filter	Factor for Blue Light $\lambda 4360$	Factor for Green Light $\lambda 5460$
Blue Glass Packet	0.096	0.0029
$\frac{1}{4}$ Neutral	0.202	0.280
$\frac{1}{2}$ Neutral	0.404	0.532
Dark Neutral	0.0108	0.116
Green Chance	0.0036	0.220
$CuCl_2 + Nd(NO_3)_2$	0.0036	0.262

Blue Light λ 4360.

The standard arrangement used for the production of blue light was a single blue glass in conjunction with the 1 cm. cell containing cuprammonium sulphate. This arrangement gives the intensity of light given in Table 3 under Blue Light alone. These filters were permanently kept in position when any exposures involving the use of blue light were made. Any reduction in the blue light intensity was achieved by inserting other glass filters as listed in Table 2.

Blue light cut down in intensity by the presence of the $\frac{1}{4}$ Neutral filter gave a direct reading on the galvanometer scale of 37.4; 37.9 scale divisions when the photoelectric cell had been placed in the position usually occupied by the thallous bromide plate. The transmission factor of the $\frac{1}{4}$ Neutral for blue light is 0.202 and thus the light transmitted by the permanent arrangement of blue filters was taken as $\frac{37.4}{0.202}$, $\frac{37.9}{0.202}$ i.e. 185 and 188 scale divisions. An average value 187 scale divisions was used for all other calculations.

Since throughout the experimental work the intensities of blue light used had to be varied for different purposes, Table 3 was drawn up in which the intensity of blue light transmitted by various systems is shown. By using the transmission values for/

for each wedge square the actual number of scale
divisions of blue light passing on to the plate
through the individual squares can be calculated. In
Table 3 the calculated values for the least dense
and the densest wedge squares are shown. In the
experimental results which follow an indication of the
light intensity used is given, but for the purposes
of graph drawing the logarithms of the light inten-
sities in scale divisions transmitted by each of the
wedge squares have been calculated and are shown in
the appropriate places in the graphs.

Table 3 /

Table 3.

Filter System for Blue Light	Intensity in scale div. transmitted.	Range of intensities of light passing through wedge in scale divisions.
Blue light alone	187	127.0 - 2.64
¼ Neutral	37.8	25.7 - 0.50
¼ Neutral + Dark Neutral	0.41	0.28- 0.006
¼ Neutral + ½ Neutral + Dark Neutral	0.16	0.11- 0.002
Dark Neutral	2.02	1.37- 0.029
¼ Neutral + Blue Glass Packet	3.63	2.5 - 0.051
½ Neutral + Dark Neutral	0.82	0.56- 0.012
Dark Neutral + B.G. Packet	0.194	0.13- 0.0027
Blue Glass Packet	18.00	12.2 - 0.25
¼ Neutral + Dark Neutral + B.G. Packet	0.039	0.027-0.00055
¼ Neutral + Dark Neutral + B.G. Packet + Green Chance	0.00014	0.000096-0.000002
¼ Neutral + Dark Neutral + Green Chance	0.0015	0.0010 - 0.000021

Green Light $\lambda 5460$.

The production of monochromatic green light was achieved by first removing the stable arrangement for blue light production and then using either the Green Chance or the copper chloride and neodynium nitrate filters. Both filter systems separately were used as stable arrangements for the production of green light and any reduction in intensity was effected by using the neutral glass filters.

In a similar manner as described above for blue light the galvanometer deflection caused by green light produced by the stable arrangement of copper chloride and neodynium nitrate filters cut down by the $\frac{1}{4}$ Neutral filter was 33.7 scale divisions. Thus, since the transmission factor for the $\frac{1}{4}$ Neutral is 0.280 for green light, the intensity of green light produced by the above arrangement was taken as

$$\frac{33.7}{0.280} = 120 \text{ scale divisions.}$$

In the same way the galvanometer reading caused by the green light produced by the second stable arrangement, i.e. the Green Chance glass in conjunction with the $\frac{1}{4}$ Neutral filter was 19.8 scale divisions. Thus the green light intensity produced by the Green Chance glass is $\frac{19.8}{0.280} = 70.7$ scale divisions.

Again /

Again for convenience the intensities of green light transmitted by various filter combinations are given below in Table 4.

Table 4.

Filter	Green Light produced by $CuCl_2$ + $Nd(NO_3)_2$		Green Light produced by Green Chance	
	Intensity sc.div.	Intensity range through wedge in sc.div.	Intensity sc.div.	Intensity range through wedge in sc.div.
Green Light alone	120	81.6-1.7	70.7	48.1-1.00
+ Green Chance	26.4	17.95-0.37	-	-
+ Dark Neutral	-	-	0.82	0.56-0.012
+ { $\frac{1}{2}$ Neutral $\frac{1}{4}$ Neutral	-	-	10.53	7.17-0.15

Absolute Calibration of Blue Light.

When calibrating the light, use was made of the photochemical decomposition of uranyl oxalate. This was thoroughly investigated by Leighton and Forbes(56). and was used successfully by J.A.Thom (11).

In presence of uranyl sulphate blue light is absorbed by oxalic acid solution which is decomposed according to the equation $(COOH)_2 \longrightarrow CO_2 + CO + H_2O$. Leighton and Forbes found that the quantum efficiency of/

of this reaction at 12°C. is 0.6 for λ4360 A.U.

The oxalate solution used for the calibrations was prepared by dissolving 4.202 g. uranyl sulphate ($UO_2SO_43H_2O$) and 6.24 g. oxalic acid $(COOH)_22H_2O$ in water and making up the solution to 1 litre. The solution is 0.01 M and 0.05 M respectively. Exactly 100 ml. of this solution was measured into a glass cell which had two polished plate glass sides 2 cm. apart. The cell was placed in the light beam so that the front wall of the cell was in the position usually occupied by the thallous bromide plate. A black mask with an aperture of 5.25 sq. cm. was placed immediately in front of the cell, between it and the light source. The cell was illuminated by mono-chromatic blue light produced from the mercury vapour lamp by using the single blue glass and the cuprammon-ium sulphate filter, for a noted length of time and then the lamp was switched off. The contents of the cell were added to 30 ml. of dilute sulphuric acid in a conical flask. The flask was heated to 80°C. and the remaining uranyl sulphate-oxalic acid solution titrated in red light against standardised potassium permanganate. A similar experiment was carried out omitting the illumination and from the difference in results the amount of oxalic acid decomposed by the blue light in a given time is obtained.

The/

The transmission and reflection coefficients of the cell and the uranyl sulphate-oxalic acid solution were determined directly using blue light of an intensity suitable for galvanometer scale deflections.

Readings.

Blue light alone	= 36.3 sc.div.
Blue light + empty dry cell	= 31.4 "
Blue light + cell containing distilled water	= 33.8 "
Blue light + cell containing solution	= 18.0 "

Area of aperture   =   5.25 sq. cm.

Time of illumination =   361 minutes.

Intensity of illumination = 187 sc. div.

Normality of potassium permanganate   = 0.184

Initial titration(without illumination) with 0.184 N $KMnO_4$ = 52.37 ml.

Final titration(with illumination) with 0.184 N $KMnO_4$ = 51.45 ml.

Difference   =   0.92 ml.

Calculation
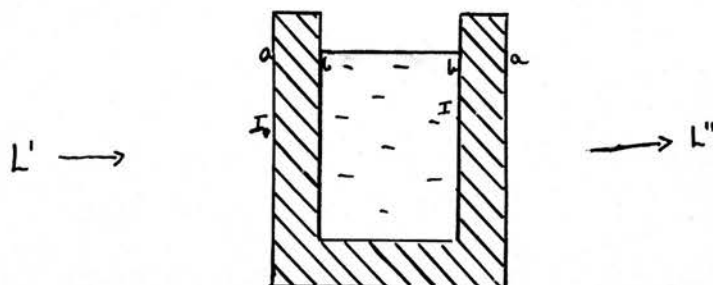
In the diagram

a = transmission coefficient for air-glass surface.
b = transmission coefficient for glass-solution
     surface.
s = transmission coefficient of the solution.
L^1= intensity of incident light.
I_o= intensity of light at front glass-solution
     surface.
I = intensity of light at rear solution-glass
     surface.
L''= final transmitted light intensity.

When the cell is empty and dry a = b. Then neglecting
reflected light, since the light passes through four
air-glass surfaces

$$L'' = L' \times a^4$$

i.e. $a = \sqrt[4]{\dfrac{L''}{L'}} = \sqrt[4]{\dfrac{31.4}{36.3}} = 0.96$

When the cell is filled with water

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

$$ab = \sqrt{\dfrac{L''}{L'}} = \sqrt{\dfrac{33.8}{36.3}} = 0.96$$

$$b = \dfrac{0.96}{0.96} = 1.00.$$

Assuming that the transmission coefficient b is the
same for the cell when it is filled with solution the
intensity of the incident light at the front surface
of the solution is calculated as follows:

$$I_o = 36.3 \times 0.96 \times 1.00 = 34.85$$

The/

The light transmitted by the solution i.e. I

$$= \frac{L''}{ab} = \frac{18}{0.96 \times 1.00} = 18.75$$

Therefore the transmission coefficient s of the solution $= \frac{I}{I_o} = \frac{18.75}{34.85} = 0.538$.

Let L be the intensity of light falling on the front air-glass surface then the amount of light absorbed by the solution taking also into account the reflections from the rear glass-air surface, a, is given by

$$I_{abs} = \{L \times ab - L \, a.b.s\} + L \, a.b.s.(1-a)(1-s)$$

$$= Lab \{1 - s + s(1-a)(1-s)\}$$

This gives after inserting the figures for this calculation

$$I_{abs} = L \times 0.453$$

As given before L = 187 scale divisions

$$I_{abs} = 187 \times 0.453 = 84.71 \text{ sc. div.}$$

Since 1000 ml. N potassium permanganate = 0.5 g. Mol oxalic acid

$$0.92 \text{ ml. } 0.184 \text{ N} \qquad " \qquad = \frac{0.5 \times 0.92 \times 0.184 \times 6.06 \times 10^{23}}{1000}$$

molecules oxalic acid

Since the concentration and the quanta absorbed change only by very small amounts during the time of/

of illumination the quantum efficiency (γ) can be taken

as $\dfrac{\text{The total number of molecules decomposed}}{\text{Total number of quanta absorbed}}$

instead of the usual expression

$$\gamma = \frac{\text{No. of molecules decomposed per sec.}}{\text{No. of quanta absorbed per sec.}}$$

The results of Leighton and Forbes showed that $\gamma = 0.60$

The total number of quanta absorbed per sec. per sq.cm.

$$= \frac{0.92 \times 0.184 \times 0.5 \times 6.06 \times 10^{23}}{1000 \times 0.60 \times 5.25 \times 361 \times 60}$$

The light absorbed was equal to 84.71 scale divisions
and therefore

1 scale division $= \dfrac{0.92 \times 0.184 \times 0.5 \times 6.06 \times 10^{23}}{1000 \times 0.60 \times 5.25 \times 361 \times 60 \times 84.71}$

$$= 8.9 \times 10^{12} \text{ quanta per sq.cm. per sec.}$$

In a confirmatory experiment the final result was

1 scale division $= \dfrac{0.87 \times 0.184 \times 0.5 \times 6.06 \times 10^{23}}{1000 \times 0.60 \times 5.25 \times 361 \times 60 \times 77.8}$

$$= 9.1 \times 10^{12} \text{ quanta per sq.cm. per sec.}$$

Thus 1 scale division deflection produced by blue
light illumination was equivalent to 9.0×10^{12} quanta
of blue light falling per second on 1 square centi-
metre of the plate surface in the predetermined position.

———

Green/

Green Light Calibration λ 5460.

From a previous calibration 6.4×10^{12} quanta (blue light) per sq.cm. per sec. falling on the photoelectric cell registered as 1 scale division on the galvanometer scale. With the cell in the same position 4.1×10^{12} quanta (green light) per sq. cm. per sec. also registered as 1 scale division. The ratio of the sensitivity of the cell for green and for blue was thus taken to be $\frac{4.1}{6.4} = 0.641$.

In the present case 9.0×10^{12} quanta (blue light) per sq. cm. per sec. register as 1 scale division using the same photoelectric cell. Therefore for green light 1 scale division $= 5.8 \times 10^{12}$ quanta per second falling on 1 square centimetre of the plate surface in the predetermined position.

EXPERIMENTAL RESULTS.

General Speed of Thallous Bromide-Iodide Plates

All emulsions used for plate-coating were made by the method as given under Experimental Procedure and contained potassium iodide to the extent of 5% of the potassium bromide present.   This was chosen from the previous work by J.A.Thom in which 5% iodide emulsions appeared to be the fastest.   The only exceptions to this are the emulsions used to determine the effects of the presence of different amounts of potassium iodide.

The majority of the results which follow was obtained from emulsions prepared from the gelatin which gave the fast plate.   This gelatin is called gelatin I and unless otherwise stated all emulsions are prepared with it.   For other purposes such as comparing the gelatin sensitivity, gelatin supplied by Nelson, Dale and Co. was used.   This for convenience is termed Gelatin (standard).   One emulsion was prepared for comparison purposes from the gelatin used by J.A. Thom, but mention of this is made in the appropriate place.

Prints made in the usual way with Ilford Contact Paper, from four typical thallous bromide plates obtained during the experimental work are shown in Plate I.   The numbers on the plates in the print do not refer to the numbered experiments in the text but only/
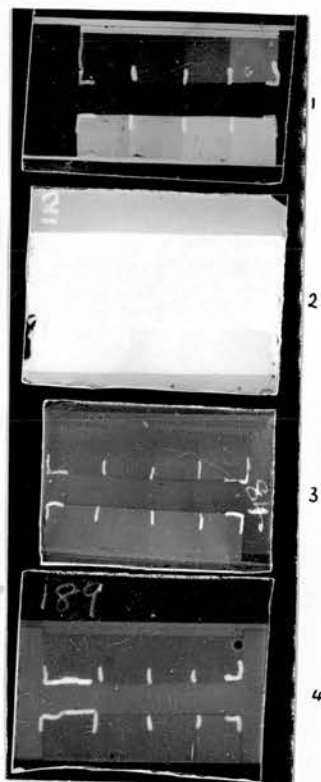
Plate I.

only to the original experimental work. The first small plate 1 shows the effect of exposing a plate for 10 sec. to a blue light intensity of 0.28-0.006 scale divisions. The wedge pattern is very obvious. The second small plate 2 shows the effect of a low intensity blue light secondary exposure on a very high primary density, the wedge squares just being visible. The third plate shows a distinct bleaching limit while the fourth plate shows a building up effect just becoming apparent in the square where the light intensity falling on the plate is the greatest. But even in this square the intensity is not enough to give a forward process of latent image formation. For all these four plates since they are prints from negatives and therefore reversed, the bottom right-hand square of the wedge pattern is the square through which the intensity of light falling on the plate is the greatest.

To obtain a general idea of the speed of a thallous bromide-iodide emulsion containing no added 'bromine' acceptors, plates were exposed to blue light λ4360 of two different intensities: (a) a high intensity of

127/

127-2.64 scale divisions and (b) a low intensity
0.28-0.006 scale divisions. In all cases the plates
(1" x 1½") were exposed with the step-wedge in position
and the plates were processed and developed in the
normal way as described above.

(a) High Intensity Blue Light (127-2.64 scale divisions)

Three thallous bromide-iodide emulsions were pre-
pared. The first emulsion I was given a ripening time
(digestion) of three hours before it was chilled. The
other two emulsions II and III were only given one and
a half hours before chilling. Densities above fog are
recorded in the following tables, such densities being
obtained by subtracting 0.10 from the measured developed
density. This value of 0.10 is that obtained for an
unexposed but developed plate, thus being the density
of the glass plate and gelatin layer. A value similar
to 0.10 was recorded in the unexposed portions of such
plates as were exposed behind the wedge at low incident
light intensities. For exposures at high incident
intensities the unexposed portions of the plate showed
usually a considerably higher 'fog-level'. A typical
figure obtained was 0.90. This high value was regarded
as due to light scattered at the edges of the wedge
sectors. Here also the value 0.10 was subtracted from
the recorded densities in the exposed areas.

In the following tables there are eight columns
in which the densities above fog, produced by each of
the/

the eight wedge sectors are recorded. A ninth column is added for interest in which the actual fog levels obtained in unexposed portions of the plates are recorded.

Table 5.

| Expt.	Time of exposure in mins.	log I	2.11	1.84	1.64	1.42	1.18	0.95	0.72	0.42	Fog Level
Emulsion 1.											
1	5		1.01	0.76	0.47	0.31	0.12	0.04	-	-	0.14
2	15		1.85	1.29	1.07	0.88	0.37	0.37	0.35	0.35	0.64
3	30		0.54	0.37	0.17	0.05	0.02	0.02	0.00	-	0.14
4	45		0.14	0.10	-	-	-	-	-	-	0.27
Emulsion II.											
5	5		0.11	0.07	0.05	0.04	0.00	-	-	-	0.18
6	15		0.21	0.13	0.10	0.07	0.04	0.03	0.02	0.00	0.15
7	30		0.29	0.17	0.13	0.09	0.10	0.07	0.04	0.03	0.11
8	45		0.46	0.30	0.22	0.16	0.09	0.05	0.02	-	0.13
Emulsion III.											
9	5		1.64	1.44	1.28	1.23	1.10	0.99	0.88	0.85	0.73
10	15		2.18	2.01	1.88	1.79	1.61	1.44	1.28	1.21	0.92
11	30		2.20	2.02	1.80	1.72	1.63	1.50	1.40	1.35	0.90
12	45		1.88	1.88	1.88	1.84	1.79	1.44	1.34	1.12	1.02

Fig. 5/

Emulsion I
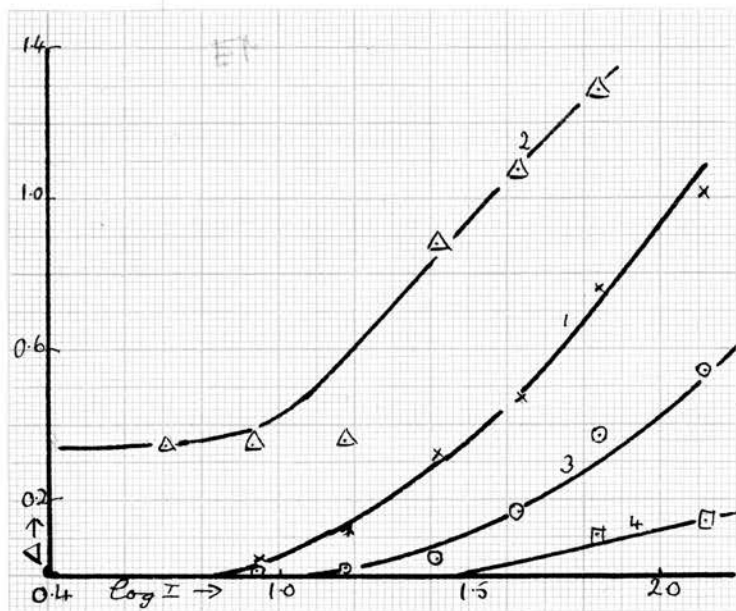
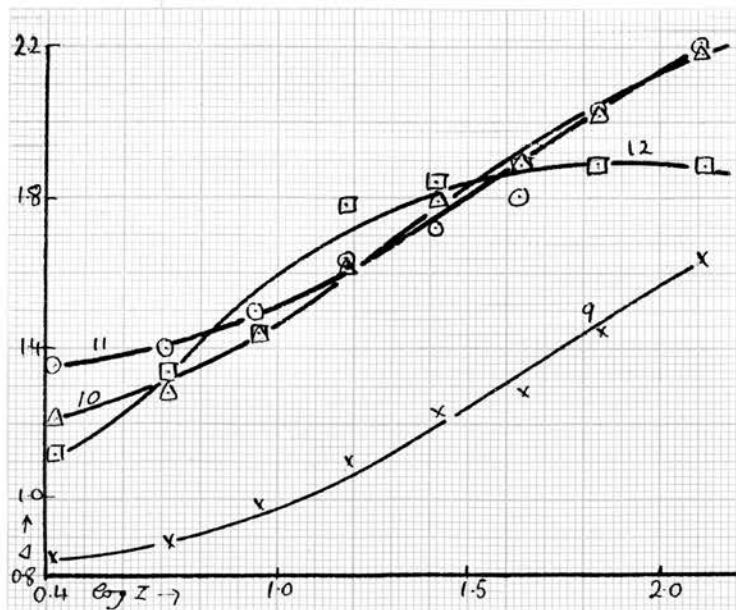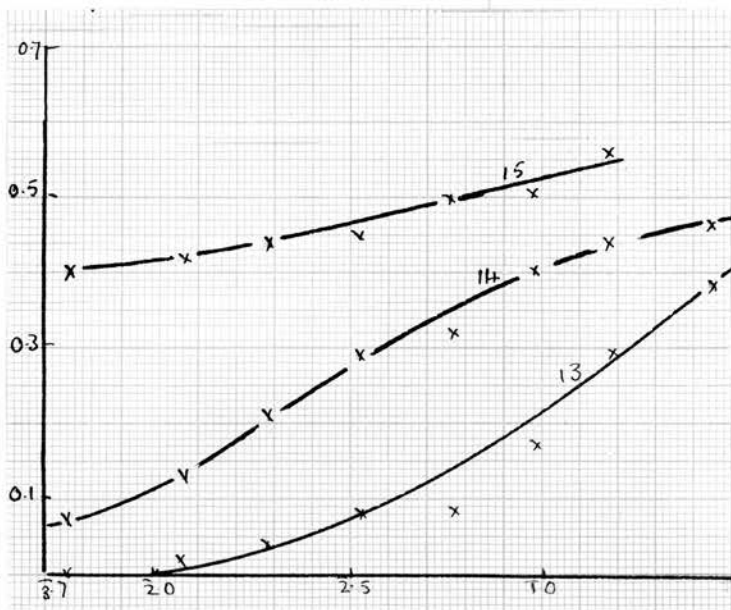Fig. 5.

Emulsion II
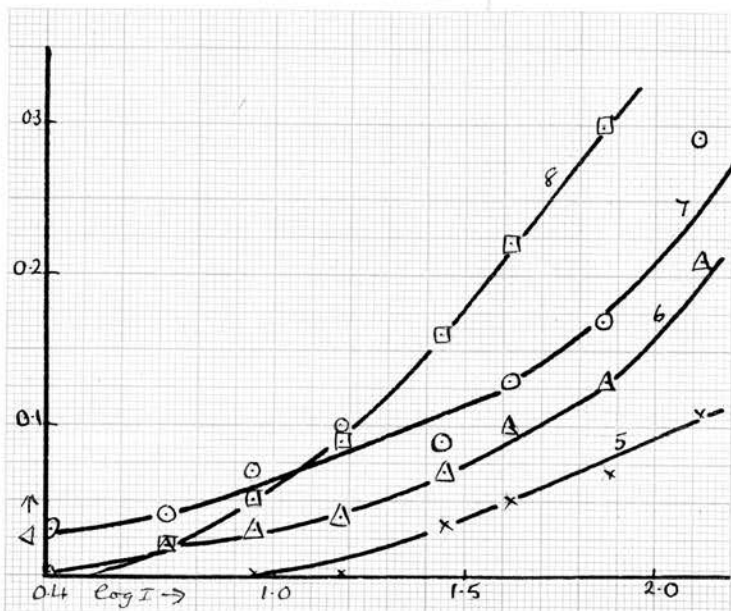
Fig. 6.

Emulsion III

Fig. 7.

Fig. 8.

In the graphs, figures 5,6,7, density above fog
is plotted against log I, the log of the intensity
falling on each wedge square. From the graphs it is
seen that there must be an effect similar to solaris-
ation present in plates from Emulsion I because in-
creasing the exposure time decreases the density. It
is obvious that increased time of digestion (emulsion
I) favours this effect. Emulsion II and III show the
normal H and D curves but in III the density produced
by the light has reached a maximum.

(b) Low Intensity Blue Light (0.28-0.006 scale divisions)

In view of the results obtained in Table 5, it
was decided to cut down the intensity of the light
used by a considerable amount. The emulsion used to
coat the plates for these experiments was given a
digestion time of one and a half hours as Emulsions II
and III. The results of exposures are shown in Table
6 and Fig. 8.

The speed of these thallous bromide-iodide plates
is quite surprising in view of the previous work. A
very small supply of the gelatin used by J.A.Thom was
available and one plain thallous bromide-iodide emul-
sion was made using this gelatin. Directions for the
preparation of this emulsion were found (11) and
followed so that the emulsion would be comparable to
the previous slow emulsions. Plates coated with this
emulsion and exposed to the intensity range 0.28-0.006
scale divisions blue light showed on development no
density/

density whatsoever.

Table 6.

Expt.	Exposure time in sec.	log I	$\bar{1}.45$	$\bar{1}.18$	$\bar{2}.97$	$\bar{2}.76$	$\bar{2}.52$	$\bar{2}.28$	$\bar{2}.06$	$\bar{3}.76$	Fog Level
13	3		0.38	0.29	0.17	0.08	0.08	0.04	0.02	0.00	0.11
14	10		0.46	0.44	0.40	0.32	0.29	0.21	0.13	0.07	0.08
15	15 min.		-	0.56	0.51	0.50	0.45	0.45	0.42	0.40	0.21

It was only when the high intensity (127-2.64 scale divisions) was used that an appreciable developed density was obtained (see Table 7).

Table 7.

Expt.	Exposure Time	Intensity range of exposure in sc. div.	log I	$\bar{1}.45$	$\bar{1}.18$	$\bar{2}.97$	$\bar{2}.76$	$\bar{2}.53$	$\bar{2}.28$	$\bar{2}.06$	$\bar{3}.76$	Fog level
16	2 sec.	0.28-0.006		-	-	-	-	-	-	-	-	-
17	10 min.	0.28-0.006		-	-	-	-	-	-	-	-	-
		127-2.64	log I	2.11	1.84	1.64	1.42	1.18	0.95	0.75	0.42	
18	10 min.	127-2.64		0.19	0.15	0.13	0.10	0.08	0.06	0.04	0.04	0.09
19	30 min.	127-2.64		0.31	0.26	0.22	-	0.18	0.14	0.12	0.10	0.15

These results are in agreement with those of J.A.Thom and the plates were of the same order of speed. The results of Expts. 18 and 19 are shown in Fig. 9.
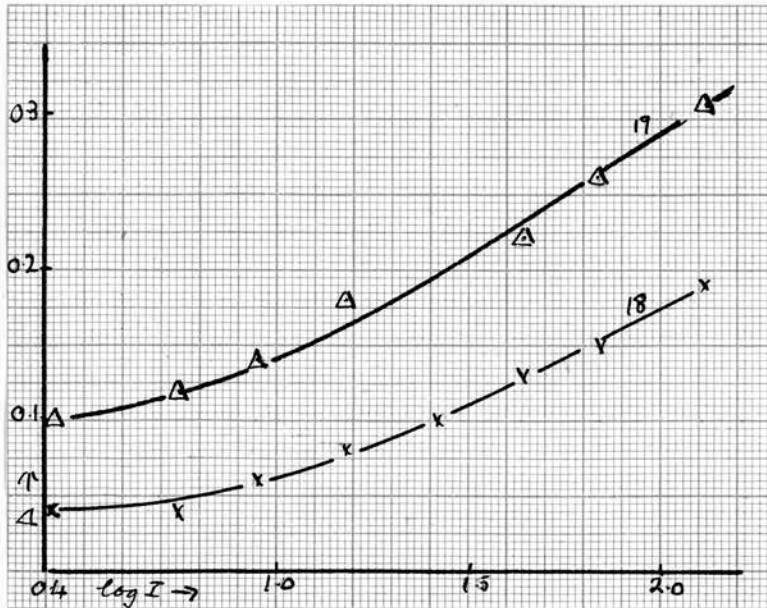
Fig. 9.

From these results it was obvious that the plates
prepared in the present work were of a very much higher
order of sensitivity than those prepared by apparently
similar methods by J.A.Thom. Such a difference could
possibly be due to the fact that a different gelatin
was employed although Farrer found that thallous bromide
emulsions prepared from 'fast' and 'slow' photographic
gelatins differed in speed by relatively small amounts.
On the other hand it was possible that such an increase
in speed was due to accidental contamination with the
silver nitrate used in the processing since the washing
of the emulsion was carried out on the same wooden
bench/

bench. It is known that thallous salt additions to
silver bromide emulsions in small amounts increase the
speed of the silver bromide plates prepared from such
emulsions (50). No data was available on the reverse
addition of silver to thallous bromide emulsions.
Accordingly the present 'fast' emulsions prepared with
gelatin I were tested for the presence of silver. The
effect of adding silver nitrate to the emulsions was
also investigated.

Tests for Silver.

The reagent used for silver detection was p-di-
methylaminobenzylidene rhodanine (57) which easily
detects 5 micrograms (Υ) of silver in 0.2 N nitric acid
in the total volume of solution as given below in the
test. The order of addition of solutions for the test
and the total volume of solution were always kept
constant during tests. The order of addition using a
standard drop arrangement is: 1 drop test solution, 1
drop 10% potassium cyanide, 5-10 drops reagent (5%
solution in methyl alcohol), 2-3 drops 0.2 N nitric acid.
The reagent was tested for possible interference effects
and it was found that the red complex produced from
5^{Υ} Ag was easily detected even in presence of large
quantities of thallium salts. The absence of silver
in the substances used for the emulsion manufacture
was confirmed. Tests on gelatin and liquid emulsions
were also done, the material being first heated gently
with/

with conc. nitric acid and perhydrol in a crucible,
and the colourless residue being taken up in 1 drop
water and 1 drop of cyanide solution. 1 Ml. portions
of several emulsions were tested at different stages in
their manufacture but no evidence of the red silver
complex was seen. Even when 5 ml. portions of emulsion,
to increase the amount of possible silver, were used
for the tests, nothing was detected.

The Effect of Adding Silver to a Thallous Bromide Emulsion.

Since no information is available as to the presence
of very small quantities of silver, the effect of adding
silver deliberately to the emulsion was investigated.
5 Ml. of a silver nitrate solution containing 20 γ
silver per ml. was added to 20 ml. of the plain thallous
bromide-iodide emulsion. The addition was accomplished
slowly, in red light, with constant stirring. Two
plates were coated and left to dry. Two other small
squares of a plain thallous bromide-iodide emulsion
were dipped one in silver nitrate solution containing
20 γ silver per ml. and the other in a similar solution
containing 1000 γ silver per ml. These also were left
to dry. These plates were exposed to blue light with
the step-wedge in position, the times of exposure and
intensity of light used are given in Table 8.

Table 8 /

Table 8.   Intensity = 0.28-0.006 sc. div.

Expt.	Silver content	Time of exp. sec.	log I	$\bar{1}.45$	$\bar{1}.18$	$\bar{2}.97$	$\bar{2}.76$	$\bar{2}.52$	$\bar{2}.28$	$\bar{2}.06$	$\bar{3}.76$	Fog level
20	5 γ	3		0.30	0.21	0.13	0.07	0.02	0.00	–	0.00	0.09
21	20 γ	3		0.34	0.28	0.21	0.14	0.06	0.02	0.00	0.00	0.09
22	1000 γ	3		0.42	0.36	0.30	0.20	0.10	0.02	0.02	0.03	0.15
13	–	3		0.38	0.29	0.17	0.08	0.08	0.04	0.02	0.00	0.11

The last experiment was included as a comparison and a plain thallous bromide-iodide plate was used.   The results shown in Table 8 are plotted in Fig. 10.
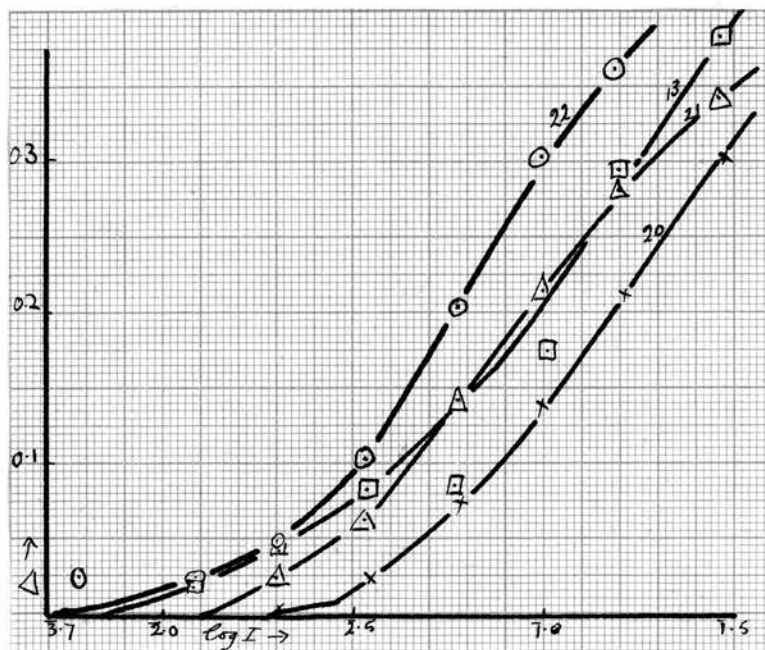
Fig. 10.

From the graph it is seen that the effect of adding
silver salts to the thallous bromide emulsion is very
small. It was therefore concluded in view of the
similarity of all other processes that the difference
in speed as compared with previous emulsions is due to
the gelatin used. It is also to be noted that in such
a fast emulsion long exposures at high intensities
tend to produce decreased densities as recorded in
Fig. 5 and Table 5.

In connection with the property of Gelatin I
which is thought to cause the additional speed in the
thallous bromide-iodide plates, tests were carried out
to assess in a general way the lack of restrainers
present in the gelatin. The test used has been
mentioned before (48) and was found and reported by
A. Steigmann.

When a gelatin rich in restrainers is used for
preparation of a silver halide emulsion, the growth of
the silver halide crystals and sensitising silver and
silver sulphide specks is curtailed. Absence of
restrainers favours the rapid formation of larger
nuclei. The new test shows the effect of various con-
tents of restraining substances (occurring naturally or
artificially added) contained in different gelatins on
the growth of silver sulphide nuclei in a boiling
system:- gelatin dissolved in water - ammoniacal silver
nitrate/

nitrate - ammonium sulphite.

The excess of sulphur dioxide and ammonia is
added to the gelatin so that reducing ammonium sulphite
is formed in presence of excess ammonia. The addition
of sulphur dioxide also brings the sulphur dioxide
content present in the tests to a comparable level.
The reduction of ammoniacal silver nitrate by the
ammonium sulphite at 90-100°C. is strongly inhibited
by many natural and synthetic restrainers. But ammon-
ium sulphite alone at low concentrations is not a reduc-
ing agent for ammoniacal silver nitrate in totally
inert gelatin. The presence of a catalyst is necessary.
This catalyst is the silver sulphide nuclei formed by
the sulphur containing bodies in the gelatin (sensi-
tisers).

The test is carried out as follows, the reagents
being added in the following sequence and well mixed:-
0.50 g. gelatin dissolved in 5 ml. water at 60°C.;
1 ml. of dilute sulphur dioxide solution (10 ml. of
3-4% sulphur dioxide + 90 ml. water); 1 ml. of 0.1 N
silver nitrate; 0.5 ml. of dilute ammonia (25 ml.
ammonia of specific gravity 0.88 + 75 ml. water).

To carry out the test the test tubes containing
the above solutions and one prepared with standard
gelatin were immersed in boiling water and the darken-
ing in the test tubes due to the formation of
colloidal/

colloidal silver, was noted every three minutes during
24-30 minutes. The more rapid the darkening, the less
restrained is the gelatin and vice versa.

In the present tests the gelatin solution made
from Gelatin I and, as a comparison, another gelatin
solution prepared from gelatin supplied by Nelson,
Dale and Co., were subjected to the test simultaneous-
ly. The darkening of the two tubes was compared at 3
minute intervals.

    After 3 min. both gelatins were slightly yellow.
      "   6 min. Gelatin I was turning orange, the
               standard was still yellow.
      "   7 min. Gelatin I was definitely orange, the
               standard yellow.
      "   9 min. Gelatin I was turning brown, the stan-
               dard orange.
      "   20 min. both gelatins were brown.

The darkening of gelatin I was very rapid as compared
with the standard gelatin. It would appear that
Gelatin I was a fairly unrestrained gelatin. Another
test was done in which the Gelatin I solution was
first treated wit h hydrogen peroxide which is known
to destroy the sensitising substances, and then sub-
jected to the test. The time of darkening was very
much increased, no change being seen even after 20
minutes.

A thallous bromide-iodide emulsion prepared from
the gelatin supplied by Nelson Dale and Co. gave a
plate speed of the same order as those obtained from
plates made with the old gelatin used by J.A.Thom.
The/

The Effect of 'Bromine Acceptors'

In previous work the effects of sodium nitrite and to a smaller extent sodium arsenite as bromine acceptors were investigated. The next section deals with first the effects of added sodium nitrite and secondly of added sodium arsenite on the 'fast' emulsion. In all the following experiments the density above fog produced by the incident light is shown by a point on the graph for each of the eight wedge squares. No further tables of densities are included. An indication of the ranges of intensity used, the times of exposure and any other particular information will be given. The graphs, unless otherwise stated, are plotted with abscissa log I and ordinate 'Density above fog', $\triangle$, the fog being of the order of density 0.10.

The effect of Sodium Nitrite.

Preliminary experiments were done to find the effects of comparatively large quantities of sodium nitrite on thallous bromide-iodide plate speeds. The quantities used were 0.25 and 0.50 g. sodium nitrite per 100 ml. emulsion. Even the smaller of these two quantities increased the speed of the plate. The plate containing the larger quantity of sodium nitrite showed a distinct print-out effect before immersion in the silver nitrate. In both cases it is seen that large quantities of nitrite do have an increasing effect/

effect on the plate speed.

To investigate the effects of small quantities
of sodium nitrite, 10 ml. of a 0.10% sodium nitrite
solution were added slowly, with stirring, to 100 ml.
of finished thallous bromide-iodide emulsion. Several
plates were coated and left to dry. This quantity of
nitrite was the same as used by J.A. Thom to assess
the effects of nitrite on the slow emulsions.

The intensity of blue light used throughout these
experiments was 0.28-0.006 scale divisions, and the
plates were exposed for various times (see Table 9)
behind the step-wedge. The results of increasing the
exposure times are plotted in Fig. 11.   From Fig. 11
it is possible to work out the reciprocity relationship.
It is seen from the graph that the process of latent
image formation is relatively very efficient and it
was therefore thought that the reciprocity law would
be obeyed. From Fig. 11 the intensities required to
give a chosen density can be read off. The densities
chosen were 0.3, 0.35, 0.45, 0.55. The time required
to produce these densities at the particular intensity
is also given in Table 9. For the reciprocity curve
log I (Intensity needed to produce the chosen density)
is plotted against log I.t. The results are seen in
Fig. 12. Each line represents the reciprocity relation
existing at each chosen density. From the graphs it
is evident that low intensity reciprocity failure
exists/

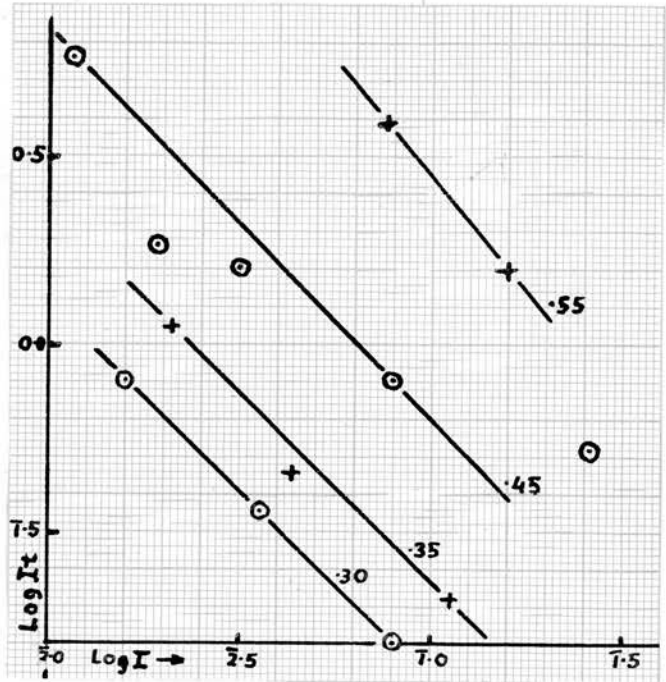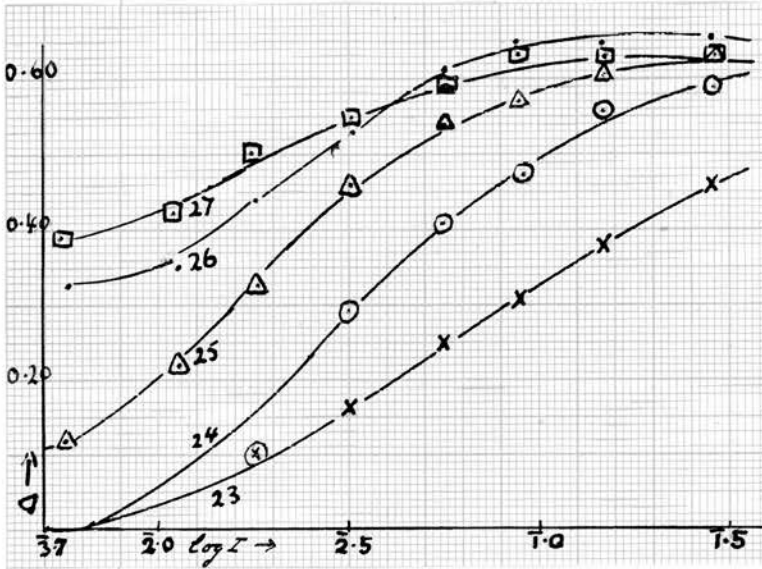exists, agreeing with previous work done (11) by

J. A. Thom,

Fig. 11.

Fig. 12.

Table 9.

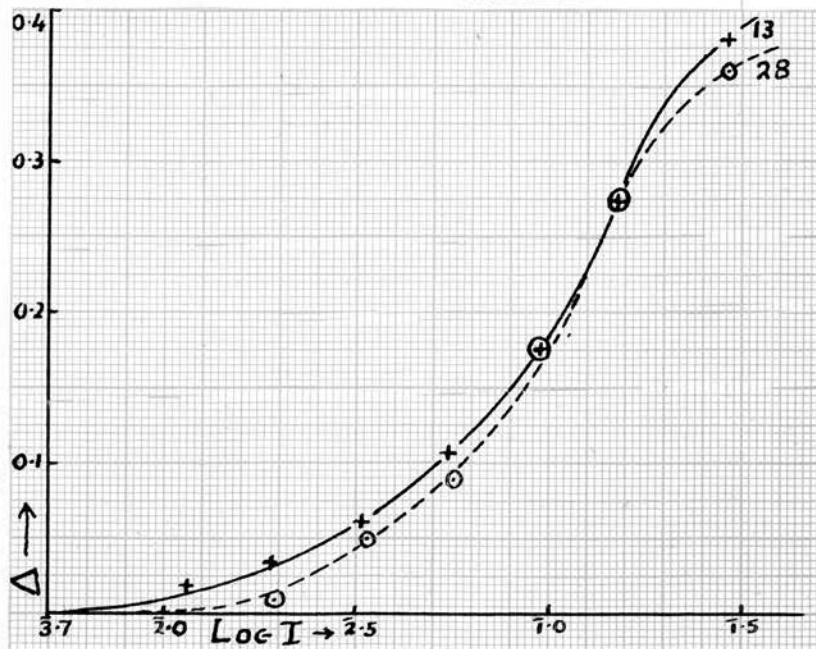| Expt.	Time of exposure.
23	2 sec.
24	10 "
25	50 "
26	88 "
27	250 "

Fig. 13.

The gelatin used is such as to produce a relatively fast plate in which the forward process of latent image production is relatively predominant. In the slow emulsions prepared by J.A.Thom the small quantity of sodium nitrite (10 ml. 0.10% $NaNO_2$ per 100 ml. emulsion) produced an appreciable increase in speed. In the present instance therefore the same amount of sodium nitrite might be expected to show little increase in speed. This was confirmed in the results which are shown in Fig. 13. Experiment 13 is done with a plain thallous bromide-iodide plate, experiment 28 is done with a plate containing nitrite in the quantities stated above. Both plates were given a three second exposure to a blue light intensity of 0.28-0.006 scale divisions with the step-wedge in position. Every effort was made to keep the conditions of processing the same for both plates.

The Effect of Sodium Arsenite.

In silver bromide emulsions sodium arsenite is known to act as a fogging agent. This was first shown by Perley (58). Clark (44) showed that the action of sodium arsenite on an unexposed silver bromide plate was identical to that of light and also that the fog did not appear as the result of chemical interaction of the arsenite with silver bromide.

Preliminary/

Preliminary work was done by J.A.Thom on the effect of sodium arsenite on thallous bromide-iodide plates which already contained a small amount of sodium nitrite, and an increase in the speed of the plates was found.

This work was continued using thallous bromide-iodide plates prepared with the 'fast' Gelatin I. All arsenite additions were made as slowly as possible to the finished emulsions.

Preliminary Investigation

The first question was to find if the sodium arsenite affected the thallous bromide-iodide plate or if the effects on the plate speed were due to the action of the sodium arsenite on the silver bromide after the exchange had been carried out. Two plain thallous bromide-iodide plates were given the same exposure to the same blue light intensity with the step-wedge in position. Both plates were processed in as similar a manner as possible up to the end of the 45 min. wash in tap water. One plate was immersed in 0.02% sodium arsenite and the other in water for 3 minutes. Both plates were given a 5 min. wash in running tap water and developed. Very little differ-ence was found in the developed densities and it was concluded that any effects which might be found would be due to the action of the sodium arsenite when the thallous bromide-iodide plates were being exposed.

For/

For preliminary work on the effect of sodium arsenite, amounts, equivalent to 0.25 and 0.50 g. sodium nitrite per 100 ml. emulsion, of sodium arsenite were added to two portions of a plain thallous bromide-iodide emulsion. The third portion was left with no additions. Plates were coated with these emulsions and left to dry for 4-5 days. It was noted that in the case of the emulsion containing the largest amount of arsenite the plates were tacky and difficult to dry.

Exposures of 15 min. to a blue light intensity of 127-2.64 scale divisions were given to small squares from these plates. On development after processing it was apparent that the plate containing the smaller quantity of arsenite had a considerably darker developed density than the plain thallous bromide-iodide plate. The plate containing the larger amount of arsenite showed the wedge pattern before the immersion in the silver nitrate but during processing the emulsion floated off the glass. Attempts were made with no avail to use chrome alum hardener to prevent this.

These preliminary results thus confirm the conclusion that in certain circumstances arsenite has a pronounced acceptor action. This, however, did not appear to hold for all conditions.

Three emulsions were prepared which contained relatively small quantities of sodium arsenite.

The first was made in the usual way with a

ripening/

ripening period of three hours.   The emulsion after
washing was divided into four portions.   The first
portion was left untreated but a 0.02% aqueous sodium
arsenite solution was added at the rate of 7.2, 14.4,
21.6 ml. per 100 ml. emulsion to the 2nd, 3rd and 4th
portions respectively, with the usual precautions.
Plates were coated with these four portions and left
to dry.   The plates when dry were exposed to a blue
light intensity range of 127-2.64 scale divisions.
The results of the exposures are given in Figs. 14-17,
on which the times of exposure given are stated and
increasing arsenite content of the plate is indicated
as i (7.2 ml.), ii (14.4 ml.), iii (21.6 ml.).   The
plain thallous bromide-iodide emulsion was abnormal
in that increasing times of exposure to a constant
blue light intensity did not produce increased den-
sities.   This is shown in Figs. 14, 15, 16 and 17,
where an effect resembling solarisation in silver
bromide plates is apparent at higher exposures.

When a short exposure was given (5 min.) to each
of the four emulsions, it is observed that the plain
emulsion is affected most (as measured by developed
density) and the emulsion containing the smallest
amount of arsenite, least.   As the arsenite quantity
increases, so the density measured increases (Fig.14).
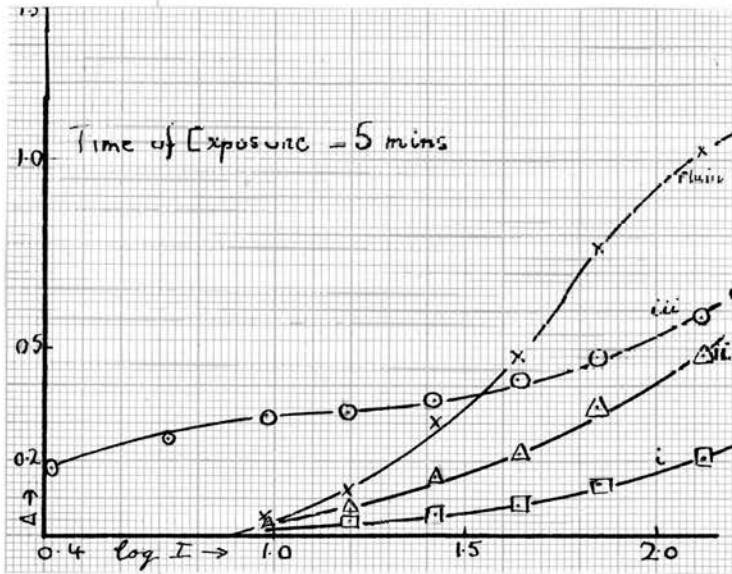
With a 15 min. exposure (Fig. 15) the effects
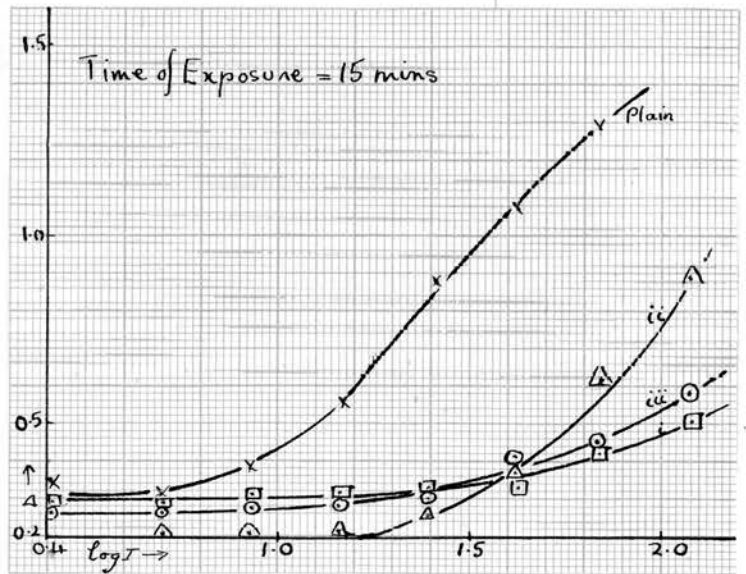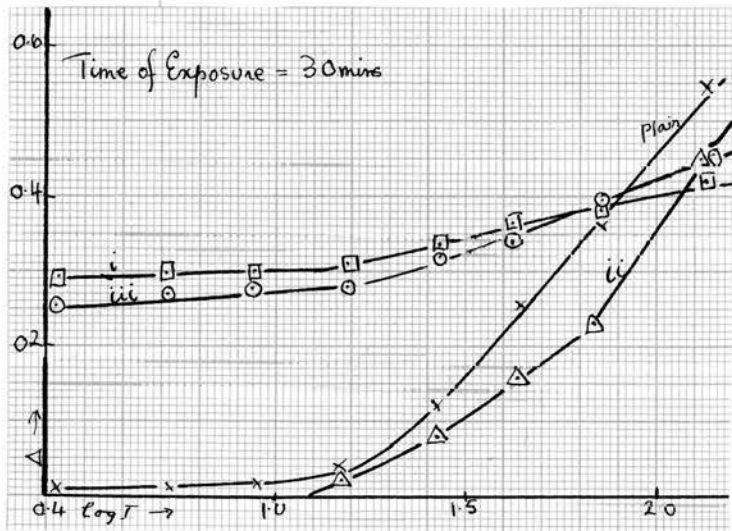produced/
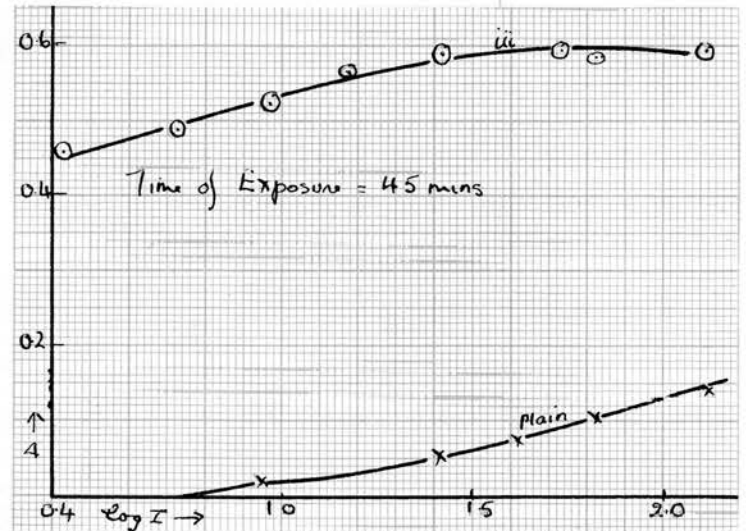
Fig. 14.

Fig. 15.

Fig. 16.

Fig. 17.

produced at low intensities on the four emulsions are very similar, the plain emulsion if anything having the greater density. At higher intensities, however, curve iii tends to occupy a position intermediate between curves i and ii, the plain emulsion still having the greater densities. If anything curve iii is less than curve ii at the highest intensities.

The effects of a 30 min. exposure (Fig. 16) at higher intensities is much the same as that of the 15 min. exposure with the exception that the curve for the plain emulsion is showing the solarisation-like effect. At lower intensities curve iii occupies a higher position than curve ii or the curve for the plain emulsion.

At 45 min. (Fig. 17) exposures the curve for the plain emulsion is everywhere less than that for the highest arsenite content. With the exception of the 15 min. exposure the intensity at which the curve for the highest arsenite content intersects or passes above that of the plain emulsion increases with increasing time of exposure.

The experiments were repeated using the same range of blue light intensity and the same times of exposure with plates coated with an emulsion for which the time of ripening was cut down to one and a half hours. It would now be expected that the size of/

of the grain and the number of latent image centres
would be reduced and the effect resembling solarisation
would be less in evidence. That this is so, is appar-
ent from the position of the plain emulsion
curves in Figs. 18-21, where increasing exposure times
produce increased densities on the plate coated with
the plain thallous bromide-iodide emulsion. Portions
of the same emulsion were used for the additions
which were made at the rate of 3.6 and 7.2 ml. 0.02%
sodium arsenite per 100 ml. emulsion. The results of
exposing plates coated with these emulsions to
similar conditions of intensity and time as above, are
shown in Figs. 18-21, where i represents the smaller
and ii the larger arsenite content. For a 5 min.
exposure a small amount of arsenite (3.6 ml.) again
reduces the sensitivity initially but further
additions produce increased densities (ii). For
longer exposures 15, 30 and 45 min. (see Figs. 19, 20,
21) the retarding effect of the arsenite is more
evident. With increasing times of exposure the effect
of the arsenite increases, and greater arsenite
additions cause bigger retardation effects. All these
effects are uncomplicated by any obvious reversing
effect like solarisation.

The experiments were repeated with a third
emulsion, the ripening period being again one and a
half hours, but somewhat greater amounts of sodium
arsenite were added, viz. 7.2, 14.4, 21.6 ml. per 100
ml./

ml. emulsion. The plates were dried and exposed
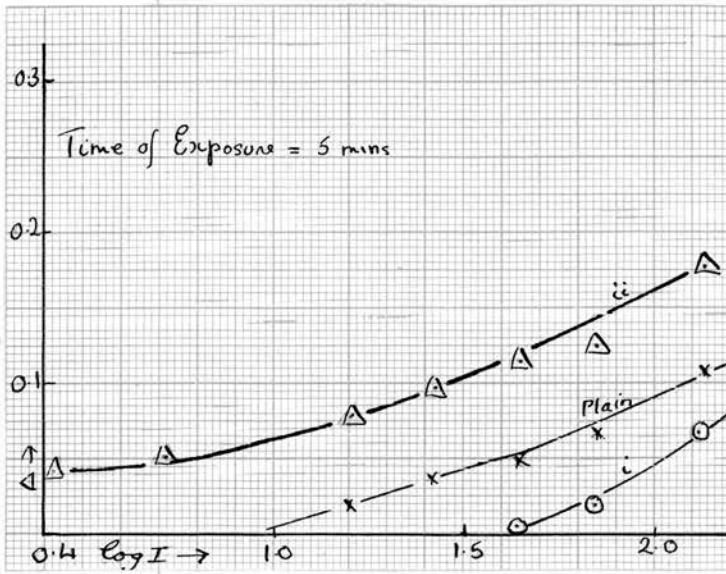under the same intensity conditions as before.
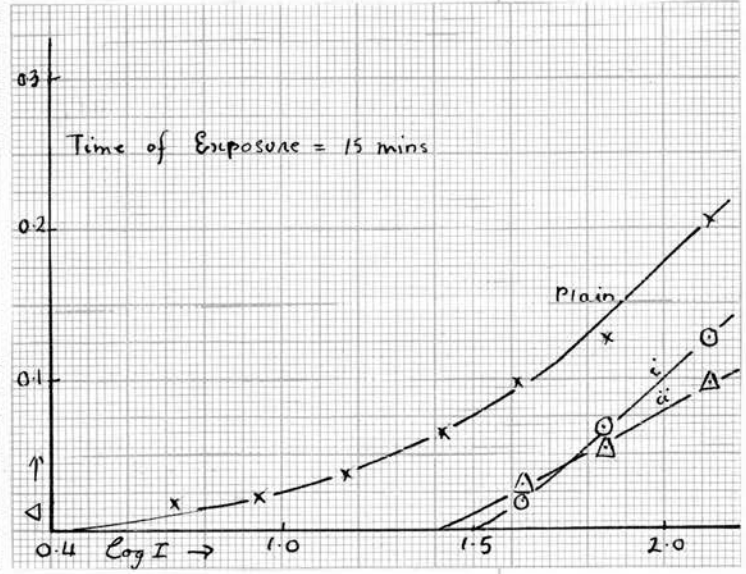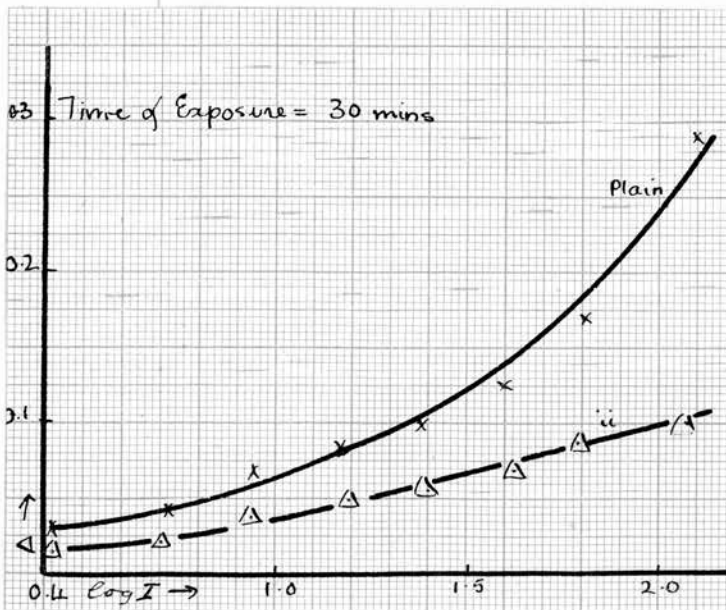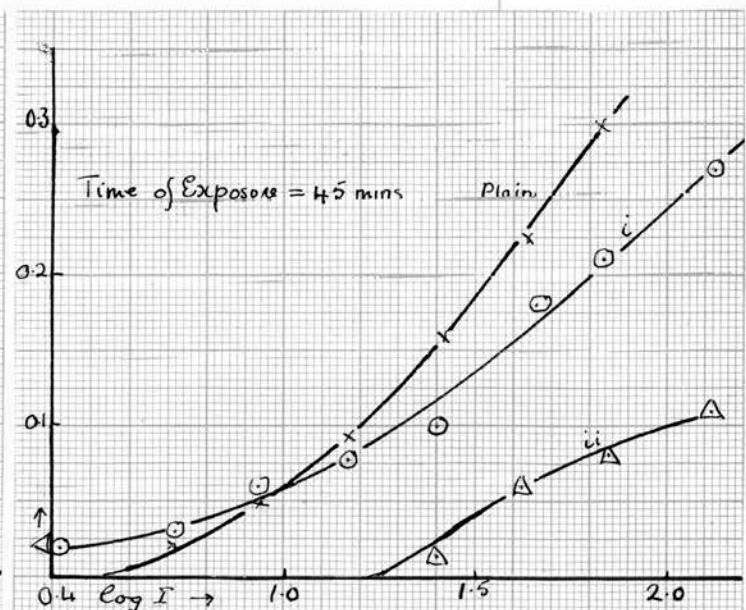

Fig. 18.

Fig. 19.

Fig. 20.

Fig. 21.

In the Figures 22-25 as before increasing quantities
of arsenite present in the plates are designated i<
ii < iii. From the curves obtained from exposing the
plain emulsion it is evident that in this case the
emulsion is intermediate between the first two arsen-
ite containing emulsions as regards the solarisation-
like effect present in the first emulsion. Increasing
exposure times do show increasing densities, but the
15, 30 and 45 min. curves are fairly close together.
Fig. 22 shows the effect of 5 min. exposures and it is
seen that the accelerating effect of relatively large
amounts of arsenite has raised the curve above that
for the plain emulsion. The tendency to reverse the
accelerating action begins t 15 min. exposures (see
Fig. 23) and is complete at 30 min. exposures (Fig.
24). At 45 min. exposures solarisation-like effects
are in evidence for the plain emulsion. The retarding
effects of increasing arsenite is still in evidence
i > ii > iii, but the accelerating effect of arsenite
at the lowest concentrations is sufficient to counter-
act the solarisation effect and produce a curve which
is everywhere above that of the plain emulsion.

the interpretation of these results may be
approached as follows:- The emulsion is a fast one
and therefore it can be regarded as relatively un-
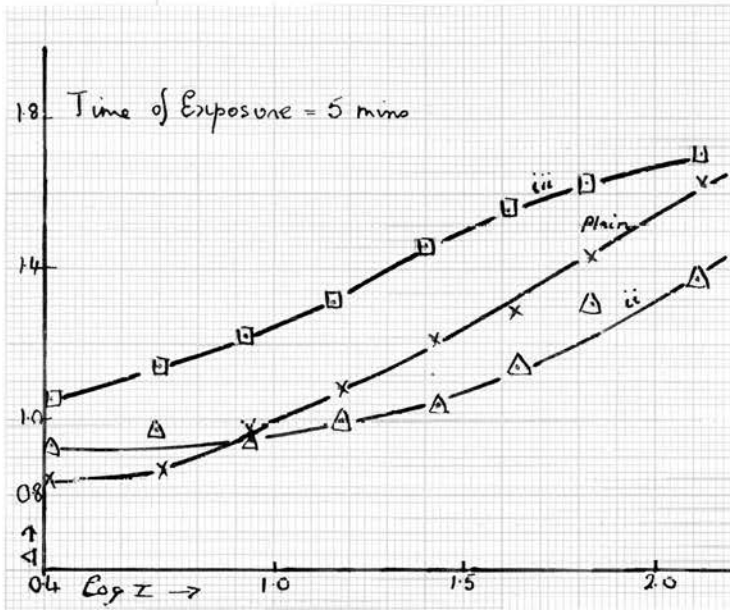restrained as compared with Thom's previous slow
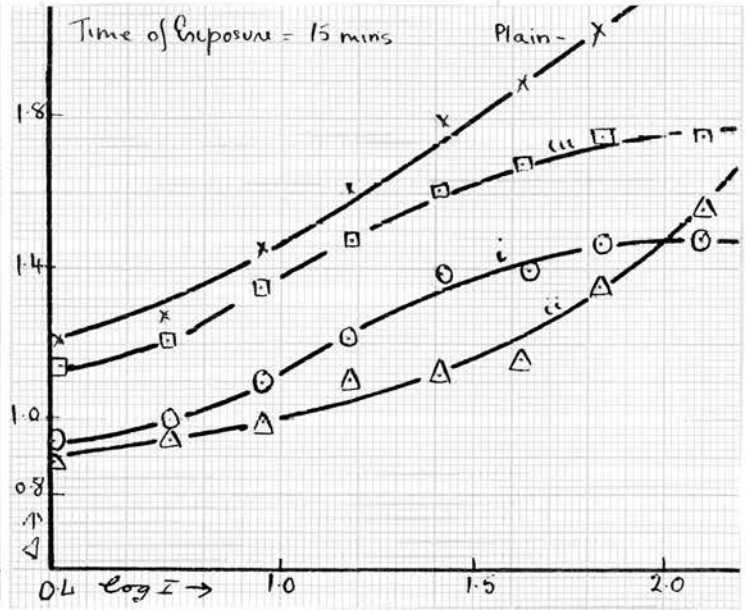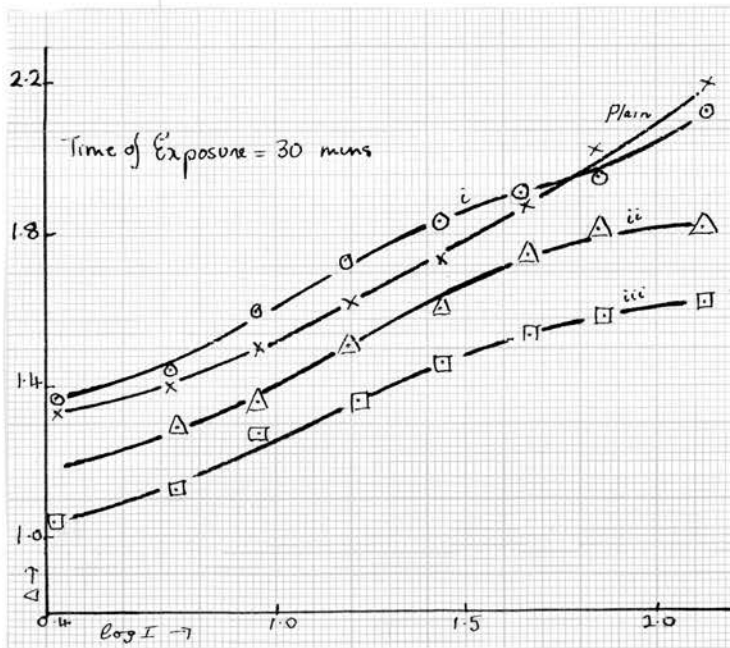emulsions/

Fig. 22.
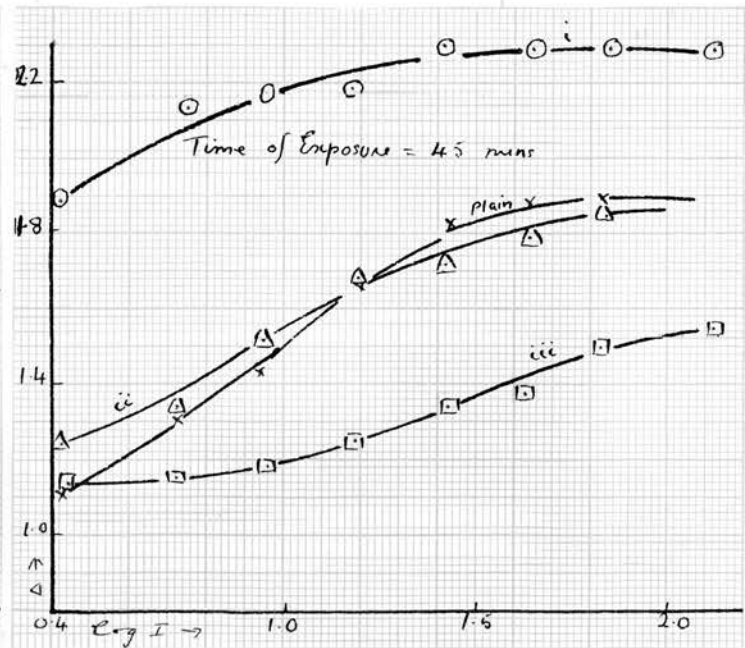

Fig. 23.

Fig. 24.

Fig. 25.

emulsions. The absence of restraining bodies will tend to produce in the three hour period of digestion large crystals and a relatively large number of latent image centres. The curves for the plain emulsion as seen from Figs. 14-17 may therefore be interpreted as due to the inability of the gelatin to remove all the bromine atoms produced by illumination, effects resembling solarisation being then in evidence.

At low exposure times as e.g. Figs. 14, 15, 18, 19, the addition of the smallest amount of arsenite reduces the sensitivity. Since the arsenite was added after the digestion process the size of the grains will not be appreciably affected and it can therefore be concluded that the number of effective latent image centres is thereby reduced. For 5 min. exposures (Fig. 14) the resultant density is on the rising part of the characteristic curve, showing that the gelatin is still able to cope with the bromine atoms produced by illumination. The effect of further additions of arsenite is, however, to increase the sensitivity in conformity with the previous conclusion that arsenite can act also as an acceptor. This acceptor action will be in addition to or in competition with that of the gelatin.

Under conditions in which the gelatin is unable to cope with all the bromine atoms produced as in Fig./

Fig. 17 arsenite may be expected to remove such atoms and produce an increased density. This is more in evidence the greater the degree of 'solarisation'. The accelerating effect of arsenite in this respect will tend to be most evident at high incident intensities and long illumination. Thus in Fig. 17 the arsenite curve is everywhere above that of the plain emulsion. 'Solarisation' is in evidence even at the lowest intensities for the 30 and 45 min. exposures of the plain emulsion (Figs. 16 and 17). In these regions the arsenite iii curve is again above the plain emulsion curve and the longer the exposure the more does this tendency become evident.

There remains for explanation the reversal of the increased accelerating effect of increased amounts of arsenite as apparent in Figs. 20, 21, 24 and 25 for high intensity regions.

At first sight it might appear that this is due to the attack of the arsenite on the latent image in the process of formation as suggested already by the reduction in sensitivity of the emulsion generally. The retardation effect of increasing arsenite content might be viewed as akin to solarisation increasing at high intensities and times of illumination. At low intensities, however, as in Fig. 22, the attack on the latent image is apparently less than the accelerating action/

action for the non-solarisation region where the
gelatin is able to remove most if not all of the
liberated bromine atoms.   This should be relatively
still more evident in the region where the gelatin is
unable to do so. Alternatively, it is suggested that
the presence of the arsenite reduces the gelatin's
capacity for such bromine atom removal. When the
bromine atom concentration is small at low intensities
the gelatin even in its reduced state may be able to
remove all the bromine atoms formed and the acceptor
action of the arsenite is in evidence; at higher
intensities the reduced capacity of the gelatin
counterbalances the arsenite acceptor action, the
greater the intensity, the greater the apparent
retardation.

In connection with the above results the effect
of sodium arsenite solution on the gelatin was investi-
gated. The restrainer test as before was used again,
the object being to find if the arsenite addition
would slow down or speed up the time of darkening,
i.e. of formation of silver. If the arsenite solution
initially destroyed some of the sensitising sulphur
compounds present in the gelatin, the emulsion
sensitivity might be expected to decrease even though
the arsenite additions were made after the emulsion
had been washed.

The/

The effects of adding sodium arsenite to the
gelatin solution before carrying out the test are
given below. Solutions used for the test were pre-
pared as given above.

To 0.50 g. gelatin I in 5 ml. water 0.50 ml. of
0.02% sodium arsenite solution was added from a pipette.
This amount corresponded to 7.2 ml. arsenite solution
added to 7 g. of gelatin as used in emulsion manu-
facture. A second test tube containing 0.50 g. of
gelatin I in 5 ml. water served as a blank. After the
reagents had been added to both tubes, the tubes were
immersed in boiling water and the rates of darkening
compared. It was found that the tube containing the
arsenite solution darkened much less quickly than the
one containing no arsenite. When half the quantity
of the same arsenite solution was added to a third
gelatin solution and the darkening time again compared
with a blank it was found that both tubes darkened at
practically the same rate as detected visually.

A second experiment was carried out in which 2.5
ml. of the same arsenite solution was added to 0.50 g.
gelatin I in 3 ml. water. The reagents were added and
after immersion in boiling water the rate of darkening
was compared with that of a blank test. It was found
that the arsenite-containing solution this time darken-
ed at a much faster rate than the blank.

These/

These results show that although arsenite in large
quantities reduces the silver salt solution as is
expected, small quantities of arsenite retard the
production of the necessary silver sulphide nuclei
either by destroying the sensitising compounds present
in the gelatin or by attacking the nuclei themselves.

Effect of Variation in Iodide Content.

The gelatin used for making these emulsions was
the photographic gelatin supplied from Nelson Dale
and Co. 2 G. of gelatin were mixed with 16.6 ml.
water in a wide necked bottle. Three such bottles
were prepared. Into each bottle 0.665 g. potassium
bromide was added. To the first bottle no potassium
iodide was added. To the second and third bottles
potassium iodide was added at the rate of 20% and
30% of the bromide present respectively. All three
bottles in turn were stirred and 16.6 ml. of a thall-
ous nitrate solution containing 4 g. per 50 ml. water
was added to each with the usual precautions. The
digestion period given was one and a half hours and
the rest of the emulsion preparation was carried out
as usual, half quantities of water being used in the
washing process. The conditions of manufacture of
the emulsions were thus kept as identical as possible.
The plates prepared from these emulsions when dry were
exposed to a blue light intensity of 0.28-0.006 scale
divisions/

divisions for 1 min. The results are shown in Fig.
26, no densities being recorded for the emulsions
containing the higher percentages of iodide. Three
more emulsions were prepared as above with iodide con-
tent 0%, 3% and 5% of the bromide present and the
results of exposing plates from these emulsions to
the same conditions of exposure are also shown in
Fig. 26. It is evident that there is a steady decrease
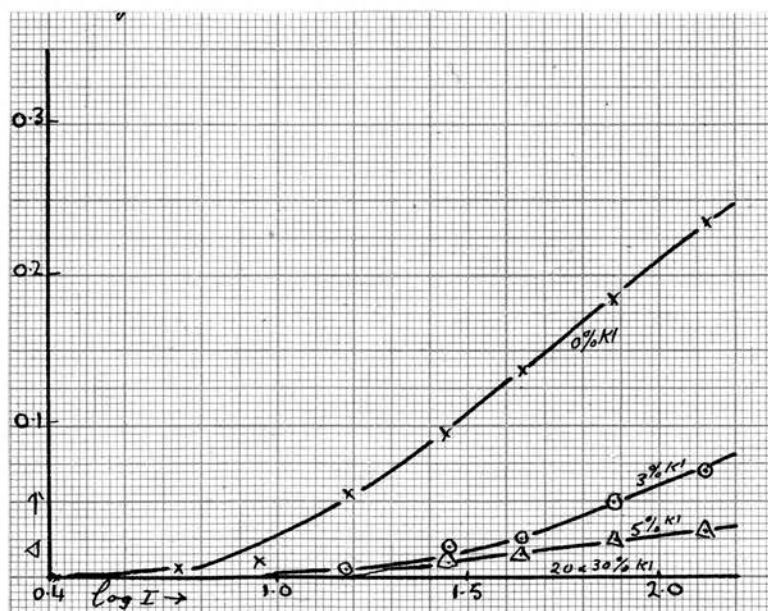of sensitivity as the iodide content rises.

Fig. 26.

This is in agreement with Farrer's original results but in contrast to Thom's very slow emulsions. It is suggested that not only the iodide content but the type of gelatin used is to be considered, but further work is necessary.

Fading of Thallous Bromide-Iodide Plates.

The fading properties of the 'slow' emulsions prepared by J.A.Thom were very prominent. Two plates coated with an emulsion prepared with the old gelatin used by Thom were exposed with the step-wedge at an interval of 4 days to the same conditions of exposure, and it was found that the decrease in density was 0.09. The experiment was repeated and a value of 0.08 was found so that these plates faded relatively rapidly as was expected. Plates coated with thallous brom-ide-iodide emulsions which were prepared with the fast gelatin I were also tested for fading. It was found that very little fading took place. At high intensity blue light exposures (127-2.64 scale di-visions) a decrease in density of 0.20 was recorded after the second plate had been kept for 10 months. Using a somewhat less intense blue light for exposures (0.56-0.12 scale divisions) a decrease of 0.01 was recorded after 3 months' delay in exposing the second plate. The second of a pair of plates exposed to a blue/

blue light intensity of 0.28-0.006 scale divisions showed again after 2 months a decrease of 0.02 at the highest intensities.

In these emulsions the latent image centres on which the latent image proper is built, is obviously fairly stable, this being in sharp contrast to Thom's results with plain emulsions where fading was rapid and such as to produce no image at all after some weeks under any exposure conditions.

In experiments done by J.A.Thom with the slow emulsions sodium nitrite and in one series sodium arsenite were added as acceptors the general result being to increase the speed of the plate and to reduce the rate of fading.   It would thus be expected that, with the inherently faster emulsion already showing a stable latent image speck system, similar additions would not appreciably affect the already slow fading rate.   This was confirmed in arsenite-containing plates where a decrease of 0.02 was recorded after the second plate had waited 7 months before being exposed to the same intensity range as the first plate.   In nitrite-containing emulsions the decrease recorded after 3 months was also of the same order, 0.01.

Fading of the Latent Image after Exposure and before Processing.

In previous work it had been found that the latent image once formed was normally stable. If the latent image in thallous bromide emulsions consists of thallium/

thallium atom aggregates, then the presence of water
and oxygen must be expected to remove partially formed
aggregates and decrease the finally developed image.
Since thallium metal is not attacked by cold water
which is free from air, immersion in cold water con-
taining little dissolved oxygen would be expected to
produce only a small effect. During the drying process
after the plate is coated with emulsion, conditions
would be more favourable for removal of latent image,
since normally the plate is then exposed to air and
the gelatin contains an appreciable amount of water.
The normal drying period for plates used in this work
was 4-5 days. It was found that after such an interval
the latent image once formed was relatively stable.
A series of thallous bromide-iodide plates was exposed
to a blue light intensity of 0.28-0.006 scale divisions.
The plates were left for 0, 10, 15, 30 and 45 min.
before processing, but the developed density on each
wedge square only differed by 0.01 in all the plates.
Three more plates were exposed to the same intensity of
blue light, one was left in air at 35°C. for 45 min.,
the next near water at 17°C. for 45 min., the third in
dry N_2 at 17°C. for 45 min., but again the differences
in developed densities over all the wedge squares,
between the plates, was 0.01.

However, another emulsion was left drying on
plates for 2 days, the plates being free from visible
'wet'/

'wet' areas.   In this case very marked decreases
in developed density were recorded for time intervals
0, 5, 10, 15 and 45 min. left before processing. The
densities recorded were 0.32, 0.20, 0.14, 0.07, 0.05,
for the highest blue light intensity. Thus for com-
parison of developed densities in normal procedure it
is obvious that adequate drying is essential.

Spectral Sensitivity of Thallous Bromide-Iodide Plates.

One of the outstanding points brought out by
Thom's work on slow emulsions was the bleaching out
effect of blue light of small intensity, in contrast
to the building up of latent image by blue light of
high intensity.   In the present case of the 'fast'
emulsions where the forward process is obviously pre-
dominant it was therefore of interest to determine
if a similar phenomenon could be established for
different conditions of critical intensity.   In this
respect preliminary experiments were carried out first
as to wavelength sensitivity limits.

The emulsion used to coat the plates was a
thallous bromide-iodide emulsion containing 0.01 g.
sodium nitrite per 100 ml. emulsion and the procedure
involving the use of 2% potassium bromide (see p.40)
was used after silver nitrate immersion, since the
plates were large.

The slit of the Hilger spectroscope was illumin-
ated first with a mercury lamp and then with a tungsten
filament/

filament lamp. A strip of thallous bromide plate was
exposed in turn for 15 min. to each radiation after
resolution by the prisms, so that the spectra obtained
would be shown side by side on the plate after pro-
cessing and development. A print of the original
plate (Plate II) is shown below. The original plate
shows (a) all the prominent lines of the mercury
spectrum up to and including λ 5460 as dark lines;
(b) the continuous tungsten spectrum also to λ5460
as a dark band; and (c) beyond λ 5460, i.e. in the
red bleaching in both spectra.
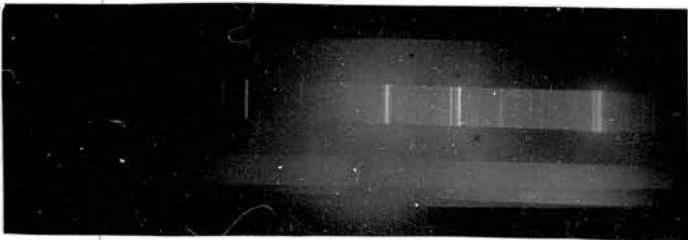
Plate II.   Plate III.

A second plate was first given an overall primary
exposure of 3 min. to white light and then given sub-
sequent exposures as Plate II. The resulting Plate
III shows (a) dark lines in the mercury spectrum up to
λ4360 but longer wavelengths, e.g. λ 5460 bleached
out; (b) similar bleaching at longer wavelengths is
shown in the continuous spectrum.

In contrast to Thom's emulsion the forward
process/

process of latent image formation is obviously pre-
dominant, in particular the present fast emulsions are
sensitive to green λ 5460 whereas the maximum wave-
length sensitivity of the slow plate was λ 4530.
Emulsions of thallous bromide-iodide containing 0.01
g. nitrite were given various ripening times, 15, 45
90, 330 min. Strips from plates coated with each
emulsion were exposed as Plates II and III.
The results showed that the general sensitivity over
all the wavelengths decreased as the ripening time
was increased. No special marked sensitivity rise or
fall was found for any one particular wavelength.

In connection with the effect of red light on
thallous bromide plates, several plates were exposed
to light produced by the Chance glass No.1. No direct
sensitivity was found which was to be expected and
when primary blue light exposures were given to plates
a secondary illumination of red light led to bleaching
of the primary image. The extent of bleaching in-
creased as the primary exposure increased. This
resembles the Herschel effect in silver bromide plates.

Green Light.

Glass plates were coated with a plain thallous
bromide-iodide emulsion for use in these experiments.
The green light was produced by filters (see p. 45)
the intensities falling on the plate through the
wedge/

wedge squares being given in Table 4. First the
direct sensitivity to green light was investigated.
The results of exposure are shown in Figs. 27 and 28.
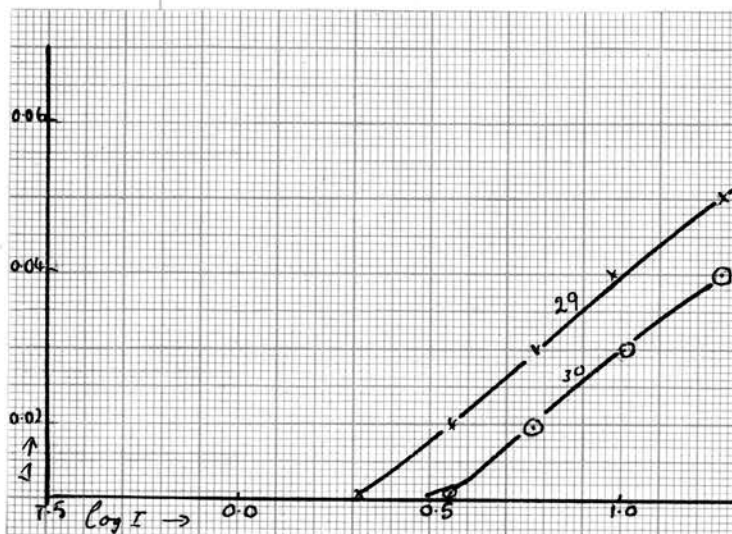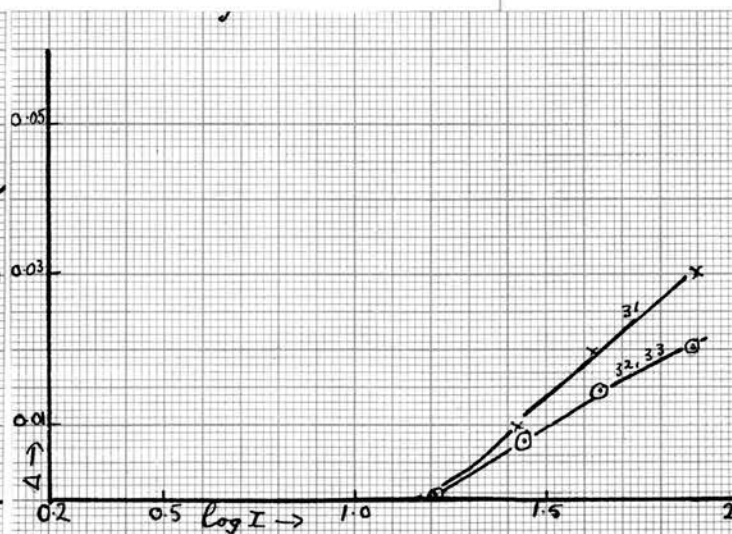
Fig. 27.   Fig. 28.

Table 10.

Expt.	Time of exposure	Intensity of Green Light
29	15 min.	17.95 - 0.37 scale divisions
30	15 "	17.95 - 0.37 "
31	15 "	81.6 - 1.7 "
32	30 "	81.6 - 1.7 "
33	3 hours	81.6 - 1.7 "

It is evident that the effect produced by green light
is only very small, so that latent image production
by/

by green light cannot be very efficient.

Reversal by Green.

Some preliminary experiments were done using
green light to produce both the primary densities and
for the post exposures, but it was soon found that the
primary densities obtained were too small and blue
light of intensity 187 scale divisions was used sub-
sequently for this purpose.   In Fig. 29 the primary
densities are given by the first point on the left-
hand side of the graph.   The time of the secondary
exposure for these experiments was 10 min. to the
green light intensity range 81.6-1.7 scale divisions.
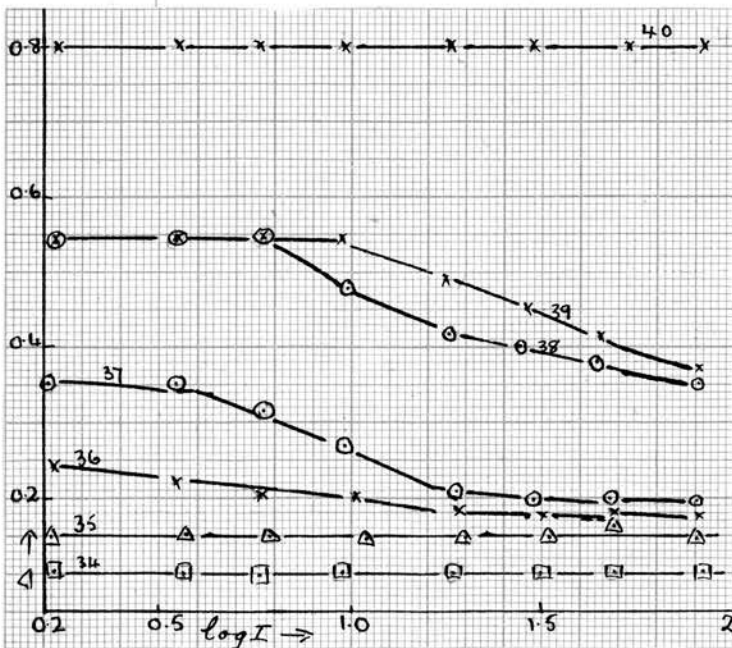
Fig. 29.

Fig. 30.

Another experiment was carried out using a secondary
exposure/

exposure of green light 100 times smaller than that used in Expts. 34-41. No bleaching was seen at all and thus the bleaching effect is dependent on the green light intensity.

The general conclusions obtained from these results may be summarised thus: (a) There is a slight forward building up process which is due solely to green light; (b) As the primary density on the plate increases so the amount of bleaching present increases; (c) The extent of the bleaching depends on the intensity of the green light used; (d) At certain very high densities there is no bleaching. This may be due to either lack of time or inability of the green light to reduce the latent image to the critical size at which bleaching shows; (e) At very low primary densities there is again no bleaching; (f) One experiment 41 (Fig. 30) showed that a forward process of latent image formation was just becoming apparent even when a very low primary density is already present on the plate.

Blue Light Reversal.

Blue light λ4360 shows again two opposing effects: (a) the forward process of latent image formation which has been discussed under the initial speed of the plates and (b) the opposing reversal effect which becomes apparent when an exposure to low intensity blue light is given to a plate on which there already exists/

exists a latent image. As the intensity of the
secondary illumination is increased a position is
reached where in preference to bleaching the forward
building up process takes place. This point where
bleaching is just beginning to show is called the
'bleaching limit'. Previous work carried out by
Thom showed that there might be a simple relation
between the primary density and the corresponding
bleaching limit. In this section attempts made to
elucidate this relationship are recorded.

The plates used were made from an ordinary
thallous bromide-iodide emulsion. For the fast gelatin
which was used here nitrite was added to the extent of
0.01g.per 100 ml. emulsion, but it was previously
shown that for this gelatin, nitrite has no marked
effect on the plate speeds. The plates used in
section 2 were made with the slow gelatin used by
J.A.Thom, no nitrite being present.

Section 1. Two sets of exposures were carried out:
(a) at high initial densities, (b) at low initial
densities. The filter systems used for reducing the
blue light intensity were altered in both cases so as
to follow the bleaching limit as the primary density
was lowered. The various filter systems used
throughout these exposures and the blue light inten-
sities they transmit through the wedge are listed in
Table 3. Ten experiments are given as examples to
show/

show the shape and position of the curves obtained at different intensity ranges. Table 11 gives the details of secondary exposures and the primary density used in each case.

Table 11.

Expt.	Pr. Dens.	Range of secondary blue light. Sc.Div.	Expt.	Pr. Dens.	Range of secondary blue light. Sc. Div.
42	1.52	0.13-0.0027	47	0.56	12.2 - 0.25
			48	1.10	2.5 - 0.051
43	1.52	0.13-0.0027	49	0.76	2.5 - 0.051
44	1.63	0.13-0.0027	50	0.27	0.027-0.00055
			51	0.30	0.0015-0.000021
45	1.31	2.5-0.051			
46	1.45	25.7-0.50			

A secondary exposure of a low intensity blue light causes reversal if the primary density is high (see Expt. 42-44). However, as the density falls to low values the effect of the same intensity secondary illumination is to cause a forward process of latent image formation (see Expt. 50). Expt. 51 shows that at very low intensities blue light causes neither a forward nor a reversal process. As the intensity of blue light increases the tendency for the forward process/

FIG. 31
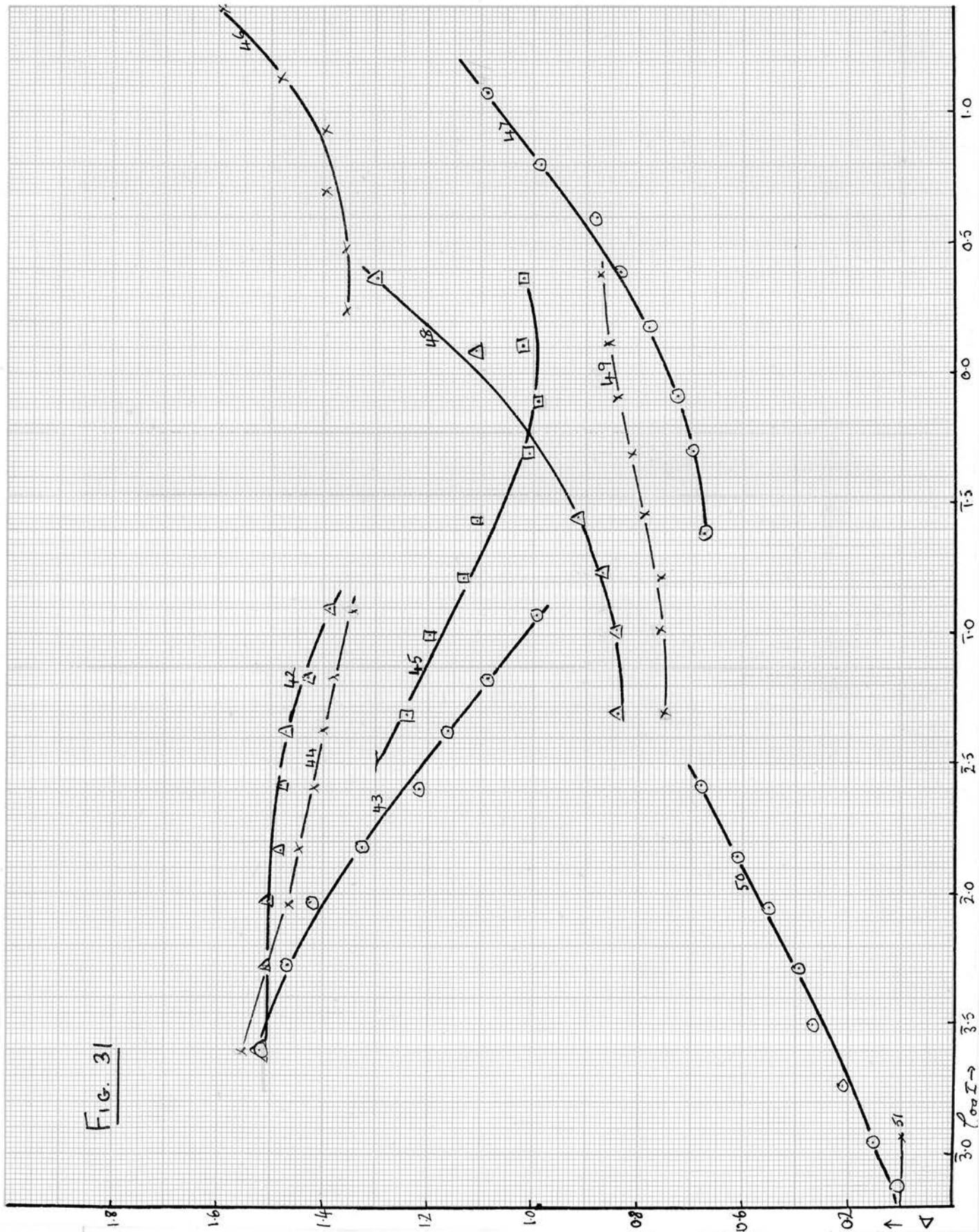
process is shown (see Expt. 48, 49) and increasing the blue light intensity further the bleaching limit is obtained even for fairly high densities (Expt. 46). Expt. 47 shows that below the general line across the graph (see Fig. 31) the forward process predominates. That is, if a fairly low primary density is given (0.56) and the secondary exposure is of a fairly high intensity of blue light (12.2-0.25 sc. div.), then the final processed and developed plate shows that even at the smallest intensity falling on the plate through the wedge a density is obtained considerably greater than the original primary density.

Several plates were exposed in a similar way to find the relation between the primary density and the bleaching limit. Exposures to various intensities of blue light were given to produce the primary density. The intensity of the secondary exposure was arranged so that a bleaching limit was clearly visible on the plate. The plates were measured in the usual way and the position where the H and D curve crossed the line representing the primary density was found in each case. The log of the intensity of secondary exposure at which the bleaching limit occurred was found from the horizontal scale. Table 12 shows the results which are plotted in Figs. 32 and 33.

Table 12.

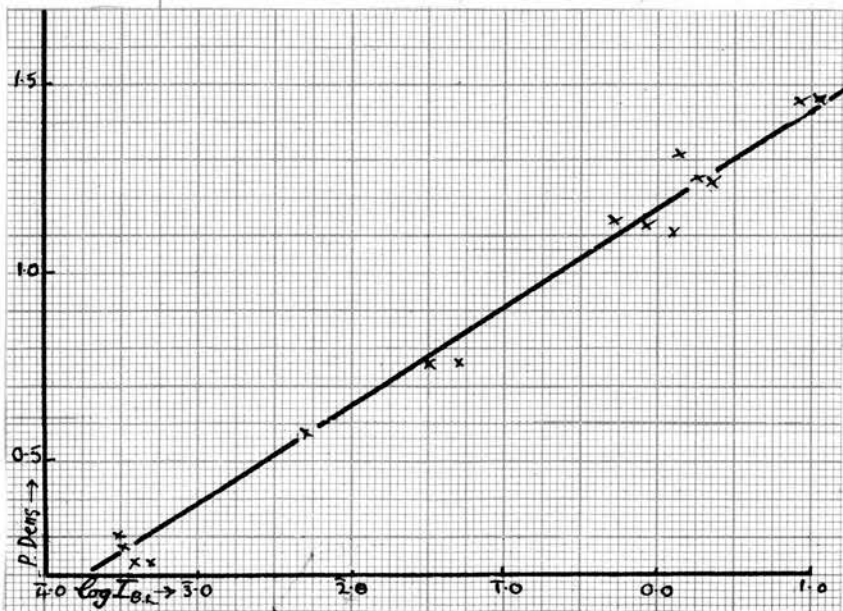| Expt.	Pr. Dens.	Log Int. B.Limit	Expt.	Pr. Dens.	Log Int. B. Limit.
46	1.45	1.04	55	1.23	0.35
47	0.56	$\bar{3}.7$	56	1.25	0.28
		(Ext.)	57	1.13	$\bar{1}.94$
48	1.10	0.12	58	1.32	0.16
49	0.76	$\bar{2}.71$	59	1.14	$\bar{1}.71$
50	0.27	$\bar{4}.5$	60	0.23	$\bar{4}.6$
51	0.30	$\bar{4}.5$	61	0.23	$\bar{4}.7$
52	1.45	0.92	62	0.30	$\bar{4}.0$
53	0.75	$\bar{2}.50$			
54	1.55	1.14			

Fig. 32.
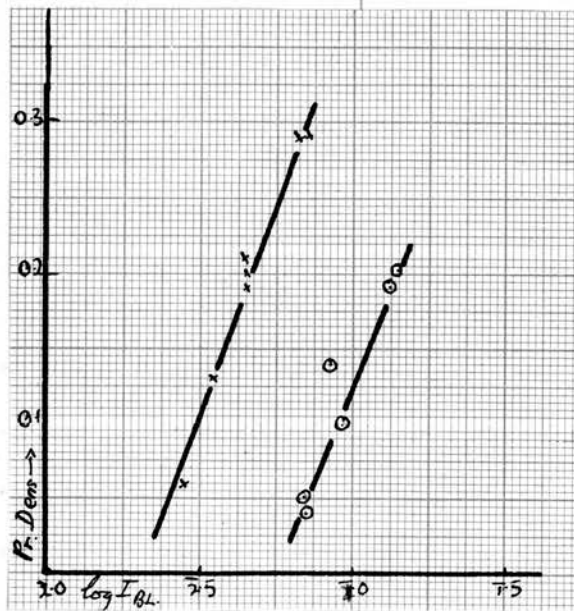
,Fig. 33.

From/

From Fig. 32 it can be seen that the relation between the primary density and the bleaching limit is a straight line. The confirmatory experiments were done with the slower plates, which were exposed to produce first a primary density and then a bleaching effect. The following Table 13 shows the primary densities and their corresponding bleaching limit. The results are shown in Fig. 33. An exact straight line relationship is again observed and a second straight line is found for results which were obtained a week later. The second line is displaced towards higher intensity ranges by an amount which is of the same order as that found in the displacement of the fading curves for the slow emulsion.

Table 13.

			One week later		
Expt.	P.Dens	Log Int. B.Limit	Expt.	P. Dens	Log Int. B.Limit.
63	0.13	$\bar{2}.56$	70	0.05	$\bar{2}.85$
64	0.21	$\bar{2}.65$	71	0.10	$\bar{2}.97$
65	0.19	$\bar{2}.65$	72	0.04	$\bar{2}.85$
66	0.29	$\bar{2}.82$	73	0.19	$\bar{1}.12$
67	0.06	$\bar{2}.44$	74	0.20	$\bar{1}.13$
68	0.29	$\bar{2}.85$	75	0.14	$\bar{2}.93$
69	0.20	$\bar{2}.65$			

Desensitisation.

Several dyes are known which have a desensitising effect on silver bromide plates. In this section the effect/

effect of two of these dyes, malachite green and methylene blue on thallous bromide-iodide plates was investigated. Small squares of coated plates were used throughout.

Three aqueous solutions of malachite green were prepared so that the concentration of the dye in the three solutions was (a) 1 in 1000 parts water, (b) 1 in 10,000 parts water, (c) 1 in 100,000 parts water. Three solutions with similar concentrations of methylene blue were also prepared, (d) 1 part in 1000 parts water, (e) 1 part in 10,000 water, (f) 1 part in 100,000 water.

The primary densities were produced by exposing the plates for various times to blue light of intensity 37.8 scale divisions. The secondary exposure was 5 min. to a blue light intensity range of 2.5-0.051 scale divisions. Between the primary and secondary exposures the plates were dipped in the prepared solutions of the dyes for three minutes, then rinsed three times in distilled water, allowing one minute for each rinsing and left to dry horizontally in a small drying cupboard. One square was exposed and not dipped, another was exposed, dipped in distilled water for 3 min., rinsed and dried. Table 14 gives the primary density and the solution used for immersion. The results are shown in Figs. 34 and 35.

Table/

Table 14.

Expt.	Pr.Dens.	Immersion solution	Expt.	Pr.Dens.	Immersion solution	
76	0.38	Undipped	80	0.01	M.Blue	(e)
77	0.08	H_2O	81	0.04	M.Green	(b)
78	1.40	M.Blue (d)	82	0.04	M.Blue	(f)
79	0.08	M.Green (a)	83	0.09	M.Green	(c)
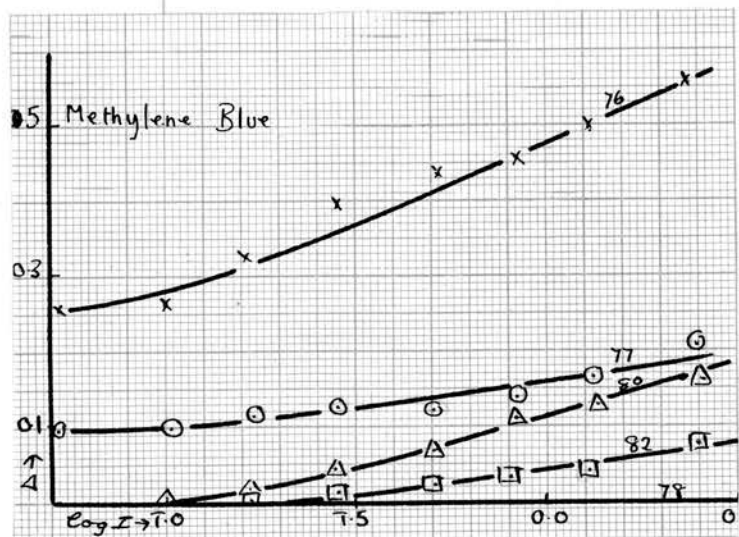
Fig. 34.
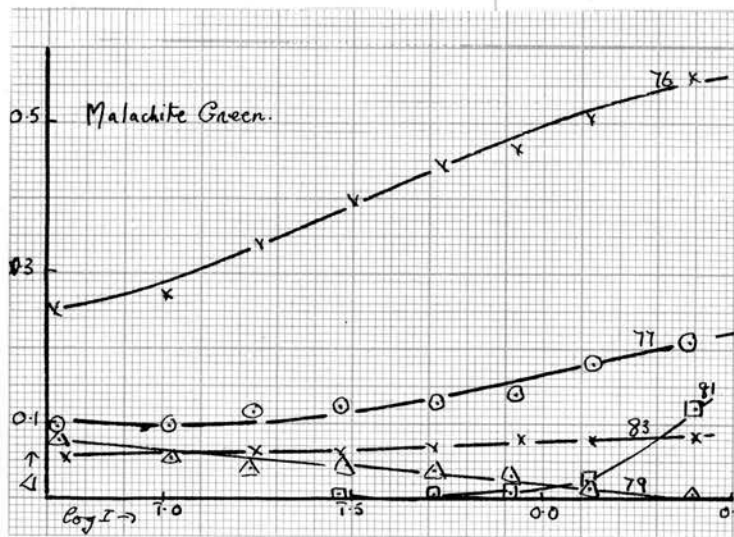
Fig. 35.

For malachite green as the concentration increases
the desensitisation increases and at concentrations
of/

of 1 in 1000 the primary density itself is bleached
out.   For methylene blue conc. (e) appears to have
not such a desensitising effect as conc. (f), but
this result depends on the fog level figures 0.78 and
0.33 very much.   A note here is included on the amount
of fogging caused by these concentrations of dyes (see
Expts. 86-91).

Malachite Green conc. (a)	fog =	0.20
(b)		0.07
(c)		0.06
Methylene Blue (d)		1.53
(e)		0.60
(f)		0.31

Since the fogging caused by the dyes is so extensive
it is difficult to obtain results which are really
comparable, but a second series of experiments was
attempted to find the effects of the dyes on the
ordinary H and D curves of the plates.

The exposures given were 10 sec. to a blue light
intensity of 0.28-0.006 scale divisions.   The exposure
was given after the plate had been dipped for 3 min.
in one of the dye solutions, rinsed and dried.   Figs.
36 and 37 show the results of such exposures, Table
15 giving additional information.

Fig./

8
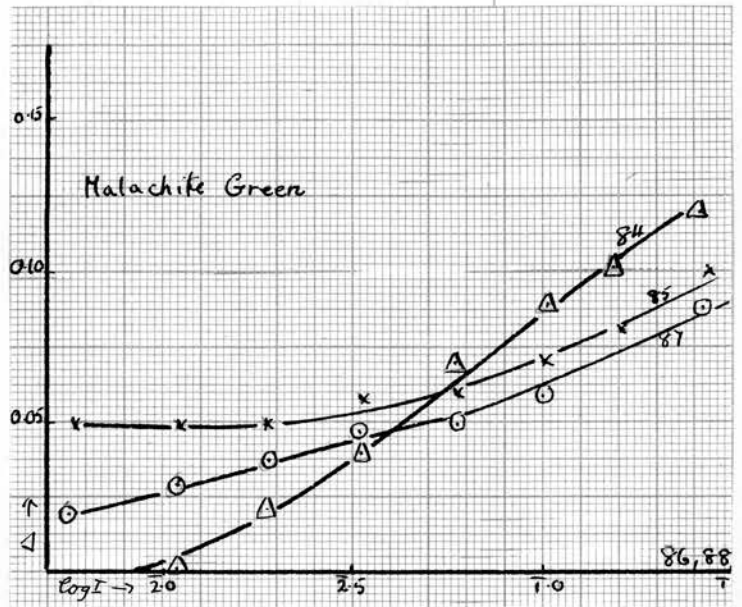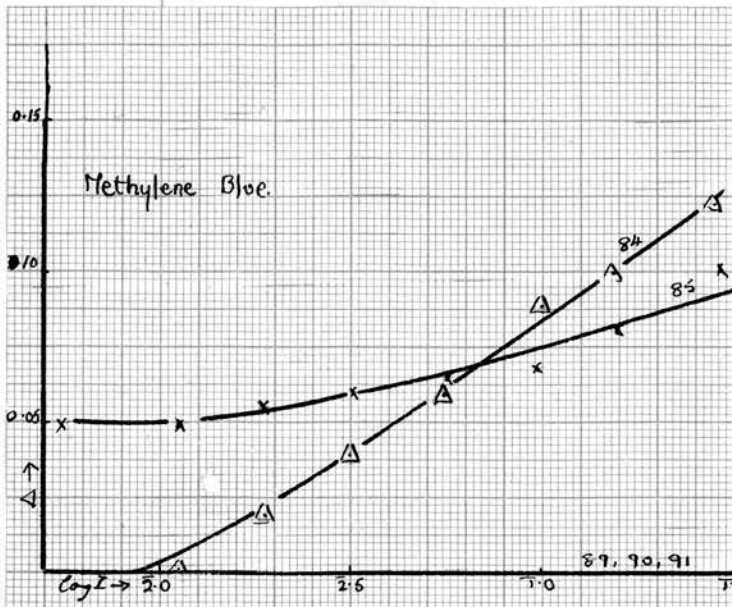
Fig. 36   Fig. 37

Table 15.

Expt.	Immersion solution	Expt.	Immersion solution
84	undipped	88	M. Green (b)
85	H_2O	89	M. Blue (d)
86	M.Green (a)	90	M. Blue (e)
87	M.Green (c)	91	M. Blue (f)

Again the general effect of both dyes is to desensi-
tise the plates and the desensitisation increases
with increasing dye concentrations.

Effect/

Effect of Malachite Green and Methylene Blue on the Spectral Sensitivity.

Two strips of thallous bromide-iodide plate were dipped in dye concentrations (b) and (f) and after drying were exposed to the tungsten and mercury spectra as Hate II.   After development no sign of the lines of the mercury spectrum were visible in either case and the plates must have been completely desensitised. Two other dye-treated plates were given primary exposure first and then exposed as above. For the methylene blue dipped plate even the blue mercury lines were bleached out and desensitisation was also obviously present in the case of the malachite green containing plate.   The effect of these dyes on the plates is thus a general desensitisation for all wavelengths.

Internal and External Image Formation.

Plates prepared from a plain thallous bromide-iodide emulsion were used for this work. The developers used were: (a) ordinary M-Q developer, (b) 'surface developer' prepared by Stevens which attacks the surface image only, and (c) 'total developer' also prepared by Stevens which contains a silver halide solvent and thus attacks all the latent image present. Stevens' developers were originally prepared for use on silver bromide plates (59).

In/

In the case of silver bromide the presence of the internal image was shown up by first destroying the surface image with a dichromate bleacher and then using a total developer to reveal internal image specks. The composition of the dichromate bleacher (stock solution) used was 0.75 g. potassium dichromate to 0.50 ml. conc. sulphuric acid added to water to make in all 100 ml. Since the effect of the double decomposition with silver nitrate is to replace the thallous bromide system with an identical silver bromide system in all respects, the presence of an internal image originally present in the thallous bromide grain could be revealed, by first using a dichromate bleacher and then a total developer if the effects of the bleacher and developer are essentially the same for the newly formed silver bromide as for the silver bromide plates for which they were originally intended.

Solutions of dichromate bleacher were made up thus:-

```
(a) 1 part bleacher to none of water
(b) 1     "          3 parts water
(c) 1     "          7     "
(d) 1     "         15     "
(e) 1     "         31     "
(f) 1     "         63     "
```

The plates were exposed in pairs for 5 sec. to a blue light intensity of 0.11-0.002 scale divisions. Both plates were processed and developed under conditions which were as nearly identical as possible. After the

45/

45 min. wash the plates were immersed in the particular
bleacher solution for 2 mins., washed a further 10 min.
and developed for 5 min. with the surface developer.
The results of these experiments are shown in Fig. 38
and Table 16 gives the solutions used in each case.

Table 16.

Expt.	Solution used.
92	H_2O
93	(a)
94	(b)
95	(c)
96	(d)
97	(e)
98	(f)
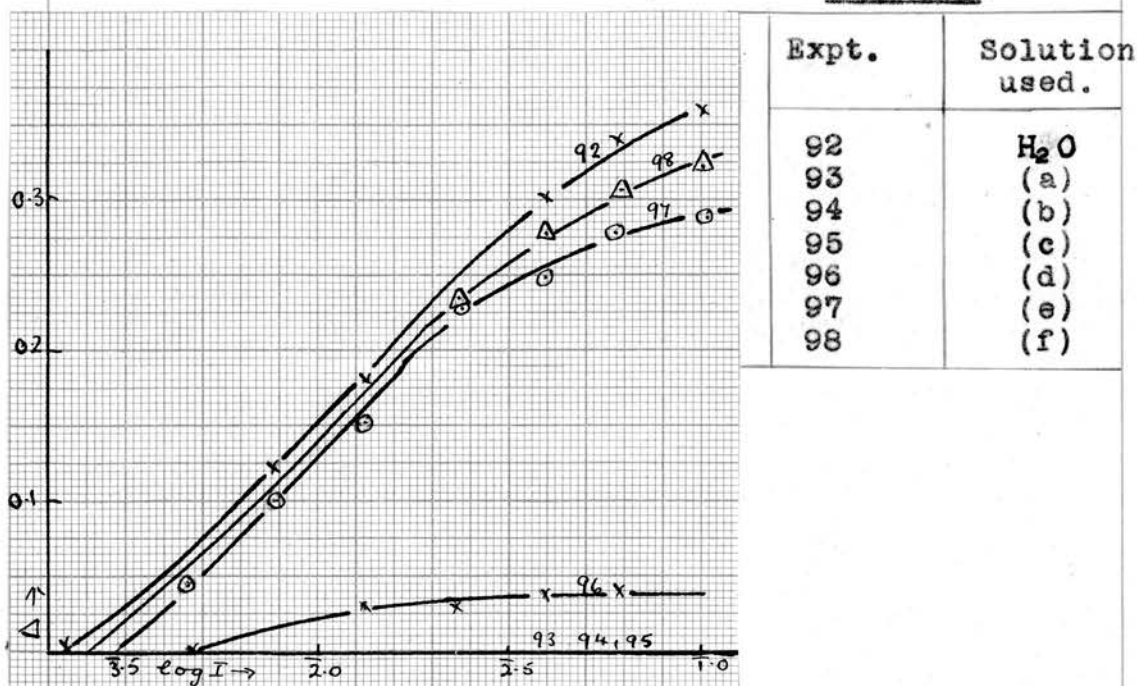
Fig. 38

The graph shows two things: (a) that the surface
developer does act on the grain surface in this case,
and (b) for concentrations of dichromate greater than
1 in 7 parts water there is no evidence of a surface
image. With more dilute bleacher solutions more and
more of the surface image is revealed by the developer.
A similar graph to Fig. 38 was found for silver bromide
plates. Two plates were exposed for 10 sec. to a
blue/

blue light intensity of 1.37-0.029 scale divisions.
Again the conditions of exposure and processing were
kept as similar as possible.   One plate was surface
developed for 5 min. and the second was totally
developed using the total developer containing 10 ml.
10% hypo, for 3 min.   The results of the exposures
are given in Fig. 39.
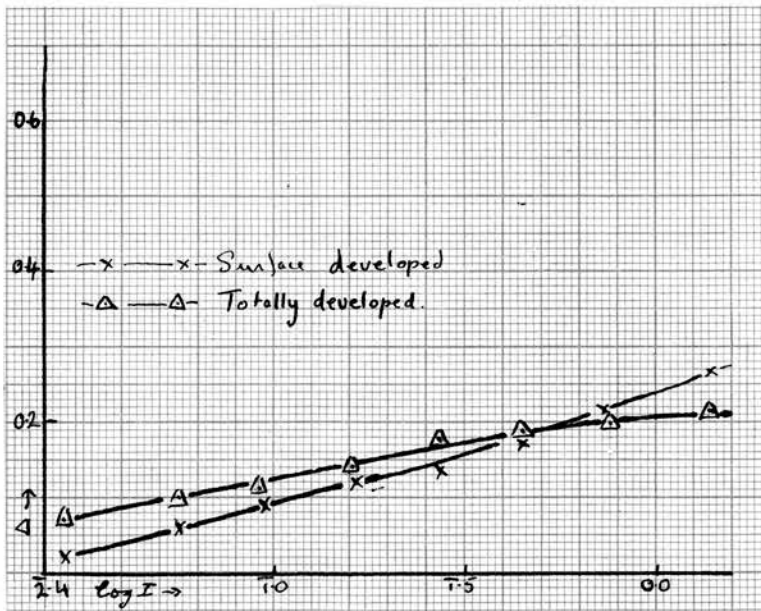
Fig. 39.

These results show that light acting on thallous
bromide-iodide plates forms latent image specks on the
grain surface, but no information can be obtained as
to whether there is any internal latent image formed.
The large number of surface specks tends to swamp any
additional/

additional developed density due to the internal specks
which might be thus revealed.

There yet remains the question as to whether,
once the surface image has been removed, there remains
any internal specks.

Two plates were exposed to a blue light intensity
of 0.11-0.002 scale divisions. After the 45 min.
wash they were immersed in bleacher solution, (a) for
2 mins., washed and one plate (99) was surface developed
for 5 min. and the other (100) was totally developed
for 3 min. The results were repeated except that
bleacher solution (c) was used. (101) was surface
developed, (102) totally developed. Both surface
developed plates showed no wedge squares. Wedge
squares were clearly visible in plates 100, 102.
Plates 103, 104 were immersed in water instead of
bleacher/, 103 being surface developed and 104 totally
     solution
developed . All these results are shown in Fig. 40.

Fig. 40 /
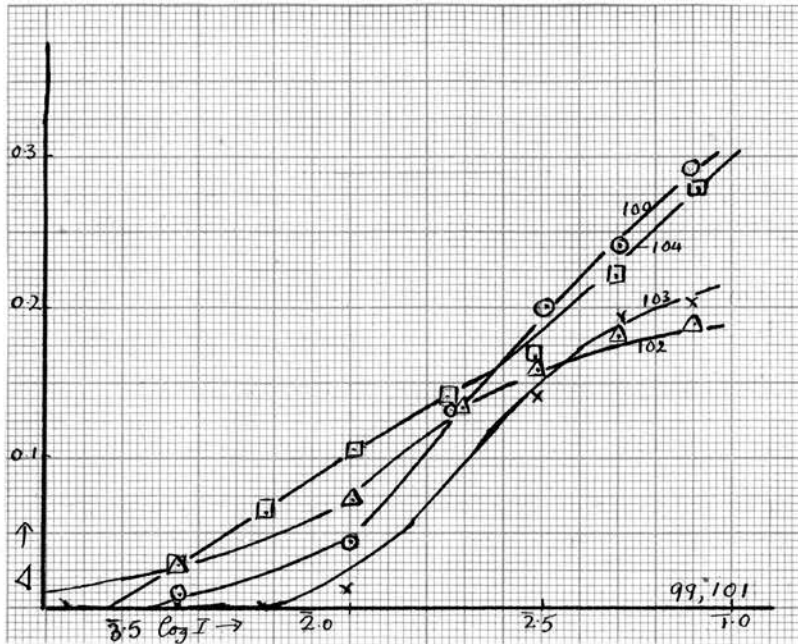
Fig. 40.

Reversal and the Internal Image.

The Herschel effect in silver bromide plates is
the destruction of an already formed image by low
intensity red light. The surface latent image is dis-
persed, the electrons being set free from the image
and the resulting silver ions travelling back into the
grain. For silver bromide it has been shown that the
electrons which are released go into the conductivity
level and fall into internal traps forming an internal
latent image. Thus the internal latent image is built
up at the expense of the surface image.

In thallous bromide plates the reversal of the
image is caused by low intensity blue light. An
enquiry/

enquiry was made into whether this effect was confined
to the surface latent image, the internal image being
increased as in the case of silver bromide plates.

Two plates were exposed to a high blue light
intensity. Half of both plates was covered and the
rest exposed to low intensity blue light. After pro-
cessing one plate was surface developed and the other
totally developed for the usual times. The densities
recorded are shown in Table 17 and it is apparent that
the amount of internal image remains constant although
no increase was apparent.

Table 17.

Developer	Unbleached portion	Bleached portion
Surface	0.58	0.42
Total	0.65	0.49
Internal	0.07	0.07

Finally an attempt was made to find in thallous
bromide plates a reversal similar to that found in
silver bromide plates known as the Albert effect.

Plates were exposed to a blue light intensity
of 127-2.64 scale divisions with the wedge in position
for 12 min. The secondary exposure given was to a
blue light intensity of 19.0 scale divisions for 5 min.
The plates were left in running water for various times,
10/

10 and 30 min. and dried before the secondary exposure. The object of this was to wash off the surface of the grain, thus taking the surface image away. After processing and development it was found that the secondary exposure had caused a reversal, the lowest densities produced by the first exposure being the darkest on development. Although for thallous bromide plates the reversal effects are complicated in that they are not confined to red light, it was thought here that a true Albert Reversal had taken place. A third plate was immersed in dichromate bleacher solution after the first exposure, and then dried. The secondary exposure was given as above and after processing and development in MQ developer, a very faint pattern of the wedge squares was visible, unreversed.

DISCUSSION.

DISCUSSION

From previous work it was known that the speed
of thallous bromide plates was likely to be very slow
in comparison with silver bromide plates. Accordingly
as the results show, plates were exposed to the same
order of blue light intensity for the same lengths of
time as was previously found necessary (11). The
plates after development usually showed high densities
and extensive fogging proved due to scattered blue
light in unexposed regions of the plates. It was
therefore clear that the plates as prepared above had
relatively high speeds and this was shown to be
caused by the gelatin used for their manufacture. For
these emulsions a ripening time of 3 hours gave plates
which showed effects resembling solarisation when
illuminated with high intensity blue light. The extent
of these effects was reduced considerably when the
ripening time was cut down to one and a half hours.
Longer ripening times decreased the sensitivity of the
emulsion, a ripening time of five and a half hours
causing the thallous bromide to dissolve in the gelatin
rendering the resulting plate almost insensitive. In
connection with the speed of the emulsion it was found
that no silver was present and that added silver
nitrate caused no great effects on the plain emulsions.
The amount of restrainers present in the gelatin was
compared with the amount present in the standard
gelatin/

gelatin and it was found that the gelatin used in
plate manufacture was relatively unrestrained as com-
pared with the standard gelatin. An emulsion prepared
with the standard gelatin gave plates with slower
speeds comparable to the speed of the slow emulsions.(11).

Previous work done by J.A.Thom showed that small
quantities, 0.01 g. per 100 ml. emulsion, of sodium
nitrite caused an increase in speed in the emulsions.
Experimental results obtained here showed that although
large quantities of nitrite did show the increases
expected, the same small quantities of nitrite used
by Thom added to emulsions gave no marked increases
in speed. The reason for this was taken to be that
the gelatin itself had apparently such a large capacity
for accepting bromine atoms that the effects of the
nitrite were swamped.

In general the same thing holds for sodium
arsenite present in emulsions. J.A.Thom had shown
that small quantities of sodium arsenite present in
a nitrite-containing thallous bromide-iodide emulsion
caused increases in speed. Results obtained for the
fast plates showed that large quantities of sodium
arsenite gave the increases as expected either from
the point of view of the accepting of bromine atoms
or of the reduction of the thallous bromide, i.e. a
continuation of the reaction initiated by light. (A
parallel effect of arsenite was shown by Clark to be
present/

present in silver bromide plates). Results obtained
from three emulsions containing relatively small
quantities of arsenite showed that in general three
effects were present: (a) an initial retardation of the
speed of the plates; (b) the expected increase attri-
buted to the acceptor action of the arsenite; (c) a
marked retardation which is thought to be due to either
an attack on the latent image centres by the arsenite
or a reduction of the gelatin's power of accepting
bromine atoms. From the experiments on the restrain-
ing properties of the gelatin it was found that arsen-
ite of the same concentration as was used in the
emulsions (as regards gelatin present) had the effect
of reducing the rate of formation of silver, i.e. the
darkening. This retardation could be due to an
attack of the arsenite on the silver nuclei which are
the catalysts in the system, such a reduction in the
nuclei leading to a reduction in the total rate of
darkening. Alternatively the retardation could be
due to a desensitisation by the arsenite of the
gelatin's sensitising compounds present. A reduction
in the concentration of sulphur-containing compounds
would thus lead to a reduction in the number of nuclei
present. It was found that large quantities of arsenite
did increase the rate of darkening and this was to be
expected from the reducing action of sodium arsenite.

A strip of fast thallous bromide plate exposed

in/

in the spectrograph showed direct sensitivity to
blue and green light but not to red. The green light
also caused a reversal effect on a pre-exposed plate.
Accordingly experiments were done first with red
light where a reversal effect was shown similar to the
Herschel effect in silver bromide plates, and secondly
with green light where in addition to the reversal
effects, the extent of which depended on the intensity
of illumination and the primary density a definite
forward process of latent image formation was shown
to take place although the extent of this process was
small. Extensive experiments were carried out on
the reversal found to take place (11) when low
intensity blue light illumination was given to an
already pre-exposed plate. It was found that very
low intensities of blue light gave extensive reversal
effects on plates which already had a high primary
density. As the intensity of secondary illumination
increased, the bleaching reached a maximum and then
a forward process of latent image formation became
apparent, a bleaching limit being observed when the
intensity of secondary illumination was such that the
rate of the forward process superceded that of the
reversal process. As the primary density fell the
bleaching limit moved towards lower intensities of
secondary illumination. For these fast plates it
was/

was found that at fairly low primary densities (0.30) no reversal effects at all could be found with very low intensities of secondary illumination, the wedge squares seen after development on these plates appearing to build up from the primary density. Experiments, using plates prepared from the old 'slow' emulsion showed bleaching limits clearly even at such low primary densities (0.10-0.30). The bleaching limit was obtained for several primary densities for both emulsions and it was found that on plotting log intensity at which the bleaching limit occurred against the primary density, a straight line was obtained in the case of both the 'fast' and 'slow' emulsions.

A general desensitisation was shown to take place when thallous bromide plates are treated with either of the dyes,malachite green or methylene blue. For malachite green the extent of the desensitisation depended on the concentration of the dye. For methylene blue the extent of fogging caused by the dye was so great that plate measurements were difficult but it was clear that complete desensitisation resulted from even the lowest concentration of dye. A few experiments were carried out where primary densities were first given to the plates which were then immersed in dye solutions, dried and post-exposed with the step wedge in position. Here although again difficulties were/

were encountered caused by fogging, it was shown that
the bleaching limit was displaced towards higher
intensities as compared with a bleaching limit ob-
tained from a plate treated in a similar manner but
immersed in water only.   The presence of the dye in
the emulsion results in a general desensitisation of
the plate, i.e. a prohibition of the forward process
of latent image formation.   This would be the result
if the electrons which are set free in the conductivity
level by the illumination are trapped by the dye ad-
sorbed in the gelatin in preference to the sensitivity
specks. This 'trapping' must be essentially different
from speck-'trapping' in that no ionic process is
initiated in the grain and latent image formation is
absent. The total capacity of the dye-complexes for
trapping electrons will depend on the concentration
of the dye present, so that with lower dye concen-
trations less effects on the forward process would be
expected and this in general was found to be the case.

When the plates were exposed to blue light before
immersion in the dye solutions the secondary low
intensity blue light illumination caused the bleach-
ing limit in general to be displaced towards higher
intensity regions. The dye-adsorption complex can be
regarded as trapping the electrons released in the
conductivity level by the secondary illumination.
These/

These electrons normally are used to form a latent
image. Thus the forward process is again retarded
and the bleaching process which occurs simultaneously
will be shown as a consequent displacement of the
bleaching limit.

For silver bromide plates it was shown that
although most of the latent image was situated on the
surface of the grain there were also latent image
centres in the inside of the grain. The possibility
of the same type of latent image distribution in
thallous bromide was examined. It was first shown
that the surface developer prepared for use in silver
bromide plates did act in a similar way for thallous
bromide plates. This was shown by immersing plates
in dichromate bleacher and then developing them with
the surface developer. It was found that with con-
centrated dichromate solutions no image could be
developed up by the surface developer but that as the
concentration gradually decreased the surface image
was not destroyed and became apparent when surface-
developed (see Fig. 38). The presence of an internal
image in thallous bromide plates was shown by first
destroying the surface image with the dichromate
solution and subsequently developing the plate with
a total developer. A developed image of the wedge
squares was clearly seen (see Fig. 40).

In/

In work on silver bromide plates it was shown
that if an initial primary density present on a plate
was destroyed by non-actinic light, the internal image
was built up while the surface image was destroyed.
Attempts were made to find out if a similar phenomenon
would occur with thallous bromide plates. From
measurements made from plates' surface and totally
developed it was found that the internal image remained
constant but no increase in the internal image could be
found in the bleached portions of the plates.

Again for silver bromide plates the effect of a
primary exposure is reversed by an overall diffuse
light exposure if the plate has been treated with di-
chromate between the exposures to destroy the surface
image (Albert Effect).   When a thallous bromide plate,
already pre-exposed with the wedge in place, was
treated with dichromate and then developed in M-Q
developer after the secondary exposure, a faint
pattern of the wedge squares, unreversed, was visible.
It was thought that as M-Q developer does penetrate to
the internal image, this pattern was caused by such an
image already produced by the initial exposure. As
the effect of this treatment was a desensitisation of
the grains, the following procedure was followed. Since
the Albert effect occurred if the surface image was
destroyed after the primary exposure, the surface
image/

image formed on the thallous bromide grains by the first exposure was destroyed by dissolving away the surface of the grain. After the secondary exposure development of the plate showed a complete reversal, the latent image resulting from secondary exposure being formed in the interior of the grain.

The mechanism of the forward process of latent image formation has been shown by the Gurney Mott theory to be due initially to electrons from the conductivity level of the grain being trapped by the sensitivity specks, thus forming a latent image. A continuous regression process is not disallowed and in fact the illumination of silver bromide plates with non-actinic light leads to such a regression. Thus two mechanisms can be visualised as taking place at the same time, the first a forward process and the second the destruction process. In silver bromide plates illuminated with blue light the rate of image production is very great as compared with the rate of image destruction. So much so that no effects from the second process can be found and it is only when the rate of the forward process is considerably reduced as in the case of red light illumination that the retardation effect becomes visible.

More evidence of the coexistence of the retardation process has come from the slow thallous bromide plates which were prepared by J.A.Thom. Here the retardation/

retardation or bleaching-out effect of blue light was very obvious and the reason for this is that the process of latent image formation is not so efficient as in the silver bromide system. When the forward rate is slow, effects due to bromine acceptors in particular will be very prominent, and clear effects of speed increases caused by the acceptors were found. Fading effects which were very prominent in the slow emulsions would be emphasised when the rate of image production was slow.

A summary of the results obtained in this work has been given. From the point of view of two opposing mechanisms it is clear that these fast thallous bromide emulsions are intermediate in character between silver bromide plates and the slow emulsions. The rate of image production is considerably increased in these plates. It then would be expected that the effects of small quantities of acceptors, sodium nitrite and arsenite, would be less in evidence, and such was found to be the case. It cannot be said that the different gelatin causes a complete removal of the bromine atoms, since effects like solarisation are found to be present in some cases. In emulsions containing small quantities of sodium arsenite, the arsenite appears to affect the gelatin in some way, causing retardation of the image, presumably by reduction/

reduction of the gelatin's capacity for accepting bromine atoms.

In these fast emulsions the bleaching process caused by blue light is again found. It would be expected that since the forward process is considerably faster this retardation effect would be found only at higher primary densities and be displaced towards higher intensity regions. At densities 0.30 and below where previously (11) definite bleaching effects had been found for low intensity blue light, no retardation process was apparent in the fast plates. Only when the primary density was considerably greater 0.5-1.5 and the forward process became slower owing to the fact that most of the specks had been used was there any evidence of a bleaching process. At these high densities when a low intensity secondary illumination was used bleaching was very obvious, but as the secondary illumination was increased the forward process again became evident. In silver bromide plates for blue light illumination even at the highest densities no bleaching effects are found when the plates are post-exposed to blue light.

The fact that, in contrast to the slow emulsions where no forward process was caused by green light occurred, green light illumination of the fast thallous bromide plates caused a forward building up effect, again is expected as a direct result of the increased

plate/

plate speed. Generally speaking the bleaching effects might be expected to occur at lower primary densities and such was found to be the case. The lack of effect of green light secondary illumination on a high primary density of 0.80 may be taken as a lack of time or more likely as a lack of ability of bringing the image below the critical level necessary for bleaching to show. In many ways the bleaching caused by green light on these fast emulsions is similar to the low intensity blue light bleaching found on the slow emulsions.

Since in the fast thallous bromide emulsions there are apparently a much larger number of sensitivity specks than in the previous slow emulsions, it might be expected that there would be more possibility of internal latent image formation being made apparent. In the results obtained it is clear that there are certainly internal image specks but that analogous to the silver bromide system most of the image appears at the surface of the grain. The presence of such a small internal image made possible reversal effects, such as the Albert Effect in silver bromide, in thallous bromide systems. If the assumption is made that both forward and bleaching processes occur simultaneously reversal effects found to be present in these plates can be explained generally by a suppression of the rate/

rate of the forward process of latent image formation.

In general, derivation of an equation for developed densities must include recognition of the actual rate of growth of any one centre in a grain, the distribution and initial relative sizes of such centres, and the varying sizes of the grains. In the following section is given an attempt to develop an expression dealing with the centre growth rate for comparison with the experimental results. 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 will indicate the relative effects of various factors which otherwise are difficult to appreciate by reason of the complexity of the system.

Let the number of latent image centres, assumed to be thallium atom aggregates, in a grain be S and the concentration of 'free' electrons in the conductivity layer as a result of incident light intensity I be e. The electrons in this conductivity level are then (1) produced by adsorption of light by the bromine ions of the grain, (2) produced by reversal from latent image centres, (3) removed by combination with the bromine atoms produced in (1), and (4) removed by other traps in the grain. In (2) the rate will depend on the intensity I, the coefficient of absorption for thallium atom complexes and/

*The following is an extension of an equation partly developed by J.A. Thom.

and the 'area' of the complex exposed to illumination.
If it is assumed that only the outer surface is con-
cerned, for a reasonably large complex the number of
surface atoms will be proportional to r^2 where r is
the radius of the spherical aggregate.

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

where k = coefficient of absorption for the grain
bromine ions, and L = number of other available traps
in the grain.

Bromine atoms are (1) produced by the initial
absorption (5) removed by acceptor A (3) removed as
bromine ions by addition of electrons (6) removed by
mutual recombination probably at the grain surface as
bromine molecules (7) removed by action on the latent
image speck itself.

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

Bromine molecules are (6) formed from bromine atoms(8)
removed by action on the latent image (9) removed by
acceptor action, diffusion, evaporation. Here for
simplicity acceptor action is included in k_9 .

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

The rate of formation of latent image, i.e. the rate
of addition of thallium atoms, on the assumption that
one electron added to the speck is neutralised by one
thallium ion from some interstitial or other lattice
position/

position, is then

$$\frac{dx}{dt} = kse - k_2 sIr^2 - k_7 s(Br) - k_8 s(Br_2)\ldots\ldots (4)$$

In this equation 4, k will include a mobility factor
for thallous ion movement.   To eliminate e, Br, Br_2
the stationary state concentrations are assumed:

$$\frac{de}{dt} = o = \frac{d(Br)}{dt} = \frac{d(Br_2)}{dt}$$

With Br_2 and e given by equation 3 and 1 respectively,
substitution in equation 2 gives:

$$k_3 k_6 (Br)^3 + (Br)^2 (k_4 k_6 L + k_3 k_7 s + k_3 k A) +$$

$$(Br)(k_4 k_7 sL + k_4 k_5 AL + k_2 k_3 sIr^2) - k_1 k_4 IL = 0\ldots\ldots(5)$$

This cubic equation cannot readily be solved for Br.
The cubic term is eliminated if L = 0, which renders
the mechanism inconsistent, or if k_6 = 0. For the
present, therefore, we obtain an approximate expression
for (Br) by omitting the cubic term while retaining
in the other terms all the reactions above. Solving
the resultant quadratic for Br, we find $k_6 (Br)^2$ from
equation 2 and e from equation 1; by substitution in
equation 4, dx/dt becomes

$$\frac{dx}{dt} = \frac{VI}{(y+d)} \left[B - y(F + G/I) - My^2/I \right] \quad \ldots\ldots\ldots(6)$$

where $y = \left\{ \sqrt{(m + Ir^2)^2 + nI} - (m + Ir^2) \right\}$,

$\quad m = k_4 L(k_7 s + k_5 A)/k_2 k_3 S$,

$\quad n = 4k_1 k_4 La/(k_2 k_3 s)^2$,

$\quad a = k_4 k_6 L + k_3 k_7 s + k_3 k A$,

$\quad V = 1/k_2 k_3 s$,

$\quad B \,/$

$$B = \frac{2ask}{k_3}\left[k_1 - \frac{k_1 k_4 k_8 L}{k(k_9 + k_8 s)} + k_2 sr^2 - \frac{k_4 Lk_2 r^2}{k}\right]$$

$$F = (k_2 s)^2 k_3 r^2\left[1 - k_8 s/(k_9 + k_8 s)\right],$$

$$G = k_2 sk_4 L\left[k_7 s - k_8 s(k_5 A + k_7 s)/(k_9 + k_8 s)\right]$$

$$M = \frac{(k_2 k_3 s)^2}{2a}\left[k_7 s - k_8 s(k_5 A + k_7 s)/(k_9 + k_8 s)\right],$$

$$d = 2ak_4 L/k_2 k_3^2 s = G/M.$$

This equation may then be considered in relation to
the developed density on the assumption that the
number of developable centres bears a constant pro-
portion to the number of all centres throughout the
emulsion.

It is difficult to assess the actual effects of
increasing A, s, and r^2 in the general equation with-
out knowing all the quantities involved. But in view
of the facts already collected it is interesting to
find the general effects of such increases. In the
case of the fast emulsions the term A which includes
the gelatin's accepting capacity will be considerably
increased. If all other terms remain constant, m
will increase considerably and n will increase too
but not to such a large extent. With low intensity
ranges which have been shown to be sufficient to pro-
duce an H and D curve (0.001 - 14 scale divisions) for
the fast emulsions the term nI will be small and so y
becomes very small tending to zero. So in equation 6
both subtraction terms are very small. The term B
becomes much larger and so the forward rate $\frac{dx}{dt}$
is/

is increased. It is also to be noted that as the intensity falls the subtraction terms become larger provided y is not zero so that the rate of latent image formation diminishes. So the general result of increasing A is to produce a much faster emulsion and such is the case with the fast emulsion, the great increase in A being primarily due to the gelatin. It is also noted that if A is very large then small amounts of acceptors additionally added will not make a great difference to the general rate of image production.

The number of sensitivity centres is greatly increased in the fast emulsions as compared with slow emulsions and again the effect of increasing s in the rate equation can be estimated generally. The term y tends to zero, B increases considerably, and therefore the general rate $\frac{dx}{dt}$ increases. The increases in plate speed observed are more likely due to simultaneous increases in A and s rather than to increases in any single term.

The effects of increasing r in the equation are very complex. In general the rate $\frac{dx}{dt}$ will depend on B which depends in turn on the sign and magnitude of the term $k_2 r^2 (s - \frac{k_4 L}{k})$. Thus at a given light intensity the resulting rate of latent image production can be either positive or negative depending on the value of r. Experimentally this was found/

found to be the case (see Fig. 31). In the slow
emulsions J.A.Thom found that at certain high primary
densities no reversal was found for blue light. The
same phenomenon was found for the fast emulsions for
low intensity green light secondary exposures. It is
thought that at these densities the structure of the
grain is altered and the equation becomes inappli-
cable.

In the following sections the data obtained
from the slow emulsions was used in the equation and
the results compared with those found in experimental
work.(11).

Reversal by blue light.

Here s, A and L are taken as constant. The
effect of secondary blue illumination may then be
illustrated numerically for the intensity range
0.01 to 150, the necessary constants being given the
following values: $m = 1$, $n = 10$, $r^2 = 10$, $F = 2.0$,
$G = 0.21$, $M = 0.0798$, $B = 0.999999$ (7). These con-
stants are derived from consideration of Fig. 4[11]
with respect to the value of the bleaching limit,
the intensity at which bleaching is a maximum and the
fact that little or no difference in density, i.e.
change in dx/dt, appears at the secondary intensity
150. At this highest intensity the rate of alter-
ation of density (i.e. dx/dt) has been taken as
exactly zero; since the rate is the product of
the/

the intensity I and the difference factor

$B - y(F + G/I) - My^2/I$, it is necessary at the
higher intensities to work out the values of y and B
to several decimal places. Calculated results are
given in Table 18.

Table 18.

$r^2 = 10$ F = 2.0   G = 0.21   M = 0.0798   B = 0.999999 (7)

I	0.01	0.1	0.2	1.0	5	10	20	50	150
$\frac{dx}{dt} x\ 10^4$	-1.52	-4.30	-3.87	-1.46	-0.23	-0.1	+0.1	+0.1	0

The maximum bleaching effect thus occurs at an inten-
sity of approximately 0.1; if effects due to a rate
of 0.2 and less are regarded as negligible, with thus
no diminution in observed density over the range 5 to
150, the calculated results are in general agreement
with the experimental results of Fig. 4(11). Rates
are here compared with density on the assumption that
no change in developed density corresponds to zero
rate of change of the size of the latent image centres.

The above equation may then be applied to other
initial primary densities by consideration of variation
of r^2, it here being assumed that each density can be
associated with a particular value of r^2. The cal-
culated value of y will vary with r^2, F will be
proportional to r^2, and B may be expected to show some
variation, but all the other constants will remain as
before/

before. The value of B is taken as that which will give no change in dx/dt for a small change in r^2 at the highest intensity as before, as indicated by experiment. The values for $r^2 = 9.5$ are given in Table 19.

Table 19.

$r^2 = 9.5$ F = 1.9 G = 0.21 M = 0.0798 B = 0.999997(7)

I	0	0.01	0.1	0.2	1	5	10	50	150
$\frac{dx}{dt} \times 10^4$	0	-1.52	-4.3	-3.76	-0.895	+0.55	+0.73	+0.65	0

For the lower value of r^2, corresponding to a lower primary density, the bleaching limit shifts to a lower value of I, and for intensities just above such limits a pronounced increase in rate and density is indicated, in agreement with experiment.

The value of B may be expressed as $P + Qr^2$

when $P = \dfrac{2askk_1}{k_3} \left[1 - k_4 Lk_8/(k_9 + k_8 s) \right]$

and $Q = \dfrac{2askk_2 s}{k_3} \left[1 - k_4 L/ks \right]$

The values of B in Tables 18 and 19 for $r^2 = 10$ and 9.5 may then be given by $B = 0.9999597 + 0.000004\ r^2$; on this basis we may then calculate values of dx/dt for values of $r^2 = 9, 8, 7$ and 5. The results are given in Table 20.

Table 20 /

Table 20.

r^2	B	$I =$	0.01	0.1	0.2	1.0	5	10	50	150
9	0.999995(7)	$\frac{dx}{dt} \times 10^4$	-1.53	-4.29	-3.6	-0.235	1.49	1.7	1.6	0.014
8	0.999991(7)	"	-1.54	-4.27	-3.29	+1.5	4.04	4.34	3.7	1.2
7	0.999987(7)	"	-1.55	-4.22	-2.84	4.0	7.88	8.4	7.5	3.9
5	0.999979(7)	"	-1.58	-4.02	-1.36	13.3	23.8	25.4	24.9	19.6

Again with lower values of r^2, the bleaching limit is
altered to a lower value of I and for intensities just
above such limits increases in rate are indicated;
further, the intensity at which maximum bleaching
should occur shifts appreciably to lower intensities,
in agreement with the results of Fig. 4 (11) for
longer illumination and consequent lower r^2 values.

The above constants have also been applied to the
case where r^2 is negligible, as an approximation to
the conditions of a previously exposed plate. Results
are as follows:

Table 21.

I	0.01	0.1	0.2	1.0	10	100	1000
$\frac{dx}{dt} \times 10^4$	-1.64	-2.24	10.4	172	1340	5610	19400

The occurrence of the negative rates may be ascribed
to the neglect of the Br^3 term of equation (5), which
will be more appreciable when the other terms involving
r^2 are small. The calculated value of Br is then too
large: a smaller value would tend to remove the
negative rates. From results obtained by using both
slow/

slow and fast thallous bromide-iodide emulsions an exact straight line relationship appears to hold between the primary density and log I_{BL} (Figs. 32,33). As the speed of the emulsion increases the line is displaced towards lower intensities and higher primary densities as would be expected. The slope of the lines obtained also appears to be dependent on the emulsion and the treatment given, but for any one emulsion (Fig. 33) the slope remains constant.

If we ascribe an 'average' value of r^2 to each developed density, the relationship between r and D becomes of immediate interest. From the calculated results of Tables 18, 19 and 20, we have the following figures for the respective bleaching limits (I_{BL}) by graphical interpolation:

r^2	10	9.5	9	8	7	5
log I_{BL}	1.18	0.40	0.05	$\bar{1}.80$	$\bar{1}.60$	$\bar{1}.40$

From the graph of r^2 against these values of log I_{BL} the values of r^2 corresponding to the experimental bleaching limits for the experimental densities (11) may be directly obtained, as shown in Table 22.

Table 22 /

Table 22.

D	log I_{BL}	r^2	r^2 calc.
0.077	$\bar{1}.40$	5.0	5.0
0.100	$\bar{1}.50$	6.4	6.0
0.140	$\bar{1}.69$	7.4	7.3
0.254	0.70	9.7	9.4
0.330	1.20	1.0	1.03

It is obvious that r^2 does not vary linearly with D, but it may be well represented by the logarithmic relationship

$$r^2 \text{calc.} = 14.33 + 8.33 \log_{10} D \dots\dots\dots (7)$$

These values of $r^2{}_{calc.}$ are quoted also in Table 22 in the last column; the agreement is satisfactory.

The general rate equation. Integration of the general equation with respect to r and t, followed by substitution of r according to equation 7 above would give theoretically an equation by which the developed density could be calculated for any exposure. The general equation, however, is given as dx/dt, representing the rate of growth of the latent image speck in terms of addition of thallium atoms. If x be the total number of thallium atoms in a spherical speck, then $vx = \frac{4}{3} \pi r^3$, where v is the volume of a thallium atom. Hence $\frac{dr}{dt} = \frac{dx}{dt} \frac{v}{4\pi r^2}$, and the general

equation/

equation becomes

$$\frac{dr}{dt} = \frac{V'I}{r^2(y+d)} \left[B - y(F + G/I) - My^2/I \right] \quad \ldots\ldots (8)$$

We may first test the applicability of equation 7 in this respect by considering the reversal by green light, for which k_1 may be taken as zero, since no image is produced by such illumination in the case of the slow emulsions. Equation 8 then reduces to

$$\frac{dr}{dt} = -k_2 sI (1 - ks/k_4 L) = -V''I \quad \ldots\ldots\ldots (9)$$

On integration, $r = C - V''I(t + E)$, where V'', E and C are constants. The following equation (10) should then be valid.

$$\sqrt{(14.33 + 8.33 \log D)} = C - V''I(t + E) \ldots (10)$$

The value of C will depend on the primary density to which the green light is applied. The continuous curves of Fig. 2[11], representing the rate of bleaching of two different densities 0.35 and 0.275 have in fact been calculated by taking $E = 0$, $V'' = 0.00253$, and C equal to $\sqrt{(14.33 + 8.33 \log D)}$ for each initial density.

The experimental points fit the calculated curves very well. Complete integration of the general equation 8 with respect to r and t is obviously complex, but an approximate integration for the conditions under which reciprocity relationships have been investigated (Fig. 6)[11] may be approached numerically as follows. The nitrite-free emulsion is/

is considered for which relative constants and rates
have already been estimated for the experimental con-
ditions in question, namely low density corresponding
to an r^2 range 5 to 7, and intensity values roughly
10 to 500 divs. The actual numerical values of $Z =$
$(y + d)/1000 \left[B - y(F + G/I) - My^2/I \right]$ for such
intensities are given in Table 23.

Table 23.

r^2	$I =$	10	50	100	500
5.0	Z	0.755	2.11	3.94	20.1
6.0		1.305	3.60	6.80	36.1
7.0		2.50	6.34	11.90	66.8
8.0		6.68	12.40	23.0	135.0

Examination of these shows that the effect of alter-
ation of I is approximately the same at each value
of r^2 except at the lowest intensity for the higher
values of r^2. Thus at $r^2 = 5$, the ratios of Z_{100}
to Z_{10}, Z_{50} and Z_{500} are 5.19, 1.86, 0.195; at
$r^2 = 6$, 5.21, 1.89, 0.188; at $r^2 = 7$, 4.76, 1.88,
0.178; at $r^2 = 8$, 3.44, 1.86, 0.171. These Z values
may therefore be written as $f(r^2)$, $f(I)$, and the
general equation becomes on integration

$$f''(r^2) = \frac{KI}{f(I)} \quad (t + E) \quad \text{where E is a}$$

constant. For a given density, $f''(r^2)$ will be
constant by virtue of relation 7: corresponding
values of t and I will then satisfy the equation

$$\frac{I_1(t_1 + E)}{f(I_1)} = \frac{I_2(t_2 + E)}{f(I_2)}$$

For/

For any other density within the range considered, the same relation will apply, in agreement with the experimental results of Fig. 6[11].

An attempt to determine whether such an expression gave a linear relationship between log t and log I as shown experimentally was made by expressing values of Z by the equation

$$Z = 0.0111 \ (I + 90/I)(1 + 0.0040 \ r^8)$$

which reproduces approximately the values of Table 23. By reference to equation 7, the necessary integration constants were obtained from two experimental points on the reciprocity curve for one particular density and the entire curve was then calculated: the calculated relation between log I and log t, though not linear throughout, was approximately so at the intermediate intensities.

It is a point of interest that in the presence of nitrite the experimental reciprocity-relationships are approximately the same as before. The effect of alteration in acceptor A in the general rate equation is very complex, but an increase in A, considered in relation to the various factors involving A, always produces an increase in rate. The necessary constants being unknown, numerical illustration must necessarily be uncertain, but it is to be noted that if alteration in A is small, the constants being such that only m

is/

is affected, then we have the following rate values
for m = 1.01 in place of 1.00 as previously considered,
for a density corresponding to $r^2 = 5.0$.

Table 24.

	$r^2 = 5.0$		m = 1.01			
I	0.01	0.1	0.2	1	10	150
$\frac{dx}{dt} \times 10^4$	-1.22	-1.98	1.51	17.8	30.8	25.0

In comparison with the corresponding results of
Table 20, the positive rates are everywhere increased,
but the bleaching limit shows only a small alteration
from I = 0.23 to 0.15 divs. The general effects of
increased A for the slow emulsions is to shift the
bleaching limit to lower intensity values. These
indications are in accord with experiment.

The parallelism of the experimental reciprocity
curves suggests that the calculated results of Table
24 should be in agreement with the previous expression
$Z \propto (I + 90/I)$. That this is approximately so is
apparent from Table 24; at I values of 10 and 1,
relative rate values are 30.8/17.8 = 1.73, to be
compared with the previous value of 25.4/13.3 = 1.9.

The general rate expression derived from these
simplified assumptions thus gives a picture of latent
image/

image formation which is in general agreement with the experimental work obtained. The general Gurney-Mott theory gives for the thallous bromide system, an adequate picture of the mechanisms involved after light absorption. It may be claimed that the results so far obtained do support the present view of latent image formation.

OTHER SYSTEMS.

Other Systems

Since it was already known that some salts of lead, antimony and bismuth darken on prolonged exposure to light, preliminary investigations were carried out on emulsions containing these salts with a view to finding any possible latent image formation.

Lead Bromide

The first method of preparation of the lead bromide emulsion was based on the methods used for thallous bromide emulsions. The amounts of gelatin, potassium iodide, potassium bromide and water were kept the same (7 g.; 0.067 g.; 1.33 g. and 33 ml. respectively). When the mixture of gelatin and water was homogeneous at 35°C, 33 ml. of a lead nitrate solution containing 4.05 g. lead nitrate in 50 ml. was added. It was noticed after the emulsion had been stirred that the gelatin had coagulated, rising to the surface in rubbery lumps. The emulsion became impossible to wash and remelt into a homogeneous form necessary for coating.

The second method of making the emulsion was to prepare the homogeneous solution of gelatin and water as before. The potassium bromide and iodide were dissolved in a small amount of water in a separate beaker. 33 Ml. of the lead nitrate solution above were added slowly to the beaker from a burette. The lead bromide so precipitated was filtered, washed free/

free of excess lead nitrate and added to the gelatin solution, vigorous stirring being employed. The emulsion was stirred for 30 minutes, allowed to stand in the thermostat at 35°C. for a further 30 minutes and then chilled rapidly and left overnight. The following day the emulsion was remelted and coated on glass plates, the washing process being unnecessary. The plates so prepared after drying were not so opaque as the corresponding thallous bromide plates. A second emulsion was prepared in which twice the amount of lead bromide was added but again the emulsion had the unusual thinness.

If an unexposed piece of plate coated with either of these two emulsions was put in ordinary hypo, the lead bromide was not dissolved but remained apparently quite unchanged for a long time (4-5 hours). Actually on testing the solubility of freshly precipitated lead bromide in sodium thiosulphate it was found that the lead bromide dissolved completely. In view of this the conclusion reached was that the gelatin must have absorbed the lead bromide in some way, thus preventing rapid dissolving in the hypo.

Because of this a special emulsion was prepared in which 4 g. aluminium chloride was added first to the gelatin solution before the lead bromide. The object of this addition was to provide a trivalent ion/

ion which would be preferentially absorbed so that the
lead bromide particles would be left on the surface of
the gelatin.   This emulsion required a considerable
amount of vigorous stirring before complete homogeneity
was achieved but the emulsion after remelting on the
following day gave coated plates which had the usual
opaqueness.   The pH of the emulsion was about 18 . On
immersing a plate coated with this last emulsion in
ordinary fixer most of the lead bromide dissolved off
the plate in 15 minutes but a faint opalescence due to
lead bromide remained in the plate for some considerable
time afterwards.

Effect of White Light on Lead Bromide.

Pieces of plate from ordinary and aluminium-contain-
ing emulsions were exposed with the wedge in position
to white light from the mercury lamp for 1 hour. After
this time a considerable print-out effect was observed.
Even 30 minutes' exposure showed the effect in the
wedge squares which transmitted most light.   The
presence of aluminium chloride did not appear to have
any accelerating effect as seen from the print-out
effects.

Exchange with Silver Nitrate.

All plates were exposed to white light for 30
minutes with the wedge in position except where stated.
Exposed lead bromide plates were left for 5, 10 and 60
minutes in 10% silver nitrate. The rest of the pro-
cessing/

cessing was similar to that of the thallous bromide
plates, the developer used being ordinary M-Q for 3
minutes.   In neither of these cases was there any
sign of a latent image on development.   A small plate
was left in 20 ml. water for 40 min. and the solution
tested for lead ions by means of potassium iodide and
potassium dichromate.   A slight positive result was
apparent but it appears that lead bromide can only
be freed from the gelatin in amounts which are too
small for effective exchange with silver ions.

The effect of the presence of dilute acids in the
silver nitrate solution was investigated next.   The
addition of dilute nitric acid even one drop per 20
ml. silver nitrate resulted in a destruction of the
gelatin film.   Dilute acetic acid was also used, but
again on development there was no sign of the wedge
squares although the acetic acid did not destroy the
gelatin.

The next idea was to use an intermediatory
exchange between the lead and silver stages. Potassium
ferrocyanide and thallous nitrate solutions were both
used, but in neither case was there any evidence of
the final lead-silver exchange being effected.

Since all attempts at exchanging lead ions for
silver had been unsuccessful, direct development of
possible latent image formation in lead bromide was
attempted.

Ordinary/

Ordinary development with M-Q developer had no
effect on an exposed lead bromide plate. The possi-
bility of physical development was next investigated.
The two solutions for Odell's physical developer
were prepared ( ). An exposed lead bromide
plate was immersed in the forebath for 5 min. and
after a brief rinsing the plate was left in the
developer solution for 2 hours. Even at the end of
this time there was no sign of the wedge squares.

The effect of other reducing solutions was
investigated. Alkaline (with sodium hydroxide)
hydrazine hydrochloride and alkaline hydroxylamine
hydrochloride solutions were used on exposed lead
bromide plates, but again after several hours'
immersion no difference between exposed and unexposed
plates could be detected.

Emulsions of Antimony Salts

Two emulsions were made, one, containing anti-
mony oxybromide which darkens in daylight and the
other of a mixture of antimony oxide and antimony
sulphide which loses its brilliant orange colour on
standing in daylight.

(a) Antimony Oxybromide

This emulsion was prepared by adding freshly
precipitated antimony oxybromide to a homogeneous
solution of gelatin and water, prepared as above
for lead bromide emulsions. The antimony oxybromide
was/

was prepared by heating 4 g. antimony oxide with excess (15-20 ml.) concentrated hydrobromic acid and filtering the solution into water. The antimony oxybromide so prepared was filtered, washed and added, with vigorous stirring, to the gelatin solution. A second emulsion was prepared with the prior addition of 4 g. of aluminium chloride to the gelatin solution. Again there was no marked difference in speed, the aluminium chloride again facilitating the action of the fixer. After the addition of the antimony oxybromide the emulsion was treated in the same way as for the lead bromide emulsion.

Two small squares, one from plates coated with antimony oxybromide emulsions containing aluminium chloride and the other from a plain antimony oxybromide emulsion, were exposed to white light for 1 hour with the step wedge in place. After this time there was no visible print-out effect, the rate of formation of the image thus being very slow. Unexposed and exposed plates were given the usual silver nitrate treatment and on development in M-Q developer no difference could be detected. Attempts were made to use alkaline hydroxylamine hydrochloride as a direct developer but again after 2 hours there was no evidence of development.

(b) /

(b) An emulsion of 50:50 antimony oxide and antimony sulphide was prepared in a similar way to the previous emulsion, the antimony sulphide being freshly precipitated in red light and added with the antimony oxide to the gelatin solution. The rest of the procedure is the same as for the antimony oxybromide emulsion.

A small square of the antimony sulphide-oxide emulsion was exposed to white light for 3 hours with the wedge in position. A very slight print-out effect was visible. Again attempts to develop up a possible latent image using the silver exchange did not meet with success. The use of alkaline hydroxylamine hydrochloride again proved unsuccessful.

Thus for lead bromide and to a very much smaller extent antimony oxybromide and sulphide emulsions, it appears that there is every possibility of latent image formation as indicated by the print-out effects. It remains, however, to find some means of exchange for silver or of direct development.

Bismuth Oxybromide Emulsions.

4 G. gelatin were heated up with 50 ml. water in a beaker. Vigorous stirring was used throughout.

The bismuth oxybromide was obtained by heating up 4 g. bismuth oxide with 15-20 ml. concentrated hydrobromic acid and filtering into water. The precipitated bismuth oxybromide after washing was added/

added to the gelatin solution. The rest of the
treatment was as for the antimony oxybromide emulsion.

A small square from a plate coated with bismuth
oxybromide showed relatively rapid darkening when
left in sunlight, a visible effect being seen after
3 hours.

A small bismuth oxybromide square was exposed to
white light from the mercury lamp for 10 minutes with
the wedge in position. It was processed in exactly
the same way as the thallous bromide plates. After
the 45 min. wash the plate was immersed in 2% potassium
bromide for 3 minutes to make sure that there was no
silver nitrate left. The plate was observed while
it was in the M-Q developer and after 2 minutes in
which nothing happened, the wedge squares became
visible. The total effect is not nearly so pronounced
as in the case of thallous bromide plates but it is
present. Again the same difficulty of the slow
effect of the hypo solution was encountered. It was
found that if the plate was left in the hypo solution
overnight in the darkroom, a clear plate except for
the developed wedge squares was obtained. The long
period in the fixer apparently had very little effect
other than slowly dissolving off the bismuth oxy-
bromide which was left. In the case of bismuth
oxybromide/

oxybromide plates the silver exchange does take place
but it is by no means complete. If the time of
immersion in silver nitrate is increased to 60 minutes
the final deposit of silver obtained after develop-
ment is slightly darker, but the effect is not very
noticeable. A plate examined in daylight after a
similar exposure shows no sign of squares so that the
image present is a latent one and not merely a print-
out effect. Another small square was exposed for 10
min. to white light with the wedge in position and
was developed directly for 4 minutes in the M-Q
developer. Nothing was seen of the wedge squares.
This indicates that the deposit seen after develop-
ment must be the result of a silver exchange.

After the immersion of the plate the silver
nitrate solution was treated with excess dilute hydro-
chloric acid and the silver chloride filtered off. On
passing hydrogen sulphide gas through the clear sol-
ution a slight brown precipitate of bismuth sulphide
was formed, indicating the presence of bismuth ions
in the solution.

The next few plates were all exposed for 10 min.
to white light with the wedge in position. They were
all immersed in silver nitrate for 10 minutes.
Additions were made to the silver nitrate to try to
increase/

increase the extent of the silver exchange. In one experiment 25 ml. of dilute acetic acid were added to 25 ml. silver nitrate and in another 5 g. of potassium nitrate but neither gave any noticeable improvement. An attempt was made to use silver acetate instead of silver nitrate with the most concentrated solution possible (1%), but after 10 min. in the acetate solution and the usual processing and development, the wedge squares were not apparent; this may be due to the low concentration of silver ions present in the solution.

Attempts were made to speed up the action of the fixing solution by additions of other substances which were known to form soluble complexes with bismuth salts. Neither the addition of 2 g. potassium metabisulphite, nor the addition of potassium bromide to the fixer caused any difference in the rate of dissolving. Potassium iodide additions although dissolving the bismuth oxybromide, also destroyed the gelatin film at the same time. This occurred even with very small quantities of potassium iodide. Alkaline hydroxylamine hydrochloride was again used as a direct developer, but again no difference was found between exposed and unexposed plates.

It is known (60) that bismuth oxybromide is changed to bismuthyl hydroxide BiO(OH) by the action of potassium hydroxide, and that bismuthyl hydroxide can/

can be reduced by stannous chloride solution to bismuth monoxide BiO, which in turn is converted to metallic bismuth by the action of aqueous potassium hydroxide alone.

A small bismuth oxybromide plate was exposed for 10 minutes to white light with the wedge in position. The plate was then immersed for 15 minutes in a 20% potassium hydroxide solution. It was then given a brief rinsing and left for 15 minutes in 2.5% stannous chloride solution and here it was noticed that the plate became transparent. Again after a brief washing the plate was immersed in 20% potassium hydroxide. Immediately the plate went completely black due to the formation of bismuth metal. This treatment is apparently too drastic for the whole plate was reduced. It was then interesting to know if milder treatment would result in the stannous solution attacking preferentially any latent image formation which might be present.

A stock solution of stannous chloride-potassium hydroxide was prepared by taking 50 ml. 2.5% stannous chloride and adding 20% potassium hydroxide drop by drop until the precipitate first formed just disappeared on shaking.

A plate was exposed for 6 minutes to white light with the wedge in position and then immersed at once in 25 ml. of the stock solution for 4 minutes. A faint/

faint image of the wedge squares appeared after 2
minutes. Although the effect was only very small it
may be that this solution acts on bismuth oxybromide
plates in a similar way to the action of M-Q developer
on silver bromide plates. Since bismuth metal is not
easily attacked by air, after fixation the plate should
be reasonably stable.

As a last attempt to speed up the fixing process
dilute hydrochloric acid was used as a fixer. This
did dissolve up the bismuthyl hydroxide but unfortun-
ately the bismuth metal was attacked afterwards.
Further work on this aspect is necessary.

SUMMARY.

Latent Image formation made apparent by double decomposition with $AgNO_3$ and ordinary development has been studied in thallous bromide-gelatin systems. The plates prepared were found to be much faster than those previously made[11], relatively stable latent image formation and no reduction in capacity for such formation with time being features noted. The type of gelatin used was found to be largely responsible for the speed increases.

The speed of the emulsion was found to be increased by large amounts of bromine acceptors, but small amounts apparently had little effect. Contrary to previous work [11], the presence of iodide in increasing amounts decreased the sensitivity of the plate to blue light.

The thallous bromide plates were found to be directly sensitive to green light. Reversal was found to take place with red, green and low intensity blue light, but in the case of the blue light such reversals were only found at much higher primary densities and lower intensity values than in previous work. The straight line relation between the bleaching limit and the primary density was confirmed. A general desensitisation effect was found when malachite green and/

and methylene blue were added to finished emulsions and an increase of the intensity of light at which the bleaching limit occurred, was observed.

A study was made of the latent image distribution in thallous bromide grains, using dichromate bleachers, surface and total developers, and another reversal effect was observed, which was dependent on the internal image.

The Gurney-Mott mechanism of latent image formation is considered to be applicable in general to the thallous bromide system. An approximate general equation was extended and developed.

Finally, some preliminary work was done on the possible latent image formation in lead bromide, antimony oxybromide and bismuth oxybromide. In the last case latent image formation was shown to be present but was capable of development to a much smaller extent than in the thallous bromide system.

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