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DUFFIN / EMULSION CHEMISTRY



**PHOTOGRAPHIC
EMULSION CHEMISTRY**

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PHOTOGRAPHIC EMULSION CHEMISTRY

by

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P R E F A C E

Photographic science is at the same time a fascinating and frustrating subject. Its fascination comes from the bringing together in one subject many disciplines in science, covering as it does many branches of chemistry and physics. On the other hand, there is probably no other area of applied chemistry where the skill of the manufacturer has produced such sophisticated products while the published understanding of the process is so scanty. This is in part due to the complexity of the silver photographic system which for many years was much more of an art than a science and also because of the very great secrecy which surrounds the truly critical steps of the preparation of the emulsions.

The international character of photographic science is recognised by conferences held every two years attended by workers from many countries and many industrial corporations. This field of knowledge possesses a camaraderie second to none other among its band of devotees.

In spite of this interest and the vast amount of work which has been reported, the science of photography remains far from a tidy one. One author still disagrees with another and interpretations of the facts, and even in some cases the facts themselves differ from worker to worker. The general scientific reader or student approaching the welter of information available in research monographs and advanced books, even ignoring original scientific papers, could be forgiven for being confused rather than informed.

This book is therefore an attempt to present an overall and, wherever possible, well-defined picture of the chemistry behind the silver-halide photographic material today. The layout follows the logic of the preparation of these products going from the raw materials, through the various stages and concluding with colour and some of the non-conventional processes. Necessarily such a work must ignore some views and there will be many who cannot agree with all the conclusions. In defence of his omissions and errors of judgement, the author would plead that any attempt to take a definite view must inevitably lead to some mistakes. It is hoped nevertheless that the positive approach included in this book will assist those puzzled by so many alternative explanations of the same processes and provide a sound basis for students from which they can, if they desire, enlarge their knowledge by further reading.

In particular, this text is directed to City and Guilds and I.I.P. Final students and those reading for a Dip. Tech. degree. A knowledge of chemistry, generally around 'O' level is assumed although more basic points are explained if a clear understanding of them is vital to subsequent discussion.

The author would acknowledge his debt to his many friends and colleagues in this fascinating industry. Among these he would especially mention Mr R. B. Collins, Technical Director of the Photographic Film Division of the 3M Company at whose

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I SILVER HALIDES

Introduction

The basic constituent of practically all modern silver photographic materials is the *silver-halide emulsion*. Photographic emulsions are not strictly analogous to true emulsions, for example, emulsion paints, which are apparently homogeneous liquids consisting of a dispersion of small globules of oil in water, but are dispersions of very small solid particles, called *grains*, of *silver-halide* which are prepared in a liquid medium, usually dilute *gelatin* solution, which can be cooled, set and dried after coating on a base. These grains are in some cases too small to be detected by ordinary microscopes and can only be seen by the use of the electron microscope; the sizes range from 0.03μ diameter*, in the case of very fine-grain emulsions used for high resolution scientific work, to 2.5μ in the coarsest-grained fast negative or X-ray emulsions. Approximate grain sizes of a number of photographic emulsions are shown in Table 1.

TABLE 1.1
EMULSION GRAIN SIZES

Type of emulsion	Approx. mean Diameter μ
High Resolution Film	0.03
Chlorobromide Paper	0.2
Lithographic Film	0.35
Fine Grain Pan Film	0.7
Fast Negative Film	2.0
Fast Medical X-ray Film	2.5

A section through a typical photographic emulsion coating is shown in Figure 1.1

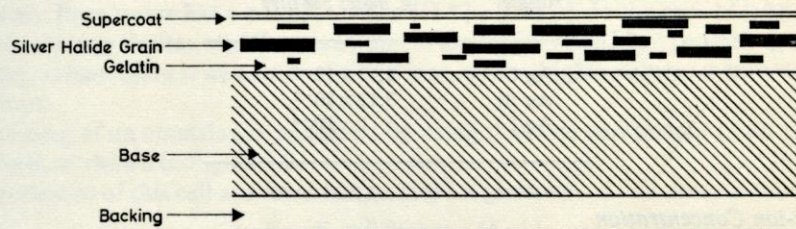


Fig. 1.1 Representation of silver halide coating

* The micron, μ , is one millionth of a metre (10^{-6} metres) and other units are the $m\mu$ or millimicron, which is a thousandth of a μ (10^{-9} metres) and the Ångstrom unit, Å, which is a tenth of a $m\mu$ (10^{-10} metres or 10^{-8} cms).

The silver-halide grains are crystalline, that is they possess some regularity of shape and, more important, the constituent parts are arranged within each crystal in a perfectly regular manner. The overall composition, shape, size and purity of the individual crystals are the factors controlling the photographic properties of the material.

Chemical Composition

A silver halide is a compound formed by the chemical combination of silver and *halogen*, which is a member of a group of non-metallic elements which are very electronegative and are very likely to pass into an electronegative state, called an *ion*. Silver-halide emulsions are never prepared commercially by the direct combination of the elements, but it is quite convenient to consider the substance from this point of view. Both silver and the halogens have a chemical combining power, called valency, of one, and it is therefore convenient to think of silver halides as silver-halogen units, one *atom* of each element being combined to make a *molecule*, although this is not an accurate picture of silver halide or of any other strongly ionic substance. The important fact is that the number of atoms of silver and of halogen are equal.

There are four halogens, namely fluorine, chlorine, bromine and iodine. The last three elements are used in photographic emulsions, silver fluoride is quite useless photographically. Using the chemical symbols for these elements we can represent the corresponding silver halides as AgCl, AgBr, and AgI.

The next important property of the silver halides is their solubility in water. Silver chloride is sparingly soluble in water and chloride ions can be used to precipitate silver quantitatively from solution. Silver bromide is less soluble than silver chloride and silver iodide is a highly insoluble substance. The solubilities of these three substances are given in Table 1.2.

TABLE 1.2
SOLUBILITY OF SILVER HALIDES
In water at 25° C.

<i>Halide</i>	<i>g. moles per litre</i>
Ag Cl	1.33×10^{-5}
Ag Br	7.12×10^{-7}
Ag I	2×10^{-8}

Silver-ion Concentration

Although the silver halides are very sparingly soluble substances, they do give some silver and halide ions in solution and the extent of this solubility is very important. The rate of solution of silver bromide, will be proportional to its concentration,

in other words

$$\text{rate} = k_1[\text{AgBr}],$$

while the rate of precipitation is similarly equal to

$$k_2[\text{Ag}^+][\text{Br}^-],$$

where $[\text{Ag}^+]$ and $[\text{Br}^-]$ are the concentrations of these ions in solution, and k_1 and k_2 are constants. At equilibrium, the state existing when silver-halide solid and solution are in contact, the rates of these two processes must be equal, otherwise either more silver bromide would dissolve or be precipitated.

Therefore

$$k_2[\text{Ag}^+][\text{Br}^-] = k_1[\text{AgBr}]$$

or

$$[\text{Ag}^+][\text{Br}^-] = \frac{k_1}{k_2}[\text{AgBr}]$$

In the presence of a large excess of solid silver bromide, the very small proportion dissolving will leave $[\text{AgBr}]$ substantially unchanged and therefore the whole of the right-hand side of this equation is a constant. Accordingly it follows that, in this system

$$[\text{Ag}^+][\text{Br}^-] = \text{a constant}$$

which is equal to 5.08×10^{-13} at 25°C .

If, therefore, more bromide ions are added to an emulsion, the silver-ion concentration will decrease. This silver-ion concentration is a very important quantity in photographic-emulsion chemistry and is expressed in a unit of pAg where

$$pAg = \text{logarithm} \frac{1}{[\text{Ag}^+]}$$

This is similar to pH, which is defined by

$$pH = \text{logarithm} \frac{1}{[\text{H}^+]}$$

because of the analogous equilibrium $[\text{H}^+][\text{OH}^-] = \text{constant}$. For example, the addition of an ionizing alkali, sodium hydroxide NaOH will increase the hydroxyl-ion concentration, causing the hydrogen-ion concentration to become low and the pH high. Pure water has a pH of 7, when $[\text{H}^+] = [\text{OH}^-]$. In the case of pAg , silver halides are very similar, and there is a point of neutrality when $[\text{Ag}^+] = [\text{Hal}^-]$; at lower pAg values there is an excess of silver ions, and at higher values an excess of halide ions.

The pAg of an emulsion is measured by using it as one component of an electrolytic cell, as shown in Figure 1.2.

The potential of this cell at a fixed temperature is given by

$$E = E_0 + 0.06 \log_{10} [\text{Ag}^+],$$

where E is the potential determined by an accurate voltmeter, taking negligible current otherwise the results will be faulty, and E_0 is a fixed voltage which depends on

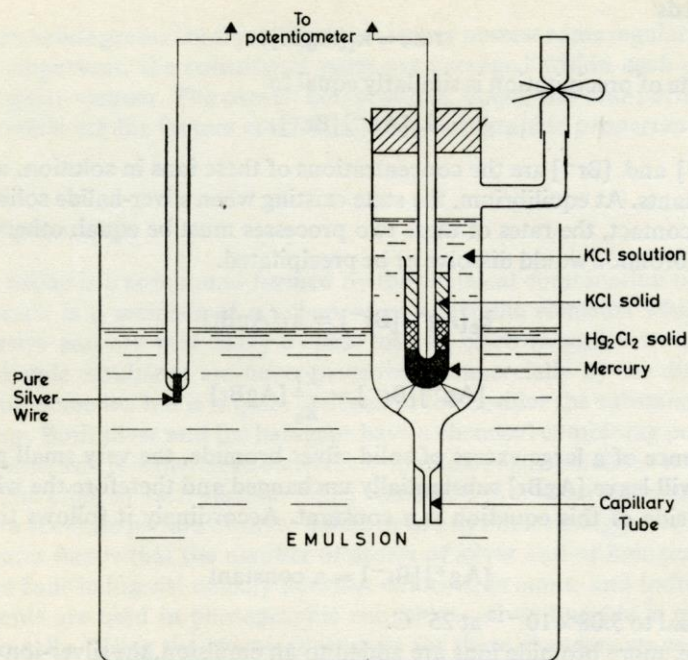
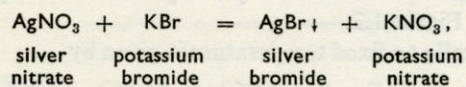


Fig. 1.2 Measurement of emulsion pAg

the other half of the cell and is determined by measuring the potential of a known silver-ion concentration and plotting a calibration curve. The pH is measured by a very similar system using a glass electrode, which responds similarly to the hydrogen-ion concentration.

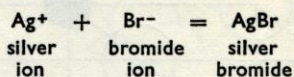
Precipitation

The low solubility of the silver halides means that if aqueous solutions containing moderate concentrations of silver and halide ions are mixed, then immediate combination will occur between these ions resulting in the precipitation of solid silver bromide. This is commonly represented as

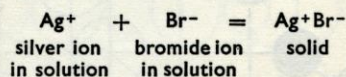


but is only partly true because the potassium nitrate exists at the end of the reaction in a completely ionized form, that is, the numbers of potassium and nitrate ions are

the same on both sides of the equation. We can therefore write the equation as



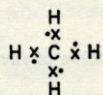
However, an even better way to consider the reaction is



Crystal Structure

The solid particles of silver bromide which are precipitated still consist of silver and bromide ions, but instead of being dispersed as individual mobile entities in the water they are now arranged regularly and at specific distances from one another in an ordered array called a *crystal lattice*. That is, silver bromide forms an ionic crystal and each unit is not Ag—Br, a kind of combination which does occur in some types of substances, particularly in those formed by carbon, called *organic compounds*.

These two types of bonding are called *covalent* and *electrovalent*. The links between individual atoms, which hold them together in compounds, are formed by the interaction of the electrons of the atoms. It will be remembered that atoms consist of a positively-charged core, the nucleus, where the mass of the atom resides, and a cloud of electrons, negatively charged and occupying definite positions in space outside the nucleus, called *orbitals*. The combining power of the atom is entirely dependent on the number and location of these electrons, and it is only those in the outermost shells which are usually involved in valency. The two types of bonds may be illustrated by the cases of methane and sodium chloride. In methane, one carbon atom is united with four hydrogen atoms. Each hydrogen has only one electron and two are needed to fill its shell, while carbon has four electrons in its outer orbit which requires eight for completion. By sharing electrons as



where the dots represent electrons originally on hydrogen and the crosses those from carbon, all the atoms are now completely satisfied resulting in a stable compound which is covalently linked. On the other hand, sodium, which possesses one electron only in its outer orbit, and chlorine, which has seven, react by the transfer of the lone sodium electron, leaving the next inner shell with its eight electrons as the outer shell, to the incomplete chlorine shell, bringing it up to its stable eight. This is shown as



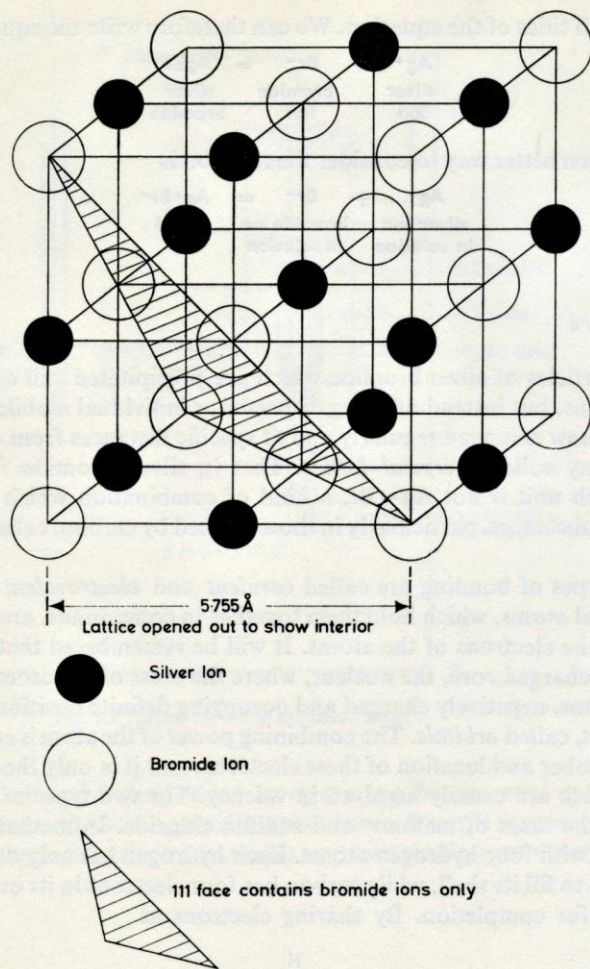


Fig. 1.3 Representation of silver bromide lattice

in which the circles stand for electrons from sodium and the ticks those from chlorine. In this form, sodium has one too few electrons and will therefore be positively charged, while the chlorine becomes negative. The electrons are not shared; both these ions contain complete outer shells and are therefore stable. The attraction between them is purely electrostatic and is therefore called electrovalency. Silver halides are of the electrovalent type. Silver bromide and silver chloride both form what is known as the *cubic lattice*; this means that the individual cell of a crystal is a cube with silver halide ions at opposite corners, as in Figure 1.3, and each crystal contains very many of these cells, as represented in Figure 1.4.

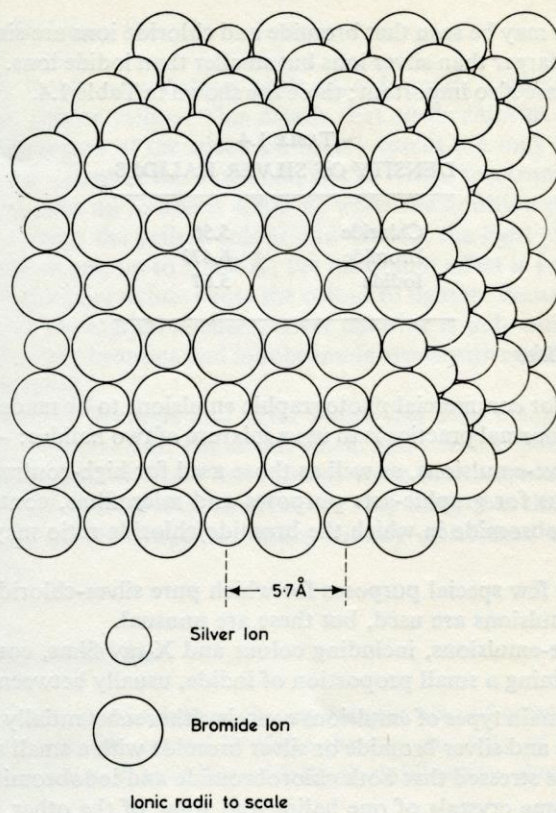


Fig. 1.4 Silver bromide lattice

The silver-iodide lattice is totally different, but no normal photographic materials use pure or substantially pure iodide and therefore the only lattice which is of photographic importance is the cubic one.

An important measurement is the distance between one silver ion and the next, which is 5.755 Å in silver bromide. The ionic radii of the elements are given in Table

TABLE 1.3
IONIC RADII

<i>Ion</i>	<i>Radius Å</i>
Ag ⁺	1.26
Cl ⁻	1.81
Br ⁻	1.96
I ⁻	2.20

1.3 from which it may be seen that bromide and chloride ions are similar in size and are considerably larger than silver ions but smaller than iodide ions. The densities of the three halides are also important, these are shown in Table 1.4.

TABLE 1.4
DENSITY OF SILVER HALIDES

Chloride	5.56
Bromide	6.473
Iodide	5.67

Mixed Silver Halides

It is very rare for commercial photographic emulsions to be made from one silver halide only. The normal practice is to use a mixture of two halides: —

1. Most positive-emulsions, as well as those used for high-contrast slower films, such as films for graphic-arts purposes and microfilms, contain mixtures of silver chlorobromide in which the bromide/chloride ratio may vary from 5% to 50%.

There are a few special purposes for which pure silver-chloride or pure silver-bromide emulsions are used, but these are unusual.

2. All negative-emulsions, including colour and X-ray films, contain silver bromide containing a small proportion of iodide, usually between 1% and 8%.

Therefore the main types of emulsions contain either substantially similar amounts of silver chloride and silver bromide or silver bromide with a small amount of silver iodide. It must be stressed that both chlorobromide and iodobromide emulsions do not consist of some crystals of one halide and some of the other, but that all the crystals are similar and contain both halides in about the same proportion. The similarity in size of the chloride and bromide ions enables them to mix freely throughout the crystals in all proportions. The overall properties of a range of silver-chlorobromide emulsions vary steadily as the proportions are changed. The much larger size of the iodide ion, relative to the others, and its very different response, in development for example, from that of the chloride and bromide, make a great deal of difference to the possible range of emulsion proportions. It is possible to include up to 20% of iodide in silver-bromide crystals without interfering with the lattice, although the emulsion would be useless photographically before that concentration of iodide is reached. The addition of small quantities of iodide has a very great influence on the properties of emulsions and a wide variety of emulsion types may be produced in the iodide range 1%–8%.

An important factor to be considered in the case of iodobromide emulsions is the location of the iodide, which may be present mainly at the centre of the crystal, distributed throughout the grain or mainly on the outside. The actual location of the iodide is determined by the preparation conditions and will clearly have an influence on the physical and chemical properties of the crystal.

Colour of Silver Halides

Silver chloride is colourless (white) while silver bromide is pale yellow and silver iodide somewhat deeper yellow. This means that silver chloride does not absorb light in the visible region of the spectrum to any extent but only in the near ultra-violet, and to some extent at the violet end of the visible spectrum. Silver bromide, however, absorbs light up to about $4,900 \text{ \AA}$, while the addition of silver iodide to silver bromide deepens the yellow colour and extends the light absorption further into the visible spectrum, up to $5,200 \text{ \AA}$, the maximum effect is produced by about 2.0% of iodide and higher values cause the colour to lighten. Because only absorbed light can have any photographic effect, silver chloride is only sensitive to u.v. and violet light, while silver bromide and iodobromide are sensitive to the violet and blue region of the spectrum.

The colour of silver bromide and silver iodide has been taken as evidence that they are not truly electrovalent. The electrovalent and covalent bonds as exemplified by methane and sodium chloride are extreme cases between which there is every possible type of intermediate state and it seems very likely that the electrons linking the silver and the halide atoms are more equally distributed than the formula Ag^+Br^- suggests.

Nature of the Crystal Surface

The outside surfaces and edges of the crystals are also of great importance. The surface of the silver-halide crystal is where the vast majority of the photographic processes take place, e.g. chemical sensitisation, stabilisation, dye sensitisation and

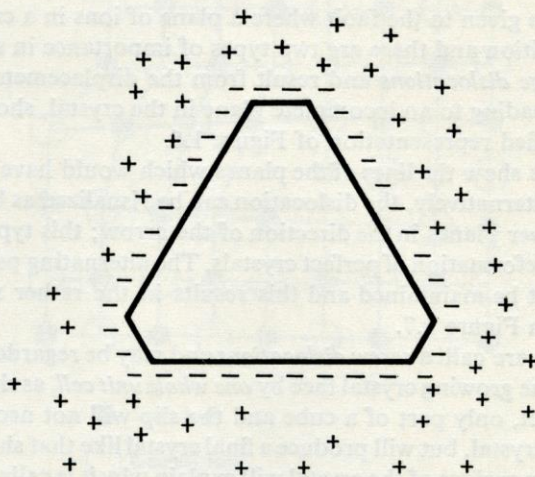


Fig. 1.5 Electrical double layer

development, and usually latent-image formation as well. In many of these steps another property of the crystal plays a part. although an emulsion crystal as a whole contains equal numbers of silver and halide ions, in suspension in a solution containing excess bromide ions, there is a layer of bromide ions closely associated with the crystal surface. This is called the electrical double layer (Figure 1.5) and results in the whole crystal being negatively charged relative to its environment. The layer is retained throughout the life of a silver-halide emulsion grain, except in certain special emulsions in the early stages of their formation, and its disappearance will immediately make the grain developable without the action of light, i.e. a fogged grain.

Also, each crystal is imperfect and not a perfectly ordered structure with flat surfaces; there may well be incomplete terraces and edges of silver and bromide ions on the faces as well as internal disorder, due to imperfect growth because of the random behaviour of the rapidly aggregating ions in the early stages of precipitation and growth or because of the presence of impurities. It is believed that these imperfections may play a vital part in giving the crystal its photographic sensitivity so the nature of some of these irregularities will now be examined.

Imperfections in Silver-halide Crystals

The imperfections which occur in silver halides are known as *dislocations* and *defects*, and these two terms have specific meanings.

Dislocations

This is the name given to the fault where a plane of ions in a crystal is displaced from its usual position and there are two types of importance in silver halides. The first are called *edge dislocations* and result from the displacement of the edge of a growing crystal, leading to an incomplete plane in the crystal, shown by the shaded area in the simplified representation of Figure 1.6.

The dotted lines show the lines of the planes which would have been formed in a perfect growth. Alternatively, the dislocation can be visualized as being produced by the slip of the lower planes in the direction of the arrow, this type of dislocation is caused by strain deformation of perfect crystals. The alternating pattern of silver and bromide ions must be maintained and this results in the rather more complicated situation shown in Figure 1.7

The second type are called *screw dislocations* and may be regarded as caused by the slip of a piece of the growing crystal face by *one whole unit cell*, as shown in Figure 1.8. This face is, in fact, only part of a cube and the slip will not necessarily be carried right through the crystal, but will produce a final crystal like that shown in Figure 1.9 the shape of the top surface of the crystal will explain why it is called a screw dislocation. With this dislocation the whole face in which the slip has occurred will be exactly

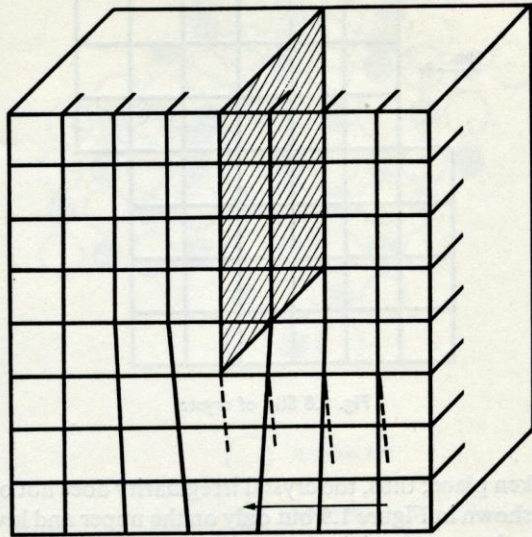


Fig. 1.6 General edge dislocation

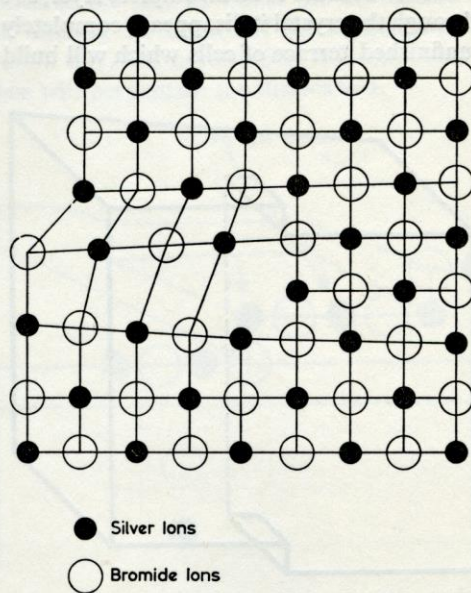


Fig. 1.7 Edge dislocation of silver bromide

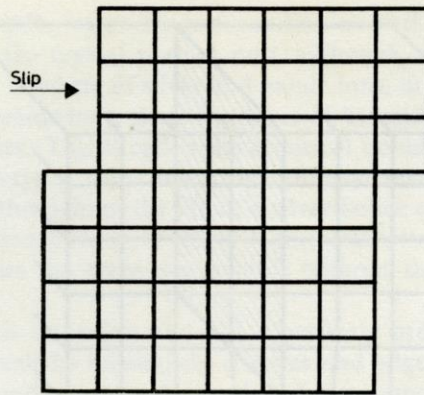


Fig. 1.8 Slip of crystal

as if no slip had taken place, thus, the crystal irregularity does not occur on the front face of the crystal shown in Figure 1.9 but only on the upper and lower faces. A screw dislocation is shown in more detail in the partial drawing in Figure 1.10, in which the silver and bromide ions have been added. It should be noted that, as with the edge dislocation, it is a whole unit cell which is dislocated; the crystal could contain both silver and bromide ions above the plane in which the dislocation occurs or might have only a one-atom terrace because of an incomplete layer, as shown in Figure 1.11. If the slip goes right through the crystal it disappears completely as a dislocation and merely becomes an unfinished terrace of cells which will build up to give a perfect cube again.

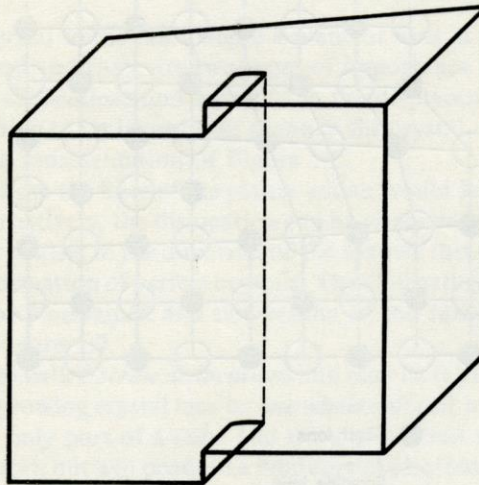


Fig. 1.9 Screw dislocation

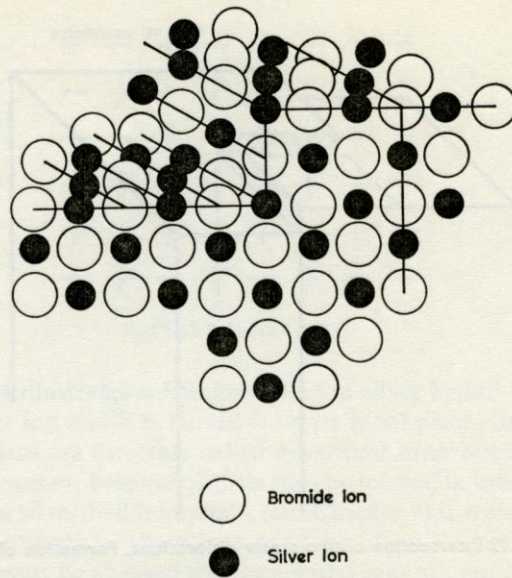


Fig. 1.10 Detail of kink in screw dislocation

Another important property of these two types of dislocation is that they cannot be cancelled out without some drastic treatment of the crystal. Growth of an edge dislocation will continue the face at which the dislocation emerges more or less indefinitely without altering the nature of the irregularity. The screw dislocation grows in a more subtle way, but nevertheless it is continued and growth upwards from the crystal face will perpetuate the dislocation.

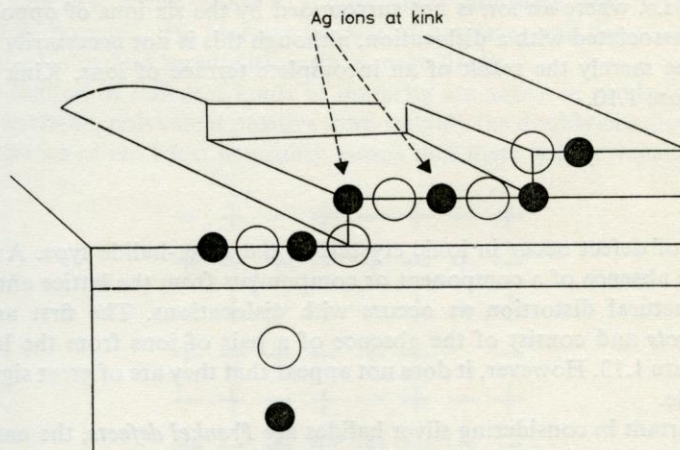


Fig. 1.11 Screw dislocation with incomplete terrace

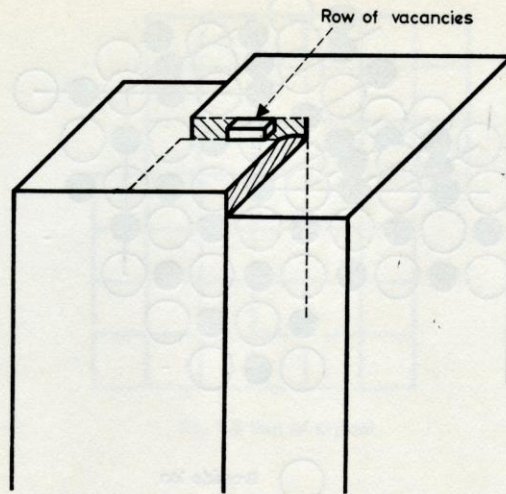


Fig. 1.12 Intersection of two screw dislocations. Formation of jog

An important further complication occurs in silver-halide crystals when two of these intersections meet one another. The discussion will be restricted to one possibility, the meeting of two screw dislocations at right angles, called a *jog* and shown diagrammatically in Figure 1.12. A row of vacancies will be produced in the space shown, in other words lattice positions will be unoccupied because of the influence of two dislocations.

Another important imperfection in silver halides, which is termed a *kink site*, consists of the actual edge ions at an incomplete part of a crystal, either internally or externally, i.e. where an ion is not surrounded by the six ions of opposite sign. This may be associated with a dislocation, although this is not necessarily the case, a kink may be merely the result of an incomplete terrace of ions. Kink sites are shown in Figure 1.10.

Defects

Two types of defect occur in ionic crystals of the silver-halide type. A defect is defined as the absence of a component or components from the lattice and implies no gross structural distortion as occurs with dislocations. The first are called *Schottky defects* and consist of the absence of a pair of ions from the lattice, as shown in Figure 1.13. However, it does not appear that they are of great significance in silver halide.

More important in considering silver halides are *Frenkel defects*, the name given to the omission of one ion from its position in the lattice and, in order to maintain electrical neutrality, its appearance at a non-lattice position, called an *interstitial*

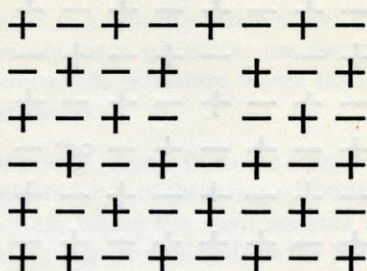


Fig. 1.13 Schottky defect

position. Figure 1.14 illustrates a Frenkel defect in silver halide which shows that it is the smaller silver ion which is moved from its usual place; the ions located in the interstitial positions are therefore called *interstitial silver ions*. The appreciably larger bromide ions cannot, because of their size, be located in interstitial positions. From recent work on silver-halide crystals, (see Chapter 9) it seems very likely that the majority of the interstitial silver ions are located on the surface of emulsion grains. However, it must be stressed that interstitial ions are not fixed like those in lattice positions but are free to move within the crystal lattice.

CAUSE OF IMPERFECTIONS. As has already been mentioned, imperfections of the above types may be produced purely from the irregular location of ions during the building of the crystal, dislocations and defects such as these are common in metallic crystals where all the ions are of one type or in very pure substances.

In silver-halide emulsion grains, however, there are deliberately introduced impurities which produce these deformations. Two of these impurities must be mentioned. The first is the iodide in iodobromide emulsions which, since it is a larger ion than bromide, will increase the size of one layer and therefore make the introduction of edge and screw dislocations more likely.

The introduction of different kinds of impurity are active in producing Frenkel defects, for example, polyvalent positive ions, notably the doubly-charged cadmium ion. Maintenance of electrical neutrality means that there will be vacancies associ-

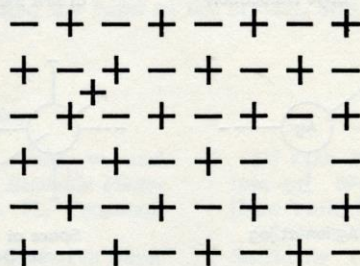


Fig. 1.14 Frenkel defect

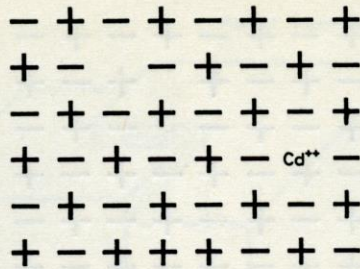


Fig. 1.15 Frenkel defect caused by cadmium

ated with each cadmium ion and also one fewer interstitial silver ion per cadmium ion. This is illustrated in Figure 1.15.

Pouradier quotes the energy of activation required to form Frenkel defects, these are 27,500 to 29,200 calories per mole for silver bromide and 38,900 calories per mole for silver chloride which suggests that the occurrence of Frenkel defects in silver chloride is fairly unlikely. It is therefore significant that cadmium salts are

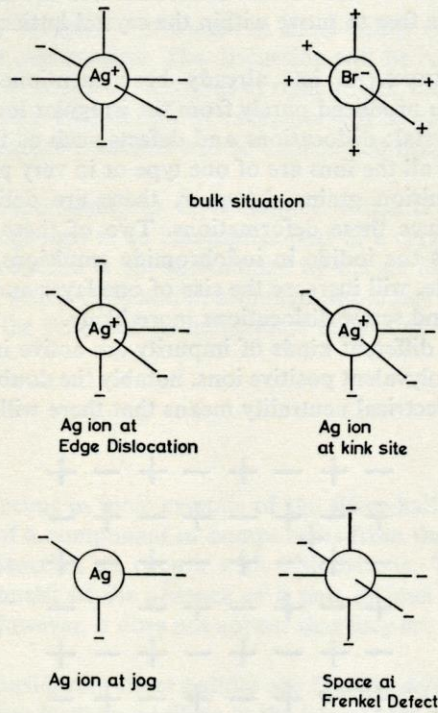


Fig. 1.16 Electrostatic balance in crystals

more frequently mentioned in connection with silver- chloride and chlorobromide emulsions, where frequently large quantities are incorporated, whereas they are used only rarely in iodobromide emulsions where the introduction of fairly small quantities produce large effects.

FUNCTION OF IMPERFECTIONS. Apart from the release of interstitial silver ions, there are other important functions of these imperfections. These are best illustrated by reference to Figure 1.16, where the environments of a silver ion at an edge dislocation and at a kink or jog are depicted. In the bulk of the crystal the charges are balanced because all the ions are surrounded by a complete group of ions of opposite charge. At these special sites, however, this is not so and, as a result, a residual charge resides on the ion in that position; this may be a residual negative charge on a kink bromide ion or a residual positive charge on a kink silver ion. These ions will, therefore, be able to attract and, to a limited extent, retain a charged entity of opposite sign, as a result of electrical attraction and are therefore called *traps*. Traps play an important part in the formation of the latent image.

Alternatively, the absence of an ion at a vacant lattice site will mean that the residual negative charge of the six surrounding ions (see Figure 1.14) is available to attract a positive entity. Therefore vacant lattice sites will act as traps for positively-charged units.

An Emulsion Grain

To summarise, an emulsion grain is an imperfect crystal, possessing basically a cubic lattice structure with a large number of internal and external imperfections. These grains may be between 0.03μ and 2.5μ in diameter, and assuming that they are cubes (this is only true of some products), it can be calculated that there are about 50 silver and 50 halide ions on each edge in the smallest crystals and about 4,000 of each in the largest crystals. In each crystal, therefore, there are approximately 1,000,000 total ions in the smallest grains and about 500,000,000,000 in the largest, or 10^6 and 5×10^{11} respectively. The immense size, in terms of numbers of ions, of the largest grains and the chances for faults and irregularities with such crystals can therefore be appreciated.

The outside shape, called the *habit* of the crystal, and crystal growth will be discussed later.

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II GELATIN

One of the important constituents of a modern photographic emulsion is the material used to suspend the silver-halide grains, namely gelatin. It was not until gelatin was introduced into the preparation of photographic materials that really satisfactory sensitivity was obtained and it became possible to make 'dry plates', that is, plates which were ready for use without further treatment. Previously other suspending substances were used, notably collodion, but emulsions prepared in this medium only retain their light sensitivity for a short while and, therefore, coatings were bathed in a sensitising silver-nitrate solution just before use, and often exposed wet. Also, it was necessary to develop these coatings very shortly after exposure. For many years the chemical principles underlying the behaviour of photographic gelatins were very ill understood. Indeed, even some fairly recent text books consider that there is an almost magical quality in the "nature of the gelatin" in advocating the view that only gelatins from certain manufacturers will function in certain types of emulsion formulae. It is the purpose of this chapter to show the present-day understanding of the action of the colloid in the preparation and properties of photographic materials.

Function of Gelatin

Gelatin plays many roles in a photographic emulsion and has marked influence of the final properties of the emulsion. The important functions are:

1. Gelatin suspends the grains during the emulsion-making process, particularly during the precipitation stage, thus preventing clumping and settling-out.
2. Gelatin influences the rate at which the silver-halide crystals grow.
3. Gelatin facilitates subsequent chemical treatments to increase the sensitivity of the grains.
4. The reversible gelling properties of gelatin, which convert the emulsion into a semi-solid form on cooling, are of great value in the coating process.
5. Gelatin contains minor constituents which affect the light sensitivity of the emulsion.
6. The subsequent physical properties of the coated layer can be modified by additions to the gelatin medium enabling the processing of the final product
7. Gelatin interacts with some of the products of the photolysis thus stabilizing the latent image.
8. Gelatin plays a vital part in rendering the unexposed grains relatively less developable than the exposed ones.

9. Coated and dried gelatin layers swell in aqueous solutions and allow the diffusion of water-soluble substances enabling processing of emulsion layers to take place.

The combination of these properties in one substance was fortunate for the development of photography as we know it today. Although modern photographic technology has grown from the widespread use of gelatin, and to some extent, may be controlled by its properties, there has also been a very large amount of research into the possibility of replacing gelatin but few of the many substitutes proposed have been used commercially. Polyamides, such as polyacrylamide or mixed polymers of acrylamide and acrylic acid, and polyvinylpyrrolidone have been quoted in patents as partial replacements for gelatin. Other substitutes less like gelatin include polyvinyl alcohol and its esters and acetals, polyvinylpyridines and cellulose derivatives in which water-soluble groups have been incorporated into the chain.

Gelatin Manufacture

SOURCES. The large number of requirements made upon present day gelatin demand very careful control in the manufacture and in the testing of production batches. Photographic gelatins are prepared from two sources—bones or hide and skin. Bones from cattle may be obtained from slaughterhouses in the manufacturing countries where the bone has to be cleaned in order to remove the residue of flesh, grease etc., or in a suitable dry clean form from India, where the combined action of scavengers and the hot sun has already performed this operation. The detailed methods of cleaning the bones are, however, outside the scope of this book.

The other source is the skins of animals, usually cattle hide, but sometimes pig-skin. In this case the residue from the edges etc. of hides, used primarily for the preparation of leather, are available for the preparation of gelatin.

Treatment of Bone

The bone, after cleaning etc., is broken into pieces about an inch cube or a little smaller in order to permit repeated access of the chemicals used to process it. Then inorganic matter, which is mainly calcium phosphate and makes up about two-thirds of the total weight of the bone, is removed. This is achieved by treating the bone with dilute hydrochloric acid at room temperature or just below, usually at about 15° C, for a few days. This treatment, as will be seen later, must not be too prolonged otherwise some degradation of the important constituents occurs. At the end of this time the pieces of bone will appear very much the same to a casual inspection as they did originally, but in fact most of the inorganic material has now been removed and the organic material, which is called *ossein*, contains a large percentage of *collagen*, a protein-like substance.

Liming of Ossein

The ossein is now freed from excess acid by washing with large quantities of water and by subsequent treatment with a little alkali, usually sodium hydroxide, and then washed again. It is important that all excess mineral acid is eliminated at this stage. The next stage is a very important process in which the collagen is broken down. This is carried out most frequently with a very long treatment, which may go up to a hundred days, with dilute lime in very large tanks which are maintained at room temperature. In some modifications of the process the lime is changed frequently, while in others, only occasionally. In addition to the use of lime alone, small quantities of alkali or ammonia and its simple derivatives may accelerate the liming treatment. The ossein does not pass into solution at any time but changes its nature—basically the larger structural chains and the links between these chains are broken up. The alkaline treatment results in a product at the end of the liming consisting of fragments having molecular weights of the order of 70,000. Physical examinations, such as X-ray diffraction, indicate that during this process the collagen is turning into gelatin. The use of lime to effect this change causes hydrolysis of the groups in the individual gelatin chains and, as a result, the gelatin contains a higher percentage of carboxyl groups than did the original collagen. This gives a product where the electrical neutrality or isoelectric point (this will be defined later) is in the region of pH 4.8–5.

Alternatively, the conversion of collagen to gelatin may be carried out by an acid treatment. In this process, the times of treatment are much shorter and the resulting gelatin contains a lower percentage of uncombined carboxyl groups, and therefore gives gelatins of a higher isoelectric point, which may be in the region of pH 8.5. Gelatins normally used for photographic purposes are those of the lower isoelectric point and, therefore obtained by the lime treatment.

The result of these treatments is a product still similar in appearance but which now consists, instead of complex collagen, of coiled single poly-amino-acid chains with most of the interconnecting links broken.

WASHING AND EXTRACTION. Before completing the process by extracting the gelatin from this limed ossein, it is important to remove excess lime. The pH is lowered, primarily by washing with very large volumes of water, and then the ossein is treated with small quantities of mineral acid to complete the deliming. A further wash is then given in order to obtain the required pH value for the final extraction stage. Extraction is achieved by treatment of the limed ossein with hot water in a series of extractions commencing at 50–60° C and then slowly raising the temperature of successive extracts until final treatments are carried out at boiling point. The pH value of the extracting water must be carefully controlled, this is generally around 6.5 and there seems no doubt that individual gelatin manufacturers can control the properties of the gelatin by variation at this stage, but these remain industrial secrets. During this treatment, the gelatin passes into solution and only useless impurities remain behind. The concentration of the gelatin solution obtained from these

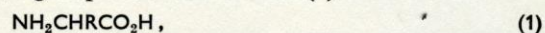
extracts is usually around 6% and as the extraction proceeds each successive fraction is of higher viscosity. The very last extract will be of very poor quality gelatin with low physical strength in the gel, and rather similar to glue.

EVAPORATION AND DRYING. The aqueous solution of gelatin is now filtered in order to remove the small particles of dirt and broken down pieces of bone, which it contains, and this filtration must be carried out very thoroughly, usually by the use of special paper filters under pressure. The clean solution of gelatin is now concentrated by evaporation, usually under reduced pressure, and is most effectively carried out in a film evaporator in which water is drawn off from a falling film of gelatin solution whose surface is being continuously renewed because of the dynamic nature of the system. This ensures rapid and efficient loss of water, avoids local overheating which can cause degradation of gelatin, and enables the gelatin solution to be concentrated up to 35%. This concentrated liquor is then run on to a chilled drum where it is rapidly changed into a gel and then scraped off the drum by a cutting edge and a scraper bar to give miniature sheets of gelatin, which are a few millimetres thick. These pieces of gelatin may then be dried by the application of warm air, the temperature of which is slightly raised as the moisture content falls. This may be carried out in a continuous system in a tunnel where the 35% gelatin enters at one end and the dry product, still containing about 15% of moisture, comes out at the other end.

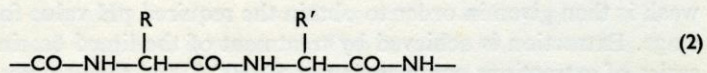
The Chemical Nature of Gelatin

The chemical nature of the resultant gelatin will now be examined.

COLLAGEN. The very important fibre-like protein which is present in both bone and hide and from which the gelatin is prepared is called *collagen*. Proteins are one of the very vital constituents of all living matter and consist of a very large number of amino-acid residues containing the group shown in formula (1)



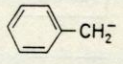
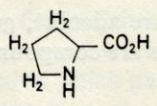
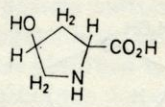


where R can represent a variety of groups. These are linked together head to tail by the elimination of water between a carboxyl group of one unit and an amino group of another, known as a peptide linkage. Simply, therefore, the structure may be represented as (2)



Nineteen different amino acids have been isolated from collagen and Table 2.1 lists the amino acids, and gives percentages by weight, which are present in collagen, and therefore in gelatin. The presence of hydroxy proline is almost characteristic of collagen and thus of the gelatin derived from it. All the other amino acids occur fairly widely in other types of animal protein and some of them are exceedingly important in their contribution to the properties of gelatin. Although the constituent amino

TABLE 2.1
AMINO-ACID CONSTITUENTS IN COLLEGEN

General formula		
		$\begin{array}{c} \text{R} \\ \\ \text{NH}_2 \text{ CH CO}_2\text{H} \end{array}$
Name	Residues per 1,000 total	R =
Lysine	24.8	$\text{NH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 -$
Hydroxylysine	5.2	$\text{NH}_2 \text{ CH}_2 \text{ CHOH CH}_2 \text{ CH}_2 -$
Histidine	4.8	
Arginine	47.9	$\text{NH}_2 - \text{C} = \text{NH NH CH}_2 \text{ CH}_2 \text{ CH}_2 -$
Aspartic Acid	47.3	$\text{HO CO} - \text{CH}_2 -$
Glutamic Acid	72.1	$\text{HO CO} - \text{CH}_2 \text{ CH}_2 -$
Serine	39.2	$\text{HO CH}_2 -$
Threonine	16.6	$\text{CH}_3 \text{ CHO} -$
Glycine	336.5	$\text{H} -$
Alanine	106.6	$\text{CH}_3 -$
Valine	19.5	$(\text{CH}_3)_2 \text{ CH} -$
Methionine	3.9	$\text{CH}_3 \text{SCH}_2 \text{ CH}_2 -$
Isoleucine	11.3	$\text{CH}_3(\text{C}_2\text{H}_5) \text{ CH} -$
Leucine	24.0	$(\text{CH}_3)_2 \text{ CH CH}_2 -$
Tyrosine	4.6	
Phenylalanine	12.6	
Cysteine*	<0.1	$\text{HS CH}_2 -$
In addition		
Proline		 makes up 129.0 units per 1,000
and Hydroxyproline		 and 94.1 units per 1,000

* Some authors refer to the disulphide, cystine, containing the $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$ link in a double molecule. However, the conversion between these is very simple and it is difficult to say which is the truly naturally occurring substance.

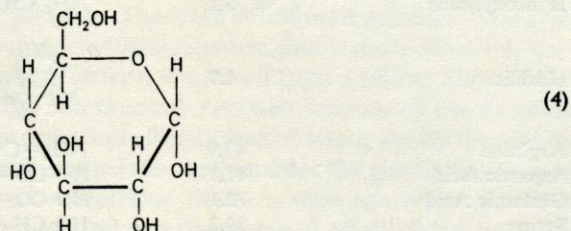
acids are known, the way in which these units are joined together in space, necessary for a full picture of the structure of the protein, is not known.

There are a number of other very important constituents which are vital for the biosynthesis and function of the protein and also for the properties of the photographic gelatin prepared from it. Two of these relatively minor constituents, in terms of quantity, are sugar-like substances and nucleic acids.

The sugar-like substances are carb, hydrates of general formula (3)

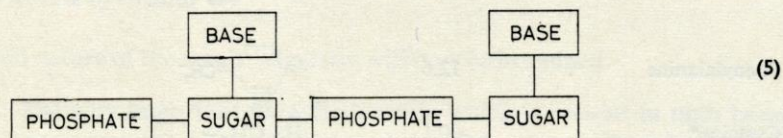


where m and n are integers, commonly equal to each other. In one type of carbohydrate the backbone of the molecule is a chain of carbon atoms all of which bear a hydrogen and an oxygen; the commonest compound of this type is glucose (4)

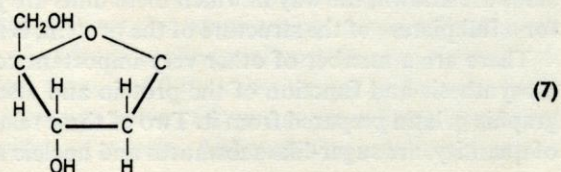
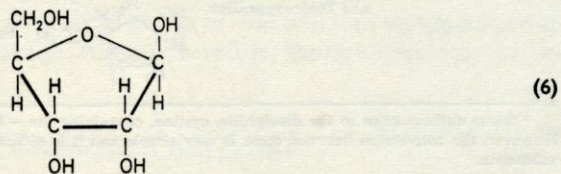


This occurs in collagen. Some of the carbohydrates present in collagen are somewhat different from glucose but belong to the similar class of compounds.

Nucleic acids are very large organic molecules consisting of a carbohydrate residue and a heterocyclic substance, containing a number of nitrogen atoms in one or two rings, and phosphate groups which unite the sugar residues together to form long chains. The general outline of these materials can therefore be represented in formula (5).



The bases present in nucleic acids are adenine, guanine, cytosine, uracil and thymine (see Chapter 5) while the sugars are compounds containing five carbon atoms, ribose (6) and deoxyribose (7).



Collagen exists as a number of twisted strands or chains of the amino-acid units carrying, at certain sites, carbohydrate molecules which are believed to play a part in providing cross links between adjacent strands, a means of 'tying' them together to make a rope.

This giant molecule can behave as an acid or a base. This is because it contains both free carboxyl and amino groups primarily due to acids such as aspartic and glutamic, which have extra carboxyl groups, and others, such as lysine and arginine, with extra basic groups. This means that it will tend to collect protons in acid solution and become positively charged, while in alkaline solution it will be negatively charged.

Two terms are commonly used with regard to gelatin and will now be defined. They are

1. The isoelectric point. This is the name given to the pH value of a solution of gelatin possessing no other non-colloidal ion than hydrogen or hydroxyl, in other words the pH of a solution of pure gelatin. It will be noted that no reference is made to the charged state of the gelatin.
2. The isoelectric point. This is the pH value of a gelatin solution when, under the influence of an electric field, the gelatin molecule moves towards neither the positive nor the negative electrode, in other words its total charge is nil, being balanced by equal numbers of positive and negative charges.

Influences of the Chemical Nature of Gelatin on the Photographic Emulsion

The chemical constituents of gelatin which influence its photographic properties will now be examined.

AMINO-ACID BACKBONE. The first of these is the general amino acid backbone which is widely thought to be responsible for the suspending properties of gelatin. Experiments have been described in which particular groups, such as the guanidino unit in arginine, are shown to possess outstanding activity. It has been shown that gelatin, and other substances of synthetic origin, with a similar chemical structure (in broad outline) to gelatin, are absorbed to the silver-halide surface. This action has two effects: first, it enables gelatin to suspend the silver-halide grain by surrounding it with an environment which protects one grain from easy access to another, which otherwise would result in clumping; secondly, it has a very important role in controlling the growth of the silver-halide crystal and enables octahedral and cubic crystals to be formed within a narrow range of grain sizes. Generally, regularity of habit is only possible in the presence of gelatin and other substances closely related to it. The use of many other polymeric substances, for example, polyvinyl alcohol and polyacrylamide, although acting effectively as suspending agents for the silver-halide grains, causes them to grow in a more random fashion or else tends to inhibit the growth to such an extent that only small ill-defined grains are produced.

It seems certain, however, that commercial gelatins are not quite so simple and many authors refer to the presence of growth inhibitors and promoters when discussing the function of certain minor constituents in gelatin. These will be considered when the ripening of photographic emulsions is discussed (Chapter 4).

The next important property of gelatin is its ability to gel. This is again a function of the general backbone of the molecule, although certain groups have an important part to play. Hydrogen bonds are formed between C=O groups and hydrogen atoms in another chain or another part of the same chain. This type of link seems to be particularly strong when the hydrogen atom is associated either with the free amino group of lysine or with the guanidino groups of arginine, both of which are quite important constituents of gelatin (Table 2.1). More attention will be devoted to this topic when considering coating and setting (Chapter 8).

CROSSLINKING GROUPS. The hardening of the final coated layer is achieved either by the reaction of gelatin with inorganic salts such as those of chromium or by crosslinking of the gelatin with an organic bifunctional reagent such as formaldehyde. The reaction of the chromium salts is considered to be with the carboxyl groups present in the gelatin while that of the formaldehyde is with the free amino groups, in particular the terminal amino group of lysine. It is clear that the relative action of a given gelatin to hardening depends upon the balance between free amino and free carboxyl groups which, of course, will be related to the isoelectric point of the gelatin.

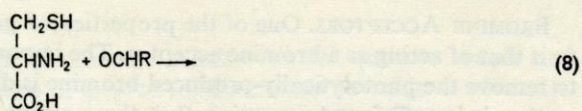
SULPHUR SENSITIZERS. The next important constituent, which will be discussed at length in the chapter on chemical sensitization, is the presence of small quantities of sulphur-containing substances, usually 10–200 parts per million of thiosulphate, which have a marked influence on the sensitivity of the emulsion. These are most likely to be produced during the liming processes by degradation of the sulphur-containing amino acid, cysteine. This, after oxidizing to the disulphide, cystine, will break down to give polysulphides which are then oxidized eventually to thiosulphate. Thus, these substances are most likely to be formed in all gelatins produced by the liming process and if it is important for them to be absent from the gelatin then they may be removed by vigorous washing and acid deliming after the liming treatment, nitric acid is particularly suitable for the removal of these substances. Conversely, only a few changes of lime during the liming period together with the minimum of washing during the subsequent purification, prior to the gelatin extraction, will give gelatins containing the maximum quantity of these types of sensitizer. Alternatively, sensitizing substances may be produced artificially by treating the gelatin liquor with sulphur dioxide when thiosulphates are formed by similar interaction with the sulphur-containing amino acids or by an oxidation reaction of the sulphite produced from sulphur dioxide, and thus a gelatin can be produced which is very similar to the natural sensitized product. Hide gelatins usually contain more sensitizer than those from ossein, this is derived mainly from the treatment used to remove the hair from the skins.

BROMINE ACCEPTORS. One of the properties of gelatin most frequently referred to is that of acting as a bromine acceptor. The importance of having some substance to remove the photolytically-produced bromine is discussed later but in the present section it is sufficient to mention that three amino acids have been considered as possible acceptors in gelatin. These are tyrosine, histidine and methionine (the formulae are given in Table 2.1), all of which possess groups able to react with bromine; by substitution as do the first two acids, or indirectly by being easily oxidized as occurs with methionine.

RESTRAINERS. For many years now it has been common to discuss restrainers as general constituents of gelatin. As with sensitizers, the function of these substances will be discussed in more detail in the ripening and digestion sections of this book, but it is pertinent to state here that the breakdown products of the nucleic acids are most likely to be present in gelatin and that these are, if not identical with the restrainers, very important components of them. It has been demonstrated that gelatins from hide contain substantial amounts (10–220 parts per million) of these products, as determined by adenine content, but ossein gelatins show a much lower content of these substances. *Gordon* and *Swann* were able to show a direct relationship between the adenine content of a gelatin and its restraining action on the rate of digestion.

As in the case of the sensitizing substances, gelatins lower in restrainer content are produced by frequent changes in the lime during a prolonged treatment followed by thorough washing and deliming. On the other hand, a short liming time, with a small number of changes, produces gelatins with a maximum natural restrainer content which may further be maintained by prolonging the preliminary acid treatment. These nucleic-acid products are undoubtedly restrainers for the digestion process but many authors suggest that they also restrain the growth of the silver-halide crystals. The whole position of growth retarders is a confused one. *Wood* has postulated that the small quantities of restrainers in the quantities of gelatin used for commercial emulsions do not effect the crystal growth. He points out that while 100 parts per million of adenine, a nucleic acid breakdown product (see chapter 5), affects sensitization, 10,000 parts per million have no influence on the crystal growth. It is very difficult, as *Wood* points out, to separate the two stages and much of the evidence produced is scanty and not generally applicable, for example, work on fine-grain emulsions under conditions very different from those existing in commercial emulsions.

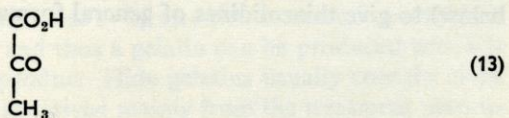
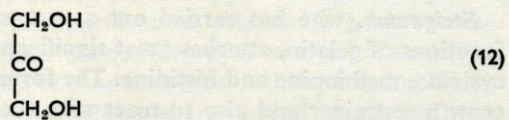
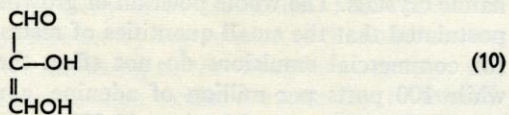
Steigmann, who has carried out a vast amount of work on the photographic functions of gelatin, attaches great significance to sulphur-containing amino acids, cysteine, methionine and histidine. The former (8) is said to be a powerful crystal-growth restrainer and also to react with the aldehydes present in the gelatin (see below) to give thiazolidines of general formula (9)



which are themselves very powerful restrainers.

In addition to compounds restraining the growth or sensitization of the crystals, there seems little doubt from a survey of the literature that the nucleic-acid or sulphur-containing amino-acid constituents greatly affect the behaviour of fine-grain emulsions used for positives. Reference is made to their effect on contrast and their desensitizing action, *Steigmann* uses the term "gradation bodies" However, no positive chemical identification has been made although they are most likely to be thiazolidines.

CARBOHYDRATES AND RELATED PRODUCTS. The true carbohydrates which occur in collagen and, therefore, in gelatin, and which are the result of breaking down large molecules containing many sugar units joined in chains, are glucose and galactose. These materials are inert photographically in the quantities present in gelatin, but in the isolation of the gelatin they are further degraded to simpler materials. This degradation is a complex reaction and all that is certain is that three-carbon fragments are the most likely products. *Landucci* and his colleagues have pointed out that reductone (10), methyl glyoxal (11), dihydroxyacetone (12) and pyruvic acid (13) are among the compounds present.



The positive identification of these aldehydes is very difficult. All these materials are very soluble in water and, therefore, must either be produced at a late stage in the gelatin preparation or must be linked to the gelatin molecules. *Landucci* has indicated that they are bound to the terminal amino groups and has suggested that proline or hydroxyproline (see Table 2.1) are involved in this function, but has not defined the link any further. Measurements of the heat of reaction show that the amino acid-aldehyde link is a weak one and the first to break in the degradation of gelatin.

The usual method for detecting these aldehyde-like substances is by the reaction of gelatin with thiobarbituric acid (14) in acetic acid



This reaction produces coloured substances of unidentified nature but which possess a number of absorption maxima, notably at about 4,500 and 5,300 Å. The vigorous conditions of this test will, of course, break down any labile substances present and it is therefore considered that it determines total aldehyde content. By standardisation with known substances, the aldehyde content can be determined and may be between 300 and 15,000 p.p.m.

It seems likely that these substances, most of which are aldehydes or closely related to aldehydes and are therefore quite strong reducing substances, are very important constituents of gelatin. It has been postulated that the formation of silver is a cause of increased photographic sensitivity but even if this is not normally the case, it is very likely that the formation of fog and sensitivity are connected with the presence of silver atoms on the crystal surface. Of all the substances present as minor constituents in photographic gelatins, the aldehyde-like sugar-derived compounds appear to be the most likely to behave in this manner.

Our present-day understanding of the presence and action of these carbohydrates is not sufficient for any detailed discussion of the effect of processing changes on the proportion present in the final gelatin.

Gelatin Modifications

Another functional activity of the gelatin, which is of increasing importance, is that of chemical modifications but generally speaking, this is not influenced by the preparation as is the presence of sensitizers and restrainers. It is related to the number and reactivity of the free amino groups and therefore will only be related to the basic structure of the gelatin and whether it is alkali or acid processed. Of the reactions of the free amino groups, most probably the ε-amino groups of lysine, the most important is acylation by treatment with an acid chloride or anhydride to produce RCONH⁻ units in which R may be an alkyl or aryl hydrocarbon group.

Other modifications described include reaction with an aryl sulphonyl chloride to give ArSO_2NH^- compounds or condensation with an active double bond, such as that of acrylic acid to yield, for example, $\text{HOCOCH}_2-\text{CH}_2-\text{NH}-$ units in place of the free amino group.

Physical Properties of Gelatin

There are two very important physical properties of gelatin which must be controlled by the gelatin manufacturer and which are important from the point of view of the emulsion chemist.

The first of these is solution viscosity. The amount of emulsion "taken-up" by the base from the coating trough or similar device is controlled by the viscosity of the gelatin. The viscosity of the extract depends upon the length of the alkaline treatment of the collagen, a longer treatment producing higher viscosity gelatin. It is important that during the extraction stage of gelatin preparation the pH is not allowed to go too low, because low-pH extraction will give gelatins of lower viscosity. The molecular weight of gelatin is another important factor which also controls viscosity, and extensive degradation, which produces increased proportions of low molecular-weight fragments with lower solution viscosity, must be avoided.

The viscosity of a gelatin solution is highly dependent on pH and is at a minimum at the isoelectric point, increasing either side of this value as shown in Figure 2.1

The gel strength of the set gelatin is also a critical factor in assessing the suitability of gelatins for photography. It is very important that, in the coating process, the gelatino-silver halide layer shall set to a strong gel very shortly after it has moved away from the coating position. The extent to which this occurs will influence its susceptibility for physical distortion in the machine during drying and its ultimate strength in the final layer.

In considering the individual amino acids and the polypeptide chain, no account has been taken of the spatial arrangement of the atoms. The atoms are not in straight lines as formula (2) might imply. The bonds around the central carbon atom of the amino acid (1) are arranged pointing to the corners of a tetrahedron with the

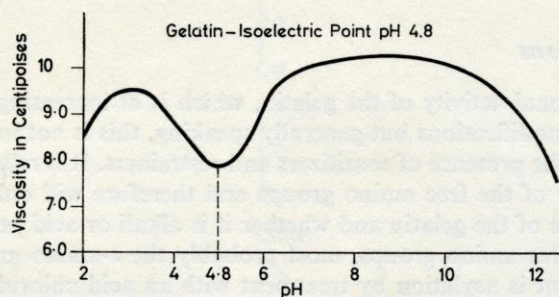


Fig. 2.1 Viscosity variation with pH

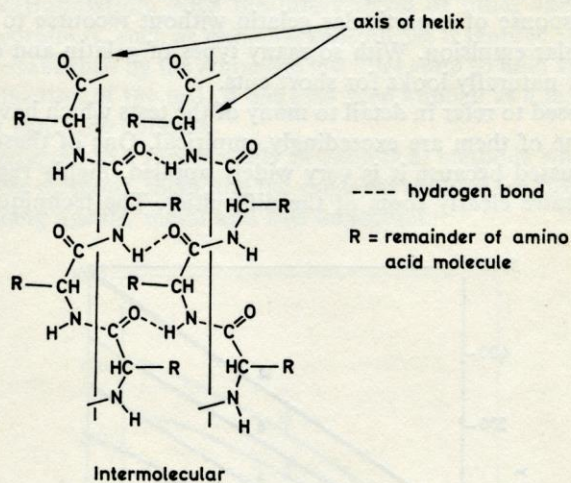
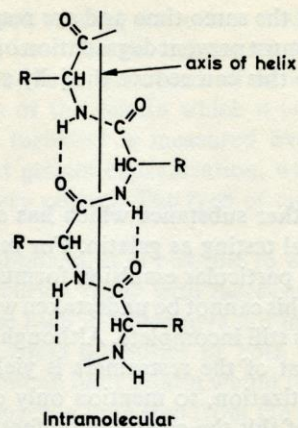


Fig. 2.2 Hydrogen bonding in coiled polypeptide chain

carbon atom at its centre. Similar angles also apply to the other atoms of the polypeptide chain (2) and this geometry results in the whole chain being arranged as a coil. In dilute solution above the gelling temperature these coils are perfectly random in their arrangement but when setting occurs a regular helical arrangement is set up in which a weak-type of chemical bond, called a *hydrogen bond* is formed between appropriately situated H-atoms from an NH unit of one peptide and the oxygen of the CO group of another. In addition, similar bonding exists between separate gelatin helices, Figure 2.2 shows both of these types of union in diagrammatic form.

Both these links exist at the same time and are responsible for the gelling of the gelatin. The manufacturer must prevent degradation of the gelatin to lower molecular-weight fragments because this can reduce the jelly strength.

Testing of Gelatin

There is probably no other substance which has stimulated so much interest in empirical or semi-empirical testing as gelatin. For many years the likely behaviour of a particular gelatin in a particular emulsion formula could not have been predicted at all and even today this cannot be undertaken with confidence since an understanding of the problems is still incomplete. Although the sulphur sensitizer problem is largely resolved and that of the restrainers is yielding its secret, the difficulties connected with gold sensitization, to mention only one of the unsolved problems, are still with us. Because of this the gelatin manufacturers, scientists working in the university, many of whom are out of touch with modern commercial technology, and the manufacturers themselves, have all sought tests which would establish the photographic response of a particular gelatin without recourse to the full testing of it in a particular emulsion. With so many types of gelatin and emulsion facing him, any worker naturally looks for short cuts.

It is not proposed to refer in detail to many of the tests which have been designed to this end, some of them are exceedingly empirical. One of these, the Ammann test will be discussed because it is very widely applied, highly regarded and also because it illustrates clearly some of the difficulties. The technique uses turbidity

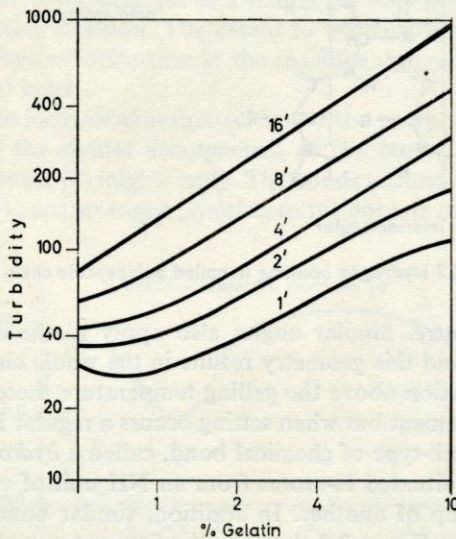


Fig. 2.3 Ammann curves — active gelatin

measurements, an approach much used by *Steigmann* and the Ammann test, called after *Ammann-Brass*, is broadly based on his techniques. A silver-chloride emulsion is prepared using cadmium chloride as the source of halide and emulsifying in the presence of different quantities of the gelatin which it is desired to classify. At a fixed temperature, the rise of turbidity is measured over a range of times and turbidity is then plotted against gelatin concentration, with a curve for each time. The experimental details are very critical. The type of curve obtained is shown in Figures 2.3, 2.4, 2.5 and 2.6.

From the shapes of curves obtained, it is possible to classify the gelatin. Those high in sensitizer content give curves rising with increasing gelatin concentration, shown in Figure 2.3, while those high in restrainers fall in that direction, as shown in Figure 2.4. Most gelatins possess quantities of both of these agents and give curves like those in Figure 2.5, but an inert gelatin would produce a series of parallel lines as in Figure 2.6. It is, however, a long step from the nucleation and growth of these particular chloride emulsions to the digestion behaviour of commercial iodobromide emulsions and there seem to be no convincing theoretical arguments to justify such an extrapolation. Also the intervention of other agents, apart from sensitizers and restrainers, such as reducing substances, is ignored. Nevertheless the general relation established by the Ammann test does seem to hold and this accounts for the wide application of the test, it has also been applied as a means of studying the behaviour of synthetic colloids.

The reader is referred to a recent study of analytical methods which gives details of the most reliable methods, including the chemical analysis for sulphur sensitizers, restrainers, reducing agents, metal and salt impurities.

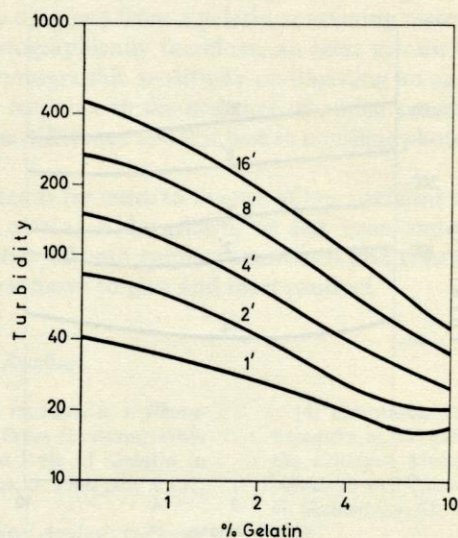


Fig. 2.4 Ammann curves — restrained gelatin

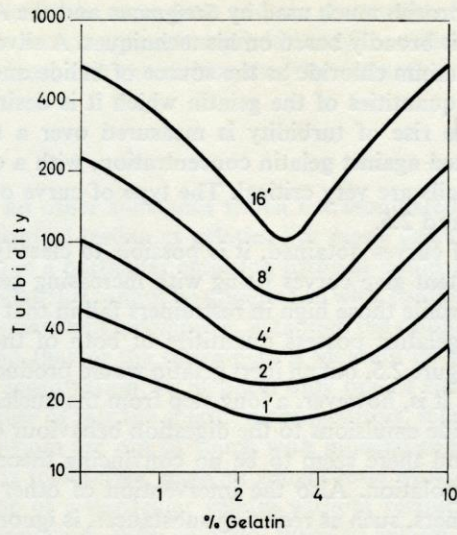


Fig. 2.5 Ammann curves — active/restrained gelatin

One general point, however, should be raised, namely the increasing use of the term *inert gelatin*. There has been much discussion and confusion about this term. If, as seems very likely, the constituents in gelatin which are responsible for the

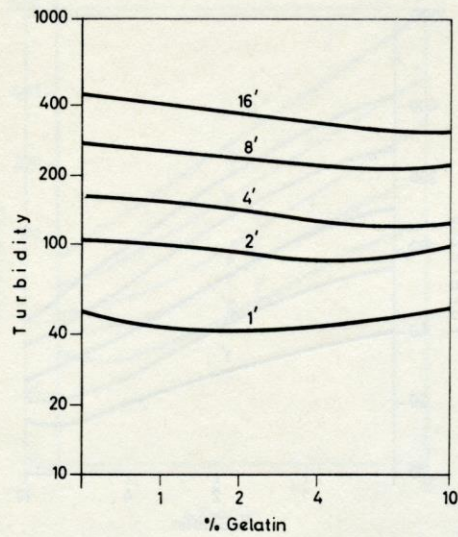


Fig. 2.6 Ammann curves — inert gelatin

sensitivity of a photographic emulsion are wholly minor "impurities", then an inert gelatin may be defined as one free from these impurities. This definition for an inert gelatin was first proposed by *Kelly* at the Liège Conference in 1959 and has been widely accepted. This very definition means two things

1. it requires a lower limit in the detection of such impurities. It is not possible to say that *none* of a certain impurity is present, merely that its concentration is below a certain value.
2. as more and more is understood about the nature of gelatin, no doubt other compounds will be added to the list of impurities.

On present-day knowledge, less than five parts per million of both sulphur sensitizer and nucleic-acid type restrainer would render a gelatin inert.

One pitfall of a loose definition for an inert gelatin can be illustrated. If a gelatin were used for an emulsion preparation and under the standard conditions of the test produced no satisfactory sensitivity, it could be classified as inert. This might arise from either of the following causes

1. the virtual absence of sensitizing substances either with or without restrainers.
2. the presence of large quantities of restrainer even if accompanied by some sensitizer.

On this evidence alone it is impossible to tell which cause accounts for the lack of sensitization. The addition of chemical sensitizer to such a gelatin would, however, immediately show the difference. If the gelatin contains no natural sensitizers or restrainers then the emulsion should now digest quite rapidly whereas little effect would be obtained from a gelatin containing restrainers unless digestion was prolonged. Photographically therefore, an inert gelatin is one which does not confer additional photographic sensitivity on digesting an emulsion on its own but gives the maximum response in the presence of added sensitizer. Clearly chemical analysis will show the difference and it is best to combine photographic and chemical testing.

Modern practice tends far more to the use of inert gelatins and these are obtained most readily from ossein. Hide gelatin, as has been stated, normally contains considerable quantities of both sulphur-sensitizers and restraining substances and, these are difficult to remove to give an inert product.

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III PHOTOGRAPHIC BASE MATERIALS

The base materials upon which photographic emulsions are coated account for a considerable proportion of the cost of a sensitized material and they can also play a considerable part in the properties of the final materials. Thus, although their preparation is in many ways a separate technology, some aspects need to be considered here.

For many years glass plates were the only suitable material with sufficient planarity and of the desired degree of inertness to use as the base. It was only the introduction of cellulose-nitrate film by *George Eastman* that led to the rapid growth in the popularity of photography and today the situation has turned full circle. The arrival of dimensionally-stable film base has resulted in the glass plate being finally displaced from its position of supremacy in the graphic-arts field. Today, only the most exact work and a number of scientific purposes, where the ability of glass to remain level without any other means of support, remain the realms of glass plates, in all other spheres film is the normal base for negative materials.

As a support for prints, paper has been used longer than film and remains, for obvious reasons, the support regarded as standard for that purpose.

The chemistry behind these support materials will now be examined briefly.

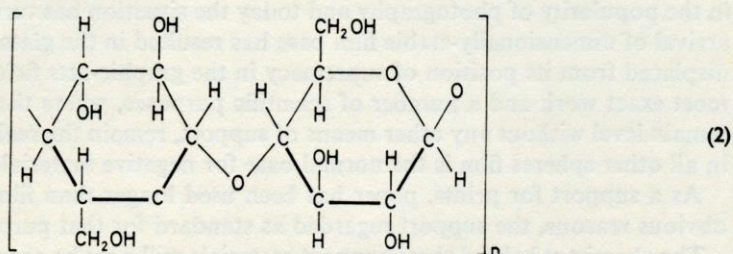
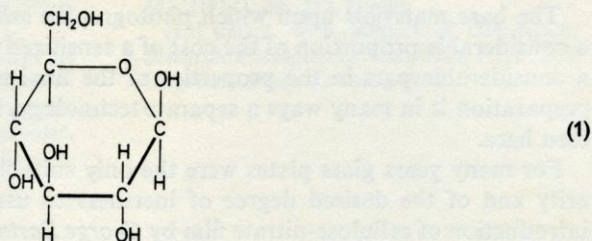
Film Base

CELLULOSE-ACETATE BASE. The original flexible film base was prepared from cellulose nitrate, and was for many years the standard material. Although possessing many satisfactory features, such as excellent mechanical properties, this ester is highly inflammable and once ignited can supply its own oxygen to continue the combustion and is therefore very difficult to extinguish. The nitrate has therefore been entirely replaced by cellulose acetate, the base originally called "safety base" because it is non-inflammable and is, in fact, difficult to keep burning. Some modern films are still marked safety films, a legacy of the days when the user liked to be sure that he was not handling the very dangerous nitrate.

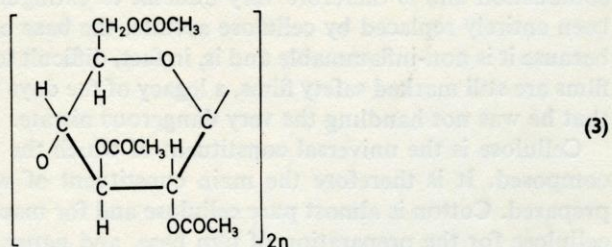
Cellulose is the universal constituent of which the structural parts of plants are composed. It is therefore the main constituent of wood, from which it may be prepared. Cotton is almost pure cellulose and for many years the primary source of cellulose for the preparation of film base, and paper, was from cotton linters, the scrap material remaining after the best cotton has been removed from the cotton seed and from rags. Today, however, cellulose is obtained almost entirely from wood pulp because modern methods of handling and purification of the cellulose make that source by far the cheapest. The isolation of cellulose will be discussed

when paper base is considered, the discussion here will be restricted to the later stages of the process.

Cellulose is a material of very high molecular weight composed of hundreds of glucose units joined together in chains. Glucose, the commonest carbohydrate has the structure shown in formula (1).



These six-membered rings are joined head to tail by the elimination of water as represented in formula (2). The molecule is linear in form and many strands of such units, with some cross links between adjacent chains, make up the cellulose fibres. Ultimate degradation, which is not easy to carry out, will hydrolyse cellulose to glucose. It can be seen that the glucose unit in cellulose contains three hydroxy groups per unit. All three of these hydroxy groups may be reacted with a wide variety of acids, acetic acid giving the *triacetate* of formula (3).



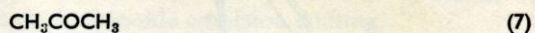
This formula contains 44.8% acetyl groups per molecule. In fact, fully acetylated material is not used for film base purposes owing to the preferred solubility of the less completely acetylated material. Earlier cellulose acetates were only 40% acetyl-

ated, called "diacetate", while more recent products are 43% acetylated and referred to as "triacetate" Material prepared from acetates with 43% acetylation is less susceptible to physical deformation in handling.

However, the preparation of the acetate is always carried out by acetylating to completion and then carrying out a partial hydrolysis. This acetylation may be carried out either in acetic-acid solution at 70° C using acetic anhydride as the acetylating agent and some concentrated sulphuric acid as a catalyst, or better, by treating a suspension of cellulose fibres in methylene chloride at 45° C with acetic anhydride and the same catalyst. In both processes an excess of acetic anhydride is present and in the latter the end of the process is determined by the viscosity reaching the required value. The completion of both these processes takes many hours.

The cellulose acetate is then washed with water to destroy the excess acetic anhydride and remove the sulphuric acid. Hydrolysis down to the required acetylation percentage is achieved by treatment with aqueous sulphuric acid, for example about 70%. This may be done as a two-phase system, the acetate being dissolved in methylene chloride throughout the hydrolysis.

The purified dried cellulose acetate is then dissolved in a suitable solvent, generally a mixture of methylene chloride (4) and another substance such as butanol (5), methanol (6) or acetone (7), for the preparation of film base. Acetone can be used as the solvent of "diacetate" but "triacetate" is not soluble in that solvent and requires the use of methylene chloride.



Another important constituent of triacetate base, which must be added, is a *plasticizer*. This is a non-volatile ester such as an ester of phthalic acid, octyl phthalate (8) for example, or a phosphate such as tri-m-cresyl phosphate (9).



The addition of these substances, incorporated at a proportion up to 20% of the acetate, prevents the base becoming brittle, probably by getting in among the chains of the polymer and assisting them to slide over one another.

The film base is formed by the method known as *casting* in which a concentrated solution of the acetate, together with the plasticizer, is run carefully, and under conditions of most extreme cleanliness, onto a moving metal surface which can be that of a very large drum many feet in diameter, or a flexible metal belt (see Figure 3.1).

These surfaces, which must be exceedingly flat and polished because the whole thickness, which is usually between 0.003" and 0.01", of the base depends on the regularity of the cast layer, can be made of copper, nickel, or, more recently, polished stainless steel. A copper surface must be coated with a renewable surface layer to prevent direct contact with the base, and a gelatin layer is suitable for this purpose. The drum or band is contained in a sealed air space from which the solvent is drawn off to a solvent recovery plant, and after nearly one circuit of the moving surface the film base is tough enough to take off, as shown in Figure 3.1. It is then carried through a further drying zone to remove the last of the solvent with the aid of hot air, and is then ready for reeling up.

Apart from the chemistry of this system, special precautions must be taken (a) to avoid the build-up of static electricity by very thorough earthing of the newly-formed base and the collection of all charge before it can build up to dangerous proportions, (b) to achieve an absolute freedom from dust both in the incoming air

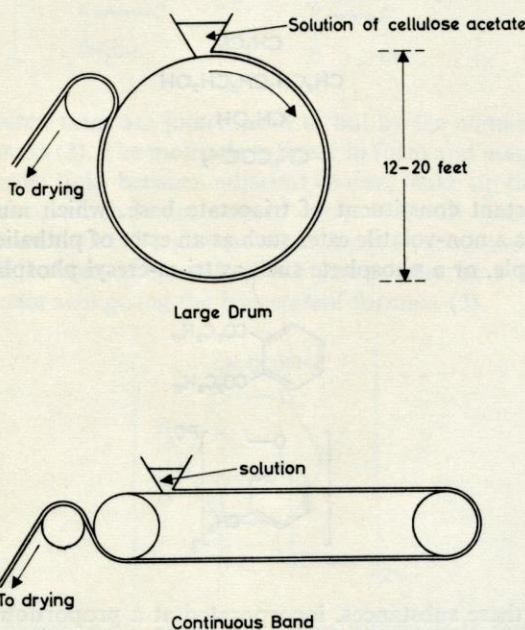


Fig. 3.1 Base-casting machines — diagrammatic

supplies and in the rooms, and (c) to provide very efficient solvent recovery both from the economic standpoint and also to trap the poisonous methylene chloride.

In addition to the acetate, mixed esters such as acetate-propionate and acetate-butyrate, where some of the acetyl groups are replaced by C_2H_5CO- and C_3H_7CO groups respectively, have also been described as suitable film bases. These are obtained by strictly comparable processes, using a mixture of the appropriate anhydrides in the acylating process.

The final film base surface is non-polar in character, as shown by the types of solvent used in its preparation. A photographic emulsion on the other hand is an aqueous suspension and this means that an emulsion would not spread evenly or adhere at all to such a film base. A further treatment, called *subbing*, is therefore necessary. This consists basically of coating a layer or a series of layers, only a few microns thick when dried down, on the film base of a material which is compatible with both film base and emulsion layers and which will therefore adhere to both. The rigorous conditions of processing used in much modern automatic machinery places additional strain on this adhesion and a very positive link is required. The formulations of these subbing layers vary widely but usually consist of water, gelatin, an organic water-miscible solvent such as ethanol or acetone, designed to effect some etching of the base, and a polymer similar to the base, such as extensively hydrolysed triacetate or even cellulose nitrate. Some subbing treatments involve successive layers becoming progressively more hydrophilic. These subbing layers are applied by methods akin to those used for emulsion coating (see Chapter 8, Figures 8.1, 8.2 and 8.3) followed by a further short drying to remove the solvents.

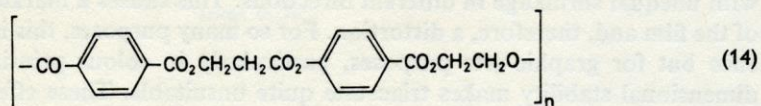
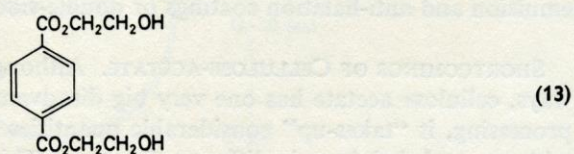
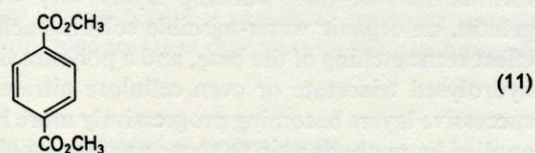
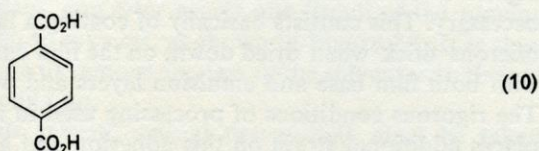
Subbing is usually carried out on both sides of the film, both to maintain flatness and also because the film will probably be coated on both sides, for example, emulsion and anti-halation coatings or double-side emulsion coating.

SHORTCOMINGS OF CELLULOSE-ACETATE. Although it is satisfactory in so many ways, cellulose acetate has one very big disadvantage. When wetted, as occurs in processing, it "takes-up" considerable quantities of water and when it dries it is with unequal shrinkage in different directions. This causes a marked change in size of the film and, therefore, a distortion. For so many purposes, this is of no consequence but for graphic-arts purposes, particularly in colour printing, this lack of dimensional stability makes triacetate quite unsuitable. These effects change with age, and re-wetting and re-drying cause still further dimensional changes. Also there are marked differences between the response of the two sides of the film, that in contact with the metal surface, the band side, and the open surface, the air side, this can cause curling of the film. The mechanical strength of acetate film also leaves something to be desired.

Acetopropionate and acetobutyrate bases were introduced as a means of improving these properties, both these bases possess lower water take-up and therefore smaller dimensional changes. Also, the newer highly acetylated base is superior in response to the older more hydrolysed product. Its introduction was made possible only when methylene chloride became commercially available in large quantities.

All these changes improve the properties only marginally and real improvements have been obtained only after the arrival of the polyester bases.

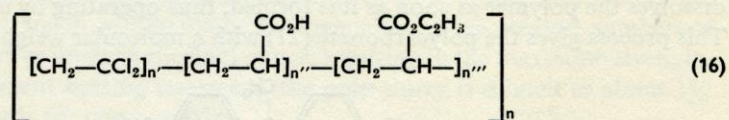
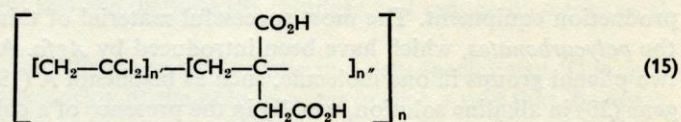
POLYTEREPHTHALATE BASE. This is a wholly synthetic material and is chemically identical with *I.C.I.'s Terylene* fibre. The starting material is terephthalic acid (10), which is available from a large number of processes, some of which enable the acid, once a rare chemical, to be produced very cheaply. This acid is then converted to its dimethyl ester (11) which is carefully purified and reacted with ethylene glycol (12) in the presence of a suitable catalyst, such as a very small quantity of sodium metal or lead oxide, to give the bis glycol ester (13).



This ester is then converted into a polymer by heating under vacuum at an elevated temperature to split off one ethylene-glycol unit between each two ester units and join the whole into a long chain containing very many terephthalyl units (14). This polymer is now ready for the next step, in which it is extruded in a molten state at a high temperature, around 250° C, and immediately after issuing from the slot it is stretched both longitudinally and laterally. The molecules arrange themselves regularly during this elongation and a short heat treatment then causes them to be stabilized in this form. The resulting film has very high physical strength and exceedingly low water take-up. This film base, which was first introduced for high

quality graphic-arts materials, is now finding wide acceptance. *Kodak's Estar* and *Du Pont's Cronar* are two very high quality bases of this type, the latter has even been introduced recently for X-ray film. Dimensional stability is so high that the exacting field of colour separation can now be tackled using film instead of glass plates. It should be noted that no plasticizer is added to polyethylene terephthalate films because none is needed and this is another factor contributing to the increased dimensional stability.

Polyester bases do possess some severe shortcomings, principally the difficulty of subbing the base to make the emulsion adhere. The polyester base is very insoluble and highly stable which makes simple etching or partial degradation almost impossible and, therefore, other methods must be used. Generally speaking, only multiple-layer treatments are satisfactory and copolymers between chlorinated hydrocarbons and organic acids are suitable for the first layer, for example vinylidene chloride-itaconic acid (15) and vinylidene chloride-ethyl acrylate-acrylic acid (16) copolymers have been mentioned, the latter being effective after an oxidation etching-treatment with permanganate. These layers are then retreated with subbing layers of the type used for acetate base.

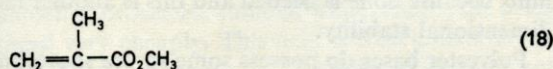
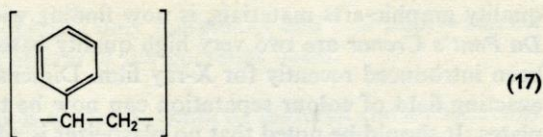


The principle behind all these treatments is similar to that of the acetate subbing except that the layer nearest the base is of a very non-polar character

Other shortcomings are that polyester film is very prone to acquiring static and is also very difficult to splice, again because of its insolubility and chemical inertness. The latter factor is probably why it has not been used so far for cine films in spite of its high physical strength.

The continued appearance of patents suggests that the manufacturers are still seeking modified polyesters in the hope of overcoming some of these disadvantages.

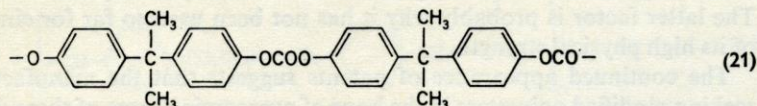
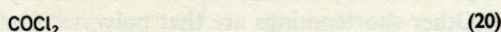
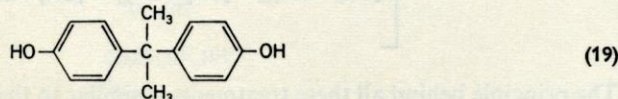
OTHER FILM BASES. Before the arrival of polyester bases, *polystyrene* (17) was introduced by a number of manufacturers as a more stable base than triacetate. This material is very brittle when prepared normally and therefore quite unsuitable as a flexible base. If, however, it is melted and then elongated, it becomes orientated along the direction of the stretching, and in this form it is suitable as a film base. Dimensional stability is achieved by the use of thicker base, and intermediate grade films on this base, for lower quality graphic-arts purposes, are still available. In addition to pure polystyrene, co-polymers



with acrylic esters, methyl methacrylate (18) for example, are also used for this type of film base.

Subbing procedures for these bases usually comprise treatment with methacrylic acid — ester copolymers followed by cellulose-nitrate layers and then gelatin layers, before the emulsion coating is made.

One important economic factor must be mentioned. Polyester and polystyrene bases are prepared by extrusion techniques which are expensive, and manufacturers are reluctant to abandon expensive film-casting machinery. A considerable search has been made for a dimensionally-stable base which could be cast from existing production equipment. The most successful material of this type is prepared from the *polycarbonates*, which have been introduced by *Agfa*. A compound containing two phenol groups in one molecule, such as bisphenol A (19), is treated with phosgene (20) in alkaline solution, usually in the presence of a chlorinated solvent which dissolves the polymer as soon as it is formed, thus operating by a two phase system. This process gives the polycarbonate (21) with a molecular weight of about 100,000.



This polymer is readily soluble in methylene chloride and gives good films of good dimensional stability, although not as stable as the polyesters. Of course, polycarbonates are also polyesters but, by custom, that term is restricted to the polyterephthalates. Patents reveal that research is still going on and many modified polycarbonates, for which superior properties are claimed, have been described.

Subbing techniques for polycarbonate base are very similar to those for polystyrene and usually involve a three-layer assembly with a vinyl or similar polymer on the base, followed by a cellulose-nitrate or partially-hydrolysed acetate layer and then a gell subbing before the emulsion coating.

Paper Base

As already mentioned, paper, which is basically cellulose, is obtained today almost entirely from wood. The raw material for the manufacture of photographic paper is pulp.

After cutting the logs to convenient lengths, the bark, etc. is removed and the clean wood is converted into small chips. These are then digested under pressure with a cooking chemical, usually bisulphite liquor. During this process the lignin, which holds the cellulose fibres together in the wood, is broken down to release the cellulose and valuable by-products, such as turpentine. At the end of the digestion period, the pressure is rapidly released by allowing the mass to blow out of the vessel, the sudden pressure release helping by blowing the cellulose fibres apart. After washing very thoroughly, the slurry is sieved to remove large particles and the filtered suspension is dried in the form of sheets. It is in this sheet form that the pulp is usually imported into this country. The fibre obtained from this process still contains some coloured materials from the wood and is usually given a further treatment with a bleaching agent, such as hypochlorite, to destroy these. Care must be taken not to bleach excessively because this can degrade the cellulose and reduce its mechanical strength.

The sheets of pulp are then disintegrated in water in a very special way. This consists of beating a 5-7% suspension of the pulp in water in such a way that the fibres are cut and split under high pressure, the object is to bring the surface area of the fibres to a maximum which will facilitate the formation of the greatest numbers of bonds between adjacent fibres in the final paper, resulting in the maximum strength. After receiving sufficient beating treatment, the pulp slurry is diluted to about 1% solids and is then ready for paper-making.

Figure 3.2 shows, in diagrammatic form, a paper-making machine. The dilute pulp is fed from the hopper, via a sluice to control the flow, onto a moving wire-mesh belt where the water drains away through the mesh, assisted by vacuum after the paper has begun to dry. At the end of the web the paper is of sufficient strength to be lifted off and pressed between rollers to further dry and strengthen it. The material is then dried by passing it over a series of hot cylinders before reeling up, at which stage it will possess only 5-8% of water.

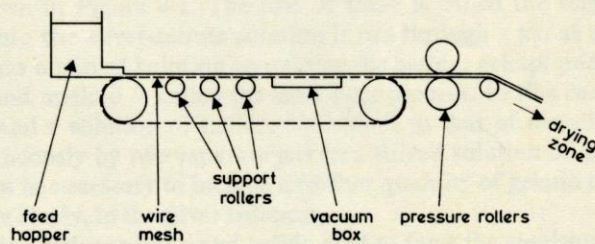


Fig. 3.2 Paper-making machines — diagrammatic

Paper in this form would still be weak and absorbent so it is standard practice to include resin of some kind in the paper to improve its surface and wet strength. Other additives for paper include fluorescent substances, called optical bleaches, which absorb near ultra-violet light and re-emit it at visible wavelengths thus increasing the light apparently reflected from the paper. These substances conceal any tendency to natural yellowness of the paper

One final process in making photographic paper, suitable for prints, is called baryta coating. This process which is applied to all high-grade papers, consists of coating a fine suspension in aqueous gelatin of a very pure form of white inert barium sulphate, of particle size $0.2-1.0\mu$, on the finished paper. The coating greatly increases the whiteness and opacity of the paper and provides a smooth base on which the highest quality emulsion coating may be obtained. This process, which is very akin to that of coating emulsion, is carried out at high speed by the use of the air-knife technique (see Figure 8.2), which will be described later. In attempts to protect paper from the effects of processing and humidity, manufacturers have coated cellulose nitrate, acetate or acetobutyrate on each side of the paper sheet before applying the emulsion layer. Such materials do possess some improved properties and are referred to as "waterproof papers" They may be regarded as intermediate between film and paper.

In conclusion it should be added that all possible precautions must be taken to remove contaminants, particularly metallic impurities, such as iron specks, which can cause serious trouble in the coated emulsion. The standards of purity for base, baryta layer and other additives are very high indeed.

References for Further Reading

[1] GLAFKIDES, P. *Photographic Chemistry*, Vol. 1., Chapter 25, Fountain Press, (London) 1958.

[2] JEFFREYS, R. A. and WAGNER, H. M.

Polymers in Photographic Materials, Reports on the Progress of Applied Chemistry p. 177, Society of Chemical Industry, (London) 1960.

IV EMULSION PREPARATION

The preparation of a silver-halide emulsion will now be considered. Basically this consists of a number of stages which are as follows —

1. The precipitation of very small silver-halide crystals (*Emulsification*)
2. The growth of these crystals to the appropriate size (*Ripening*)
3. The removal of by-products from the crystal formation and growth stages. (*Washing*)
4. The sensitization of the crystals to obtain the desired response to light (*Chemical and Spectral Sensitization*)
5. The preparation of the emulsion in its final form for coating.

Emulsification

The first stage which is called *emulsification*, or precipitation, is achieved by mixing solutions of the desired halide with a soluble silver salt, usually the nitrate, in the presence of gelatin. One of the most important factors affecting the subsequent growth and final photographic response of the silver-halide emulsion is the conditions existing during this precipitation stage. The gelatin plays a vital role, as will be discussed later, in the way in which the crystals are formed. The halide may be that of an alkali metal, such as sodium or potassium, or alternatively an ammonium halide. Except with very special emulsions, the quantities of halide and silver are never equivalent, in the vast majority of photographic emulsions, particularly those of a negative type, excess halide is always present. There are often other substances present. In many cases ammonia is used as a silver-halide solvent, particularly when it is desired to grow crystals which are thick, for reasons which will be discussed later.

Apart from more modern ways of making photographic emulsions by continuous precipitation processes in which the conditions are quite different from those of the more classical procedures, there are two broad classes of method used to form the emulsion, shown in Figure 4.1. The first of these is called the *single jet* method in this procedure the silver-nitrate solution is run through a jet, at a carefully-controlled rate, into a stirred solution containing the halide, gelatin and other ingredients. The second method is called the *double-jet* process in this case a solution of silver nitrate and a solution of halide, equivalent to that of the silver nitrate, are added simultaneously by two separate jets to a stirred solution of gelatin halide. It may sometimes be necessary to include a further quantity of gelatin in the halide solution or, more rarely, in the silver solution.

The solutions of silver nitrate and halide used to form the emulsion are frequently around normal solution strength, in other words they contain of the order of one

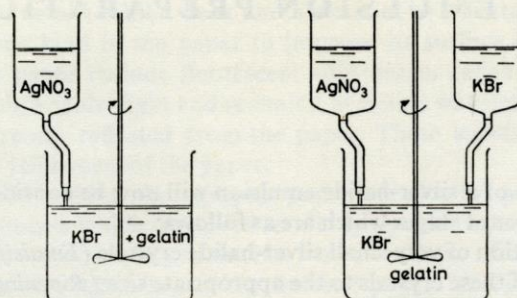


Fig. 4.1 Representation of precipitation methods. *Left*: single-jet method; *right*: double-jet method

gram molecule of silver salt or halide per litre. The very low solubility of silver halide, as mentioned in a previous chapter, means that very high supersaturation occurs as soon as the mixing process commences. This results in an exceedingly rapid formation of small silver-halide crystals which may be observed by the immediate clouding of the solution where mixing occurs, and the whole bulk of the mixture will soon become an opaque milky liquid, its colour depending on which halide is precipitated. The formation of the silver-halide lattice occurs, therefore, by the very high speed aggregation of silver ions and the halide ions. It will be obvious that the environment of these ions will be very important in controlling the exact sequence of events leading to crystal precipitation and growth, and it will be necessary to examine later the critical factors in this process.

Ripening

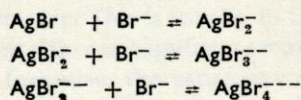
At the conclusion of the mixing stage the emulsion is given a heat treatment, during which time the crystals grow; additional halide or other silver-halide solvents or gelatin may be added at this stage. This is called *ripening*, or physical ripening to distinguish it from chemical ripening, or Ostwald ripening after *Ostwald* who first recorded the change of fine precipitates of silver iodide into coarser ones on heat treatment where a proportion of the crystals grew at the expense of the rest. This process is continued until the crystals have attained the desired grain size and grain-size distribution. The ripening may be observed by microscopy with the coarser-grained emulsions or electron microscopy with the finer ones.

This crystal growth will only occur in the presence of suitable silver-halide solvents and these will now be considered.

Complex Ions

Although the aqueous phase of a silver-halide emulsion has so far been considered as a very low concentration of soluble AgHal in equilibrium with silver ions, in fact, this is a great simplification.

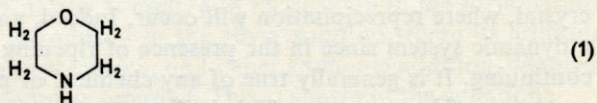
The presence of an adequate concentration of excess halide, which will be usually either chloride or bromide, renders the silver halide much more soluble than it is in pure water because of the formation of complex ions. The reactions of silver bromide with excess bromide ions to give multicharged complexes are represented by the following equations: —



The most predominant of these complex ions, in the range of excess bromide concentrations used in photographic emulsions, is the AgBr_4^{---} complex ion. However, it has been suggested that the important complex from the point of view of crystal growth is AgBr_3^{--} and this is also present in appreciable quantities under the usual conditions of emulsion precipitation and ripening.

Another complex ion, which is important in the ripening stage is formed by the action of ammonia, a common constituent of many negative and X-ray emulsion formulae. This agent produces the $\text{Ag}(\text{NH}_3)_2^+$ complex ion.

Although excess bromide and ammonia are the most common ripening agents, others mentioned in the literature include thiocyanate in place of bromide and a variety of amines such as morpholine (1) and N-hydroxyethylpiperidine (2) instead of ammonia.



When it is considered that in the very rapid aggregation of ionic species which occurs in the initial stage of grain formation, and bearing in mind that any defect or dislocation will be continually extended throughout the growing crystal, it will be seen that the form of the finished grain will be controlled by the ions which are predominant in building up a crystal. Recent work by *Moisar* and *Klein* has thrown light on the factors controlling grain growth on different faces of silver-bromide crystals. Very even-sized silver-bromide crystals in which there were nearly equal areas of (100)-(cubic) and (111)-(octahedral) faces were grown by a carefully controlled

precipitation. These crystals were then grown by using feed-stock from a double-jet precipitation in which the pAg of the suspension was carefully maintained at a constant level. At low pAg , that is low excess bromide concentration, the 111- faces are the site of growth and therefore these disappear giving finally a 100-faced-crystal. At higher bromide-concentration, however, there is a marked adsorption of bromide-ions at these faces causing hindrance to normal growth. It was proposed that a nucleation process is now necessary for any further growth on 111-faces. Additional energy is needed for this process and therefore growth can only take place easily on the (100)-faces to produce a final crystal with (111)-faces. In silver chloride, however, no (111)-planes can be observed even at very high chloride-ion concentration.

Cause of Ripening

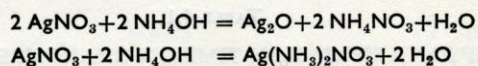
Why do crystals grow at all? The growth process normally only takes place by 'cannibalism' (although aggregation of crystals sometimes takes place) and this means that some of the crystals grow at the expense of others produced in the same precipitation process. The rate of this growth process will, of course, be dependent upon the nature of the crystals present and on the environment. In a single-jet emulsion the conditions in which the first and last crystals are formed will be very different, depending upon the concentrations of the halide and ammonia; the crystals formed earlier may be more or less soluble than those formed later. A detailed study of this subject is outside the scope of this book but the general principle by which some crystals grow at the expense of others, is important.

Growth will take place by the solution of surface ions from one crystal as a result of the action of the ripening agent, followed by their migration to a neighbouring crystal, where reprecipitation will occur. Indeed, an emulsion must be regarded as a dynamic system since in the presence of ripening solvents this process is always continuing. It is generally true of any chemical or physical system that it will tend to a state of lower energy. This is illustrated by such simple facts as water always flowing downhill or the discharge of electricity, where the flow takes place because of the high-energy state of an electron surplus at one point and a deficiency at another. In a silver-halide system, the larger the surface area of a crystal, relative to its volume, the higher will be the energy state of that crystal. In general terms, therefore, the silver-halide emulsion will tend to a state containing a small number of larger crystals because this system is in a lower energy state than the opposite arrangement, and is therefore more stable. The different modes of growth occurring in an emulsion because of changing conditions, e.g. colloid content, halide concentration etc., must mean that this is a simplification. Nevertheless, this gives a simple reason why growth takes place.

Emulsion Variables

The number of possible different conditions which may be produced with a comparatively simple emulsion formula is very large indeed. The following ten factors must be considered important.

1. The mode of emulsification, that is single or double jet.
2. Emulsification Time. This is a critical variable and may vary from a very rapid addition in 5 secs (very difficult to achieve and control industrially) to a slow mixing in up to one hour, addition times around one minute are most common.
3. The emulsification temperature. This is usually in the range 40° to 70° C.
4. The excess of halide present either in a uniform amount or a decreasing amount. In considering emulsion formulae, the usual way of describing the quantity of halide is as the percentage excess over the quantity equivalent to the silver. Iodobromide emulsions usually contain between 20% and 250% excess bromide during precipitation and ripening: those for negative purposes commonly containing the highest amounts while X-ray emulsions have the lowest. Chlorobromide and chloride emulsions rarely contain more than about 10% excess halide but it may be as low as 1% or 2% in cases where very little growth is desired. Some authors, including the Russians, refer to the strength of the excess halide in terms of normality. As it is the *concentration* of excess halide ions which controls the formation of complex ions, notably those described above, this is probably the more logical way. However, as the vast majority of emulsions are formed at roughly the same concentration, around 2,000 ml. per g. mole of silver, these two ways of looking at the halide excess may be considered to be very similar.
5. The quantity of ammonia, if any is used, and its position in the formulation. The ammonia is usually introduced in the silver solution where its addition initially precipitates silver oxide which, on further ammonia addition, dissolves to give a solution of the complex ammine. This is shown in the equation.



At this stage the silver is said to be "converted" and "ammoniacal emulsions" are those in which this quantity of ammonia has been added. Alternatively, the ammonia may be contained in the halide/gelatin solution and/or in the added halide in a double-jet formula.

6. The pH of the solution. In an ammoniacal emulsion, this is, to a large extent, controlled by the ammonia addition, but in other emulsions the pH during precipitation may be critical and is usually controlled.
7. The quantity and nature of the gelatin. Account must be taken also of the presence of microimpurities which may have a marked effect in some emulsions, particular those of fine grain.

8. The proportion of the different halides in the silver-halide crystal and their mode of introduction. This in practice will mean the inclusion of the less soluble halides present during the precipitation, that is bromide in a chlorobromide emulsion and iodide in an iodobromide emulsion; the latter, in particular, very critically influences the growth and sensitivity of the grains.
9. The cation of the halide used which may commonly be potassium or ammonia but frequently alkaline-earth salts, such as calcium chloride, or other soluble metal halides are used. The latter may be introduced in either large or small quantities for special effects. Among those specifically claimed are lead and cadmium salts.
10. The deliberate addition of organic substances for the "artificial" restraint or acceleration of grain growth. *Glafkides* mentions iminazoles, thiazoles and thioglycollic acid as examples.

Effect of Emulsion Variables

The scope of manipulation of so many factors will give some idea of the complexity of the emulsion chemists's problem. In addition to this, there is probably no other branch of applied science in which the manufacturer is less inclined to give away his secrets, all the large manufacturers are in possession of a vast amount of unpublished experience. It is not the purpose of this book to attempt a detailed analysis of the published information but to study the general principles and to illustrate a few of them from published data.

EMULSIFICATION TIME AND TEMPERATURE. In a single-jet emulsification very rapid mixing of the halide and silver solution produces a large number of small nuclei and the longer the time of the silver addition, the larger the grains will grow. This broad picture is in Table 4.1 and may be illustrated by the data interpreted simply on the basis that if nuclei produced early in the emulsification are permitted

TABLE 4.1
EFFECT OF EMULSIFICATION TIME ON GRAIN SIZE AND SPEED

<i>Time of addition</i>	<i>Mean grain area μ^2</i>	<i>Relative speed</i>	<i>Gamma</i>
0'31"	0.14	12	2.5
4'22"	0.28	52	2.08
10'12"	0.50	150	1.50
19'30"	0.82	250	1.36
42'40"	1.47	450	0.94
54'50"	2.35	630	0.83
85'10"	2.56	910	0.65

to grow to some extent, the excess halide being the ripening agent, they will then act as nuclei for the silver halide, formed later, to grow upon. On the contrary a very rapid addition of the silver solution gives a large number of similar sized nuclei which then do not ripen so rapidly

In broad outline, the double-jet method gives a more even grain distribution at the end of emulsification. Long emulsification times give a very similar opportunity for those crystals formed in the earliest additions to grow and then act as nuclei for halide precipitated in the later stages but, as the concentration of ripening agents remains fixed throughout, no initial large excess is present to cause the more rapid growth at the beginning of the process.

Generally, increasing the emulsification temperature causes faster crystal growth and therefore gives a coarser grained emulsion. This is not always the case, and in some situations alteration of the emulsification temperature may affect grain pattern considerably

MULTIPLE OR CONTINUOUS EMULSIFICATION. The fact that newly-formed small nuclei are in a high energy state ensuring that they will readily dissolve, and therefore act as a source of silver halide for larger nuclei, is frequently applied in commercial emulsion formulae where a double addition of silver halide is made. In this case the crystals are formed by a customary single-jet or double-jet emulsification and ripened to the desired size. Then a fresh stock of newly-formed crystals are introduced by the precipitation of a further quantity of silver bromide. These new crystals are very small because they have not been subjected to physical ripening, will be in a very high energy state, and therefore rapidly dissolve, the material from them being deposited on to the already present larger crystals. Frequently, this second addition of silver halide is made by adding further quantities of silver nitrate over a prolonged time so that, as soon as they are formed, the new crystals are ripened on to the preformed larger nuclei.

Two cases of the use of this technique will be given here. The first is an *Agfa* formula for a very fast emulsion, used for night photography, the details of which were published after the war. The formula is

Solution A	{	Water	70 ml.
		Potassium bromide	8.0 g.
		Potassium iodide	0.5 g.
		Gelatin	1.0 g.
Solution B	{	Water	90 ml
		Silver nitrate	9 g.

Solutions A and B were both heated to 65° C and then half of B was added to A in one minute. The second half was then added over 29 minutes, enabling the first half of the silver halide to ripen and act as nuclei for the second. Another similar formula is given by *Glafkides*

Solution A	{	Water	160 ml.
		Gelatin	60 g.
		Ammonium bromide	19.0 g.
		Potassium iodide	0.7 g.
		Ammonia (S.G 0.910)	4 ml.
Solution B	{	Water	140 ml.
		Silver nitrate	20 g.
Solution C	{	Water	70 ml.
		Silver nitrate	10 g.
Solution D		Gelatin	35 g.

At a temperature between 42°–70° C depending on the nature of the gelatin, (this is a very wide range and a modern emulsion formula using inert gelatin would require this factor to be better defined). Solution B was added to Solution A in 1–5 minutes. The emulsion was then ripened for 10–60 minutes before the second silver solution C was added, followed by more gelatin D and a second physical ripening for 15 minutes. Again the nucleation principle is being employed.

Sometimes the nuclei may comprise a lower fraction of the total silver content, for example, a recent Japanese ammonia formula uses only one third of its silver iodobromide as nuclei for the remainder.

EFFECT OF IODIDE. Another very important variable on which information is available is the function of silver iodide. Experimental work has shown that when silver nitrate is added to mixed bromide and iodide ions, silver iodide is precipitated first because of the much lower solubility of silver iodide. Equally the process of Ostwald ripening causes the dissolution of these first-formed grains and a redistribution of their iodide. Nevertheless it has been shown that the coarser grains of a broadly dispersed iodobromide emulsion contain the most iodide, suggesting that grains containing the most iodide were probably precipitated first and tend to grow more quickly. The very important effect of iodide on grain growth is illustrated by the results of *Trivelli* and *Smith* shown in Figure 4.2.

The location of the iodide in the grain has been studied and it was shown that some silver-bromide crystals contained a core having quite large concentrations of iodide. Again this suggests that once the silver iodide has been built into a crystal of medium size, it is likely to remain there because of its low solubility.

Another important function of iodide is to introduce defects into the silver-bromide lattice. This is reflected in the fact that, other things being similar, iodide has the following effects

- a) increased photographic speed, especially after chemical sensitization, which is much less likely to give fog with higher iodide-content emulsions.
- b) improved spectral sensitization.

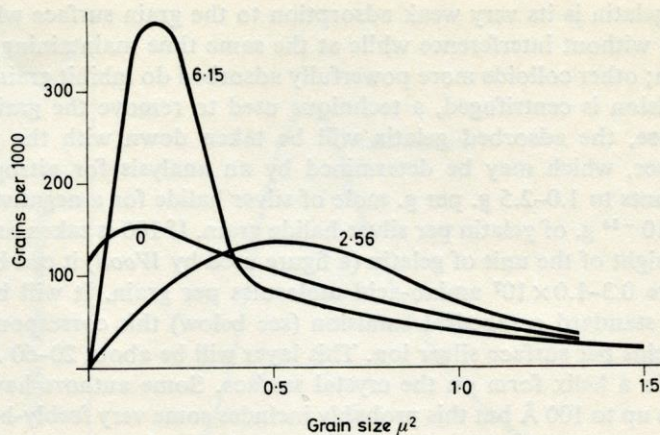


Fig. 4.2 Grain-size distribution with iodide content. The numbers on the curves are the molar percentage of iodide

If, however, the iodide percentage is increased above 10%, the photographic sensitivity falls, which has been attributed to the formation of more internal image (see Chapter 9).

GELATIN. Generally speaking, more gelatin produces slower grain growth. It is fairly certain that this is not just a viscosity effect because the influence of gelatin can produce such dramatic changes. This is a function of the basic peptide structure and due to the influence of ripening restrainers in the gelatin (see Chapter 2 — Ammann test). However, the tremendous emphasis, in the past on the nature of the gelatin is slowly giving way, and the use of inert gelatin enables the emulsion chemist to have more control of the grain-growth stage.

It may well be that the most important function of the gelatin is merely to keep the emulsion grains apart. This simple action will permit each one to ripen in a controlled manner without the intervention of adjacent crystals.

The Adsorbed Layer of Gelatin

A layer of gelatin is probably adsorbed to the crystal surface from a very early stage of its growth and in its final state will remain there. This layer has been considered to play an important part in the formation of plate-like grains but this is unlikely because crystals of that shape are formed in the presence of other colloids, or in the absence of colloid e.g. by growth in hydrobromic acid. Recent measurements of the heat of adsorption of gelatin to silver bromide have shown it to be very low indeed and this indicates that the bond between gelatin and silver bromide is one which makes use of only a little of the bonding power of the gelatin and that very little energy is needed to displace it. Therefore, it may be that the important

property of gelatin is its very weak adsorption to the grain surface which permits grain growth without interference while at the same time maintaining the crystals in suspension, other colloids more powerfully adsorbed do inhibit grain growth.

If an emulsion is centrifuged, a technique used to remove the grains from the aqueous phase, the adsorbed gelatin will be taken down with the grains. This adsorbed layer, which may be determined by an analysis for nitrogen content, usually amounts to 1.0–2.5 g. per g. mole of silver halide for a negative emulsion, or $0.3-1.0 \times 10^{-14}$ g. of gelatin per silver-halide grain. If 100 is taken as the average molecular weight of the unit of gelatin (a figure used by *Wood*) it can be calculated that there are $0.3-1.0 \times 10^7$ amino-acid molecules per grain. It will be seen that, relative to a standard octahedral emulsion (see below) this corresponds to about 1–3 amino acids per surface silver ion. This layer will be about 20–60 Å thick, and is probably in a helix form on the crystal surface. Some authors have suggested gelatin layers up to 100 Å but this probably includes some very feebly-held material. Silver-ions are retained in this gelatin shell in the form of a complex; this is shown by, for example, the relatively high opacity of these shells which makes them easily detected by electron microscopy

Types of Emulsion

Two common terms referring to types of photographic emulsion should be commented upon. These are a *neutral* (boiled) emulsion and an *ammonia* emulsion. The latter has been defined already. Ammonia emulsions, particularly those using converted silver, ripen rapidly and frequently a temperature of 40° C or 45° C is quite high enough to give a satisfactory ripening rate. In the absence of ammonia, when the only ripening agent is excess bromide ions, then much higher temperatures are needed, frequently up to 70° C. and in earlier days even higher, and these are therefore termed neutral or boiled emulsions.

Two iodobromide emulsions will now be considered in more detail, the first a bromide-ripened emulsion with octahedral grains, the other an ammonia-ripened emulsion with polyhedral grains.

An Octahedral Emulsion

This emulsion is made by the following formula, which is for 0.5 g. mole of emulsion.

Solution A at 50° C	{	inert ossein gelatin	12.5 g.
		potassium bromide	206 g.
		potassium iodide	1.66 g.
		water	to 750 ml.
Solution B at 30° C	{	silver nitrate	85 g.
		water	to 500 ml.

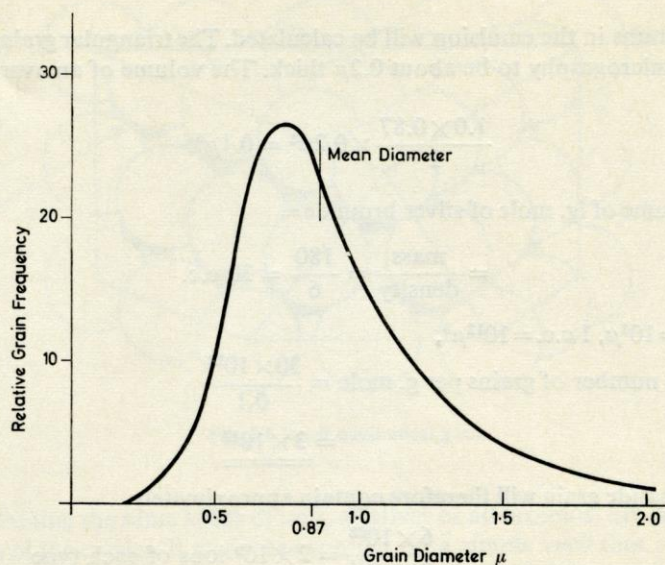


Fig. 4.3 Grain-size distribution of octahedral emulsion

Solution B is added to solution A in 60 seconds, the temperature adjusted to 50° and ripened at 50°

The important quantities are

Ripening volume	2,500 ml/g. mole
Bromide excess	244 %
Bromide ripening normality	1.0 molar
Iodide content	3.0 % molar
Gelatin concentration	25 g/mole

Plate 4.1 shows the growth of these grains during ripening and their grain-size distribution at the end of ripening is plotted in Figure 4.3. It will be seen from this diagram, as well as from the final photomicrograph, that there is a fairly broad range of grain sizes: the average grain diameter being 0.87 μ

The broad spread of grain sizes in this emulsion is characteristic of emulsions ripened in the presence of a large excess of bromide. The contrast of emulsion of this type is fairly low and this kind of grain pattern is most suitable for negative and colour emulsions when a wide range of light intensities must be recorded.

The tabular grains, which are seen as triangles or hexagons in the photomicrograph, are very common in emulsions of this type. These are flat octahedra (Figure 4.4.) and are relatively thin in their dimensions at right angles to the plane shown in the picture, usually only about 1/10th or 1/5th as thick as their diameter.

This emulsion will now be described in detail to give a clearer quantitative picture of a silver-halide emulsion, based on an average grain diameter of 0.87 μ . First the

number of grains in the emulsion will be calculated. The triangular grains are shown by electron micrography to be about 0.2μ thick. The volume of an average grain is therefore

$$\frac{1.0 \times 0.87}{2} \times 0.2\mu^3 = 0.1\mu^3$$

Now the volume of 1g. mole of silver bromide =

$$= \frac{\text{mass}}{\text{density}} = \frac{180}{6} = 30 \text{ c.c.}$$

Since $1 \text{ cm.} = 10^4\mu$, $1 \text{ c.c.} = 10^{12}\mu^3$,

$$\begin{aligned} \text{therefore the number of grains per g. mole} &= \frac{30 \times 10^{12}}{0.1} \\ &= \underline{\underline{3 \times 10^{14}}} \end{aligned}$$

Each silver-halide grain will therefore contain approximately

$$\frac{6 \times 10^{23}}{3 \times 10^{14}} = \underline{\underline{2 \times 10^9}} \text{ ions of each type}$$

Secondly, the number of surface ions in the grain may be calculated. The surface

$$\begin{aligned} \text{area of a grain} &= 2 \times \frac{1.0 \times 0.87}{2} \text{ (two triangular sides)} \\ &\quad + 3 \times 0.2 \times 1.0 \text{ (edges)} \\ &= \underline{\underline{\text{approx. } 2\mu^2}} \end{aligned}$$

The unit cell has a side of 5.75 \AA , each 1.0μ edge of a triangular grain will therefore contain $\frac{1.0 \times 10,000}{5.75} = 1,800$ silver ions, and the number of surface silver ions will

$$\text{be } \frac{2 \times 1800 \times 1500}{2} + \text{contribution from the edges } \underline{\underline{3 \times 10^6}}$$

There will also be the same number of bromide ions.

Although the crystals of this emulsion have an octahedral habit, their interior structure is still cubic and in fact represents a section of a cubic crystal in which

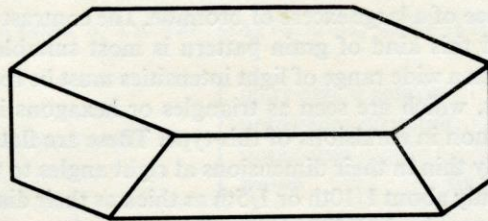


Fig. 4.4 Representation of octahedral grain

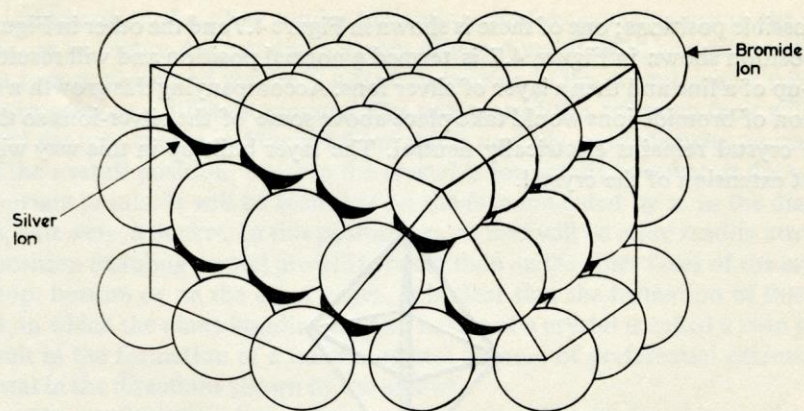


Fig. 4.5 Small octahedral grain

planes containing the same kinds of ions, all silver or all bromide, are parallel to the larger faces of the crystal. It might be expected on a simple view that a cubic lattice would produce cubic crystals, because of their unusual habit and their photographic importance, much attention has been given to discovering why, in the presence of excess bromide, silver bromide should prefer to grow this type of crystal. The most acceptable theory is that which was suggested a few years ago by *Berriman* and *Herz* in which a particular form of fault was shown to occur in a tabular silverbromide crystal.

It is now necessary to discuss the formation of this very important crystal fault. If the very large number of bromide ions and silver ions which are rapidly deposited in a more or less regular array are considered, and which it is very likely are deposited individually (it is certain that this is true of the silver ions), then it can be appreciated that there is a good chance some of these may end up in an incorrect position. A partially-grown silver-halide crystal is represented by the drawing in Figure 4.5. This contains a much smaller number of ions than probably occurs in a crystal at the critical stage of grain growth. The diagram shows the internal cubic structure of the crystal, and it will be seen that the upper layer of the crystal is made up of a plane surface composed only of one kind of ion, namely bromide. This plane is the same one as that shown shaded in Figure 1.3 (see Chapter 1) and is called a (111) plane. The latter term is given because the plane cuts each of the three lattice co-ordinates, running across, up and into the plane of paper in Figure 1.3, one cell unit away from the corner. If all the faces of a perfect crystal were made up of (111) planes, its habit would be a regular octahedron as shown in Figure 4.6. In fact crystals of this perfect shape are rarely found in silver-halide emulsions, but the eight-sided tabular crystals under consideration are sections of such a shape. *Hamilton* and *Brady* have drawn attention to the fact that when the very important growth-promoting AgBr^3- ion approaches a (111) surface, the geometry of the complex ion facilitates contact in

two possible positions, one of these is shown in Figure 4.7 and the other in Figure 4.8. The position shown in Figure 4.7 is termed a normal position and will result in the build-up of a line and then a layer of silver ions. Accompanying this growth a steady addition of bromide ions would take place above some of the silver-ions so that the whole crystal remains electrically neutral. The layer built up in this way will be a perfect extension of the crystal.

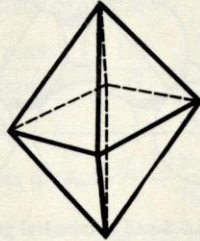


Fig. 4.6 Complete octahedral crystal showing habit of complete 1.1.1. faced crystal

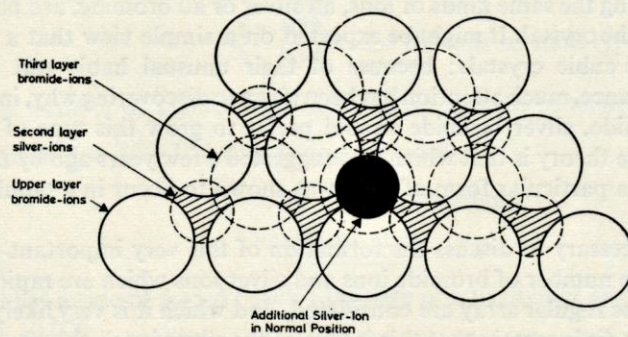


Fig. 4.7 Entry of silver-ion on 1.1.1. face — normal position

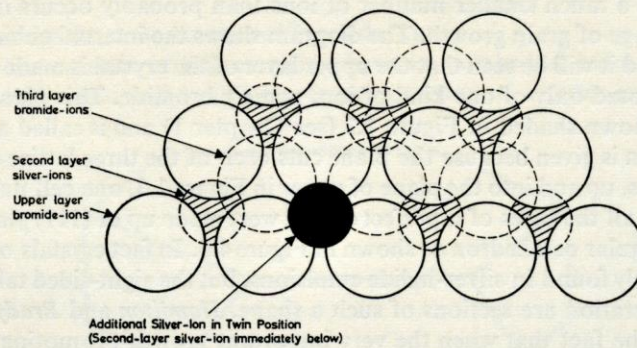


Fig. 4.8 Entry of silver-ion on 1.1.1. face — twin position

The introduction of a silver ion by the approach of the complex ion in the other position, as in Figure 4.8, produces a very different result. This second position is called a *twin* position and results in a fault appearing in the crystal, which will now cause it to grow in a different manner. The outcome of this twinning fault will be a crystal of the type shown in Figure 4.9 but this is actually an inadequate representation of the overall position, because the crystal is too small; however, it does show the important points. It will be seen that on the face indicated by \times in the diagram there is, as it were, a pocket. In this position, extra ions will be more readily attracted into a position enabling crystal growth to occur than on the other faces of the crystal, either top, bottom or on the other edges. It is clear that the formation of this kind of fault, in which the plane bonding the two halves of a crystal is called a twin plane, will result in the formation of a tabular crystal because of preferential extension of the crystal in the directions shown by the arrows.

Adequate confirmation has subsequently been obtained for this mechanism. Electron-micrograph pictures of large silver-bromide crystals, show the presence

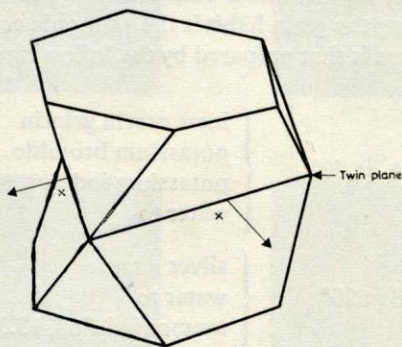


Fig. 4.9 Representation of completely-twinned crystal. X indicates pockets where rapid growth occurs

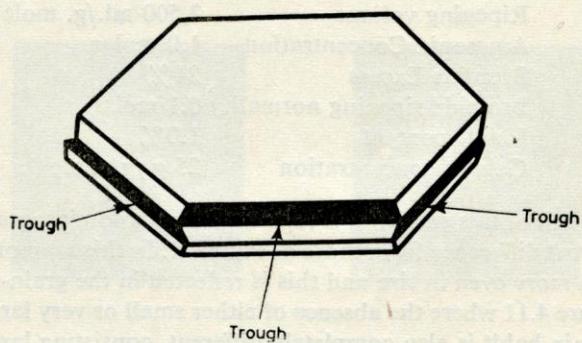


Fig. 4.10 Doubly-twinned crystal showing troughs for rapid growth on all six edges

of the type of edge which is characteristic of a twin plane. It must be admitted that these crystals are larger than those ever found in commercial emulsions, but since their conditions of formation are not vastly dissimilar from emulsion crystals, it must be assumed that an extrapolation is valid. Furthermore, the vast majority of crystals examined show not just one twin plane but two. This is shown in Figure 4.10 where the pair of twin planes in a crystal will result in pockets along all six edges in a crystal of this type, producing rapid growth on each edge and if this takes preference over growth on either of the flat surfaces large plates would be produced. There are many emulsions known in which this type of tablet growth occurs and in some of these, growth is exceedingly rapid.

An Ammonia Emulsion

The other common type of crystal formed in iodobromide emulsions is the cubic polyhedral habit which is used in X-ray type emulsions. These crystals are formed in an excess of ammonia, that is, under conditions in which the silver-complex ion responsible for controlling the grain habit is the ammonia complex $\text{Ag}(\text{NH}_3)_2^+$

An emulsion of this type is that prepared by the following formula, again for 0.5 g. mole of emulsion —

Solution A at 50°	{	inert ossein gelatin	12.5 g.
		potassium bromide	73.8 g.
		potassium iodide	0.83 g.
		water to	656 ml.
Solution B at 20°	{	silver nitrate	85 g.
		water to	500 ml.
		ammonia 0.880, 13.3N	94 ml.

Solution B is added to solution A in 1 minute, the temperature adjusted to 50° C, and the emulsion ripened at 50° C. The important quantities are —

Ripening volume	2,500 ml./g. mole
Ammonia Concentration	1.0 molar
Bromide Excess	24%
Bromide ripening normality	0.1 molar
Iodide content	1.0%
Gelatin concentration	25 g./g. mole

The grain growth of this emulsion is shown in the photomicrographs of Plate 4.2 which show a great difference from those of Plate 4.1. In this ammonia emulsion the grains are much more even in size and this is reflected in the grain-size distribution diagram in Figure 4.11 where the absence of either small or very large grains will be noticed. The grain habit is also completely different, consisting largely of rounded cubes with some almost perfect cubes, which will mean that their dimensions are the

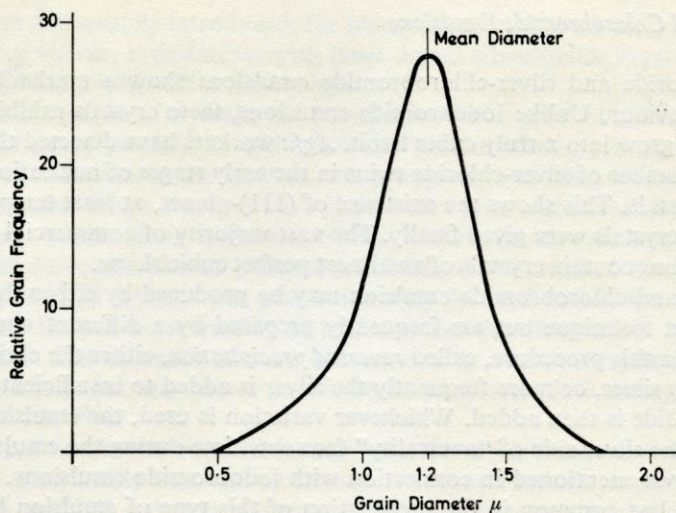


Fig. 4.11 Grain-size distribution of cubic emulsion

same all directions. Indeed, these crystals are what one might expect for silver bromide.

This emulsion will now be studied in the same detail as the octahedral one. The mean grain size is 1.2μ cube and mean grain volume is $1.75\mu^3$. Since, from the data obtained previously, 1 g. mole of silver bromide has a volume of $30 \times 10^{12}\mu^3$, then

$$\begin{aligned} \text{the number of grains per mole} &= \frac{30 \times 10^{12}}{1.75} \\ &= 1.8 \times 10^{13}, \end{aligned}$$

which is a smaller number than that obtained for the octahedral emulsion. Also, each edge of the cube will have 2,100 silver ions, 4,200 total ions per side, and therefore 3.5×10^{10} ions of each kind per grain. The surface area of each grain will be

$$\begin{aligned} &6 \times 1.2 \times 1.2\mu^2 \text{ (6 sides of cube)} \\ &= 8.7\mu^2 \end{aligned}$$

The relatively large volume of each grain and the fairly narrow grain-size distribution make emulsions of this type of high speed to the light absorbed by the silver halide, the sensitivity of each crystal being a volume relationship (see Chapter 9), and of high contrast. This makes this kind of emulsion very suitable for medical X-ray films for use with fluorescent screens. The colour of the light emitted by the screens is such that spectral sensitization is not beneficial and therefore maximum speed must be obtained from the halide alone and the high contrast is required in order to give "bright" radiographs showing good differentiation.

Chloride and Chlorobromide Emulsions

Silver-chloride and silver-chlorobromide emulsions show a markedly different growth behaviour. Unlike iodobromide emulsions, these crystals exhibit a greater tendency to grow into a truly cubic habit. *Agfa* workers have detected the presence of a small number of silver-chloride twins in the early stages of nucleation of silver-chloride crystals. This shows the existence of (111)-planes, at least temporarily but (100)-faced crystals were given finally. The vast majority of commercial chlorobromide emulsions contain crystals of an almost perfect cubic shape.

Chloride and chlorobromide emulsion may be produced by either the single-jet or double-jet technique but are frequently prepared by a different emulsification procedure. In this procedure, called *reversed precipitation*, either the entire halide is added to the silver, or more frequently the silver is added to insufficient halide, and the extra halide is then added. Whichever variation is used, the emulsion environment is on the silver side of "neutrality" for some time during the emulsification, a situation never mentioned in connection with iodobromide emulsions. The use of ammonia is less common in the preparation of this type of emulsion because the very high solubility of silver chloride in ammonia restricts its use to small quantities and even these have a drastic effect on the grain growth. Much more frequently, therefore, chloride and chlorobromide emulsions are ripened in excess chloride either in acid or neutral solution. Cadmium chloride is frequently used to obtain chloride and chlorobromide emulsion of maximum contrast and citric acid is widely used to control pH, probably because fairly large, and therefore convenient, quantities of it are needed to give a well-buffered emulsion pH of 5.0.

Generally speaking chlorobromide emulsions are of greater speed and softer in contrast as the bromide content increases. Unlike iodide which is only added to bromide emulsion within a range of about 1.0 to 8.0%, chloride and bromide are mixed in all proportions from 1 : 0 to 1 : 1.

The *Agfa* company added small quantities of trivalent rhodium chloride, used either as its ammonium or sodium complex, immediately the emulsification stage was concluded, as a means of obtaining high contrast. This particular use of rhodium seems almost unique, no other metal having been claimed to give the same effect, and only very small quantities are needed, e.g. as little as 5 ml. of 1 : 10,000 solution per kg. of silver nitrate. This corresponds to 5×10^{-7} equivalents of rhodium and therefore only a few rhodium ions per grain of emulsion. Clearly at this concentration its effect must be on the primary stage of latent-image formation, but no theory of the action has been published.

Crystal Irregularities

So far only one type of crystal imperfection in silver halides, the twin plane, has been discussed, but there is no doubt that other types exist in silver-halide emulsion crystals. Compared with transistors, another class of crystalline substances where

impurities are deliberately introduced, the published literature on silver-halide technology is very sparse, experiments with large doped silver-halide crystals may not be valid for photographic-emulsion crystals.

Electronmicrographs of crystals, the position at which print-out silver is formed as a result of heavy photolysis, and studies of partially-developed grains have all revealed lines and areas in the crystals, which appear to be unusual relative to the rest of the crystal. Many workers have shown that print-out silver in large silver-bromide slabs forms along dislocation lines within the crystals but *Swinnerton* demonstrated that quite different patterns are obtained from similar looking crystals. The etching of large crystals was also studied by *Mitchell* and it was found that etch pits were formed most quickly at points where the dislocations came to the crystal surface. The existence of such dislocations in emulsion crystals is implied and it seems likely that they play a part in heavy photolysis, influencing the formation of print-out silver.

So far it has not been decided whether a perfect silver-halide crystal would be useless photographically although most authors suggest that this would be the case. *Mitchell* has pointed out that dislocations as such may not be needed but the occurrence of surface imperfections is a part of many modern considerations of photographic sensitivity.

Emulsion Separation and Washing

At the conclusion of the ripening stage, the photographic emulsion will contain silver-halide grains of the desired size suspended in a small quantity of gelatin. In addition, however, there will be the by-products from the various reactions which resulted in the formation of the silver halide as well as the growth-promoting substances. It would be impossible for an emulsion of this composition to be coated on film because the salts, etc. still present would crystallize at the drying stage and render the physical condition of the coated layer unsuitable or, in some cases, prevent complete drying. In the cases of emulsions designed to be coated on a paper base, the presence of salts is not deleterious for drying and it was common practice in the past to coat such emulsions with these by-products still present. The great majority of modern photographic emulsions are given a subsequent chemical sensitizing treatment, commonly called digestion, and this process is retarded by the presence of excess halide. In addition an emulsion which has been ripened in the presence of ammonia will clearly be at a high pH and therefore would be even less acceptable for digestion and coating.

For these many, reasons therefore, the emulsion is subjected to what is commonly called *washing*, this term being derived from the classical procedure adopted to remove the by-products.

NOODLE WASHING. The earliest, and until recently the commonest, method of removing the impurities was to cool the emulsion, usually after the addition of further quantities of gelatin, when the solution sets to a fairly soft jelly. This is

broken up into small fragments, usually by shredding to produce noodles, which are then suspended in water. The water is changed frequently, sometimes continuously, and during this washing treatment the ions diffuse, by osmosis, out of the gelatin phase into the aqueous phase and are then removed. This process will continue until the emulsion noodles are sufficiently free from the soluble inorganic constituents, namely the by-products of the double decomposition, acid or ammonia, and excess halide ions.

The progress of the washing process may be followed by two methods —

- 1 Measurement of the total ionic strength by the determination of the electrical conductivity of the aqueous phase or of the emulsion, a small quantity of which has been taken and reconstituted into a continuous phase by melting.
2. The residual silver-ion concentration, pAg , of the emulsion may be measured by potentiometric means with a silver electrode and a standard calomel electrode as a reference (see Chapter 1 for details).

Either of these methods may be regarded as reliable because the diffusion rates of all types of ions out of the gelatin phase will be similar and thus a measurement of total ionic strength will be a reliable guide to the halide-ion concentration and vice versa. The first method is, however, only satisfactory for production-control purposes, because it will be obvious that with two emulsions of similar excess halide concentration and different total ionic strength, the reduction of the total ionic concentration to a given value will leave the halide ions at different concentrations. This is a weakness of the conductivity method and, bearing in mind that the halide-ion concentration has a critical effect on the subsequent digestion treatment whereas quite large concentrations of other ions may be tolerated, the direct determination of pAg is much to be preferred.

The classical washing procedure has, however, two very grave disadvantages and on account of these it has very largely been replaced by more modern methods. The first disadvantage is that the process is time consuming and requires special equipment and a fair amount of handling of the emulsion. This means that in production, labour charges and a great deal of space, finance and time are taken up with the process of washing the emulsion. The other shortcoming is that noodle washing allows no opportunity for concentrating the emulsion, indeed the opposite occurs. As the removal of the inorganic salts proceeds, the emulsion noodles tend to swell and absorb water and it is quite common for the emulsion concentration to have dropped to almost half its initial value by the time the halide-ion concentration is sufficiently low for digestion. This tendency to swell may be minimised by washing with a solution of an inorganic salt containing multi-charged ions, which does not interfere with the digestion process, instead of water. A common example of this procedure is to use a solution of magnesium sulphate which greatly reduces the water take-up by the noodles and which is not itself taken-up to any great extent by them. Clearly the use of this method must be limited to emulsions which are not sensitive to the addition of these ions. At best, however, this is only

a partial solution, but if it is satisfactory to coat fairly dilute emulsions, as was the case when coating was carried out on glass, then this dilution effect can be tolerated.

Modern high-speed film-coating methods commonly require more concentrated emulsion than those easily obtainable after noodle washing both from the point of view of the economics of coating and the physics of the film-coating methods.

It is worthwhile at this stage to define clearly what is meant by emulsion concentration. This may be expressed by two figures

1. The concentration of silver halide. This may be expressed in grams of silver for a given volume thus giving a uniformity to the different halides or mixtures of halides.
2. The concentration of gelatin, which again may be expressed as grams for a given volume. In this case, because of the indeterminate "molecular weight", the equivalent weight can have little significance for a substance like gelatin, so it is quite common to quote gelatin concentration as a weight/volume percentage. For satisfactory coating of emulsion by standard procedures and using gelatins of average viscosity and strength, the gelatin concentration cannot be permitted to drop appreciably below 5%.

Both of these concentrations decrease during noodle washing. When, however we are considering the light-stopping power and the attainable contrast and maximum density of a photographic emulsion, we are largely concerned with the silver halide concentration. It is the silver-halide coating weight which must be controlled in order to obtain a satisfactory photographic response. However, even a very dilute emulsion could be rendered capable of being coated in a sufficiently thick layer after adding sufficient solid gelatin to bring the solution up to a high enough viscosity. In earlier years, this was done but it increases the gelatin to silver ratio to a higher figure than would be acceptable today. Some years ago, many plate-coated emulsions had as much as 300–400 grams of gelatin per gram molecule of silver and the same was true of some film emulsions. Such a ratio gives an emulsion layer which is far too thick for present-day standards, it would possess a slow rate of development, poor drying characteristics and low sharpness. Present-day emulsions frequently have no more than 100 grams of gelatin per gram molecule of silver and therefore the addition of further quantities of gelatin after noodle washing is completely out of the question.

It is theoretically possible to ripen the emulsion under very concentrated conditions and to include only a small quantity of gelatin, relative to the silver, at the pre-washing stages of emulsion preparation in order to ensure the minimum take-up of water, but this is rarely practicable. It is far better to use an emulsion-washing method which itself involves a silver-halide concentration stage.

COAGULATION WASHING. Modern methods of emulsion washing are all based on the principle of causing the gelatin to coagulate and, therefore, separate from the warm emulsion solution when the silver halide is carried with it. The density of the silver halide ensures that the gelatin-halide mixture settles rapidly to the

bottom of the vessel as a curd-like mass from which the aqueous phase may easily be decanted or removed on a large scale by some other method. The successful operation of many of the methods described below depend on the separation conditions, e.g. correct conditions of temperature, rate of addition of the precipitant, degree of stirring, pH, and many other critical factors, which it is outside the scope of this book to discuss, but which must be controlled very carefully in practice. Unlike the classical setting and noodling technique where the excess salts are enclosed in the solid gelatin, from which they must then slowly diffuse during the washing process, in the precipitation technique, under optimum conditions, the volume of the coagulated emulsion is very small indeed and by thorough separation of the aqueous phase from the curds, a very high percentage of the unwanted salts may be removed in one stage. For example, if 0.5 molar excess bromide is used during the ripening stage as in the octahedral formula given above, then the removal of 95% of the aqueous phase, which is readily achievable, results in a bromide normality of 0.05 if the emulsion were reconstituted to half of its original volume, which is a concentration at which digestion could be carried out. In practice, therefore, no more than one such precipitation and separation sequence is virtually adequate, although it is quite common for the emulsion to be reconstituted by heating the curds in water after the decantation of the salt solution, and then subject it to a further precipitation stage. This double process will be quite sufficient to achieve the desired removal of the unwanted ions.

The more common methods used today for the precipitation washing of photographic emulsions will now be considered.

SOLVENT PRECIPITATION. The addition of a water-miscible organic solvent, in which gelatin is not soluble, will precipitate the solid phase. The commonest example of this is the use of industrial ethanol, or methylated spirit, which was probably the earliest method of coagulation commonly used in production but has now been largely displaced by newer processes. The emulsion is precipitated in rather a slimy form which is difficult to handle and a clean separation from the aqueous solution is difficult. In production, the higher cost and inconvenience of recovering the large volumes of spirit, frequently around 1 litre per gram molecule of silver, must also be taken into account.

SALT PRECIPITATION. Although there is a fair concentration of salt always present in an emulsion at the end of ripening, this rarely exceeds 1.0 molar in total content and is only likely to contain a very small proportion of doubly-charged ions. The addition of large quantities of inorganic salts containing at least one doubly-charged entity, or smaller quantities of trebly or quadruply-charged ions causes the precipitation of the gelatin from the aqueous phase. This type of precipitation is well known in protein chemistry and ammonium sulphate, frequently used in that field, is one of the commonest precipitants for emulsions. Apart from being fairly cheap, ammonium sulphate will form very concentrated solutions in water and the addition of such a solution to a photographic emulsion will produce an

immediate precipitation of the gelatin, which carries the silver halide with it. The precipitation is commonly carried out at a pH value just below the isoelectric point, e.g. at a pH value below 4 according to a *Kodak* patent.

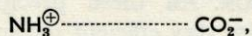
The form of this precipitate is influenced by the temperature, etc., as mentioned above, and it is easily obtained in a crumbly semi-solid state from which the supernatant liquor may readily be separated. This separation removes the greater part of the salts, including most of the precipitant, so that the emulsion coagulum is now readily dispersible in fresh warm water by stirring. The precipitation and decantation may then be repeated in order to lower further the concentration of the halide ions. Alternatively, the curds may be soaked in a number of changes of cold water and this is an easy way of removing the remaining unwanted halide ions, this operates by an osmotic diffusion process, somewhat similar to that used with the noodles in the classical method.

PRECIPITATION BY SULPHONIC ACIDS. The addition of an organic sulphonic acid or sulphate will cause the acid group of the added compound to form a salt with the amino groups in the gelatin. The result of this chemical modification is that on the acid side of the isoelectric point the gelatin will no longer be soluble, because of salt formation, and if the group attached to the sulphonic or sulphate entity is hydrophobic then the whole complex will be water insoluble. Amongst the compounds used for this type of process are naphthalene disulphonic acids and long-chain alkyl sulphates, such as the well-known anionic wetting agents.

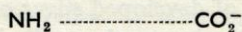
The method therefore involves the addition of the sulphonic acids followed by sufficient mineral acid to cause the gelatin to precipitate, usually at a pH value below 4. As with the earlier examples, the silver halide is carried down, forming curds which are easily separated from the aqueous layer by decantation and the emulsion redispersed by the addition of water and sufficient alkali to carry the pH above the isoelectric point. This method is clean and convenient for large-scale operation.

USE OF ACYLATED GELATIN. This process is really a logical extension of the previous method in which instead of using an ionically-bonded group attached to the amino group of the gelatin, the modification is introduced via a covalent link. Gelatin is treated under suitable conditions with a derivative of a carboxylic or sulphuric acid, in the presence of a base, so that the free primary amino groups of the gelatin are converted into their acyl derivatives.

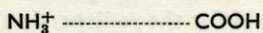
If the gelatin molecule is represented by the symbol: —



then in alkaline solution it will occur as: —



while in acid solution it will be —



It will be seen that in both acid and alkali the molecule carries an ionic charge which will aid its solubility in water. In the modified gelatin, however, the NH_3^+ group will be replaced by $\text{RCONH}-$ or $\text{R}'\text{SO}_2\text{NH}-$, and these groups do not possess the ability to go into a positively-charged form. In solution below the isoelectric point the gelatin will carry the acylated amino groups balanced by the CO_2H groups and will no longer possess the ionic character necessary for ready solubility. This insolubility may be reinforced by the rather hydrophobic nature of R or R' , which may be aromatic groups, or in an extreme case R may itself carry another acid radical, for example the gelatin obtained by reaction with phthalic anhydride where the amino groups are converted into group (3).



It is important to note that if the pH value of an emulsion using these acylated gelatins is lowered further, for example, to 3, then it will redisperse again. This is because other groups in the gelatin, such as the guanidino links of arginine and the iminazole ring of histidine (see Table 2.1), which are not readily acylated, will protonate in more strongly acid solutions and take the gelatin into solution.

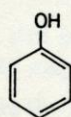
The modified gelatin is used in the emulsification stage or added at the conclusion of ripening, which is carried out above the isoelectric point of the gelatin, and acid is added to the emulsion to reduce the pH value to about 4, whereupon precipitation of the gelatin occurs and the emulsion coagulum may then be treated as in the previous method. When carried out under optimum conditions, which depend on the nature of the emulsion, the precipitation results in a fine, firm curd from which separation of the salt solution is easy.

As these gelatins carry modifications on groups which are likely to be important in the growth of the silver-halide crystals, it might be expected that emulsions grown in these gelatins would be appreciably different from those using untreated gelatins. However, there seems to be little evidence of such differences although some Russian authors have reported that benzene-sulphonated gelatin produced slower grain growth than occurred with ordinary gelatin. The grain patterns of two emulsions, one ripened in ordinary gelatin and the other in phthalated gelatin are shown in Plate 4.3.

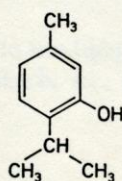
IMPORTANCE OF REDISPERSION. All these precipitation methods of washing photographic emulsions require very efficient redispersion of the precipitate when the final washing is completed. Without this, the grains will tend to clump together which will produce aggregates of developed silver on processing. Even if these are not serious enough to degrade the image, they will give a coarser-grained result than in a completely dispersed system. The redispersion stage therefore requires the use of intensive stirring and the pH for the redispersion is frequently critical.

Bacteriocides

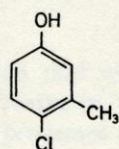
One further emulsion constituent should be mentioned at this point. The protein nature of gelatin makes it liable to attack by bacteria. Although every attempt is made to keep dirt in any form out of the emulsion, the damp, neutral, substantially salt-free silver-halide gelatin emulsion, either in noodles or in solid mass, is an ideal medium for growing such bacteria as do contaminate it. It is therefore necessary to add a bacteriocide, usually a phenol, to kill any accidental infection, whenever emulsion is to be stored for any length of time. Amongst the phenols used are phenol itself (4) thymol (5) and p-chloro-m-cresol (6). With the very active halogeno-



(4)



(6)



(5)

phenols, 0.1% of the weight of gelatin may be sufficient, with the other compounds up to 5% may be necessary

In order to delay chemical degradation of an emulsion, it is imperative that the emulsion is stored at a low temperature, usually below 5° C. This storage will enable a stable finished emulsion to be kept for several months, but undigested material is usually kept for only a few days.

References for Further Reading

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V CHEMICAL SENSITIZATION

The silver-halide crystals are now in a suitable condition for the next stage of preparation of the light-sensitive material. The final size distribution will have been achieved and the emulsion freed from impurities such as excess halide ion, high concentrations of basic materials and excessive quantities of unwanted substances from the gelatin.

However, the emulsion grains are still in a relatively insensitive condition. There are two ways in which the sensitivity may be increased. These are:

1. to cause emulsion grains to make the most efficient use of the light they absorb; i.e. *chemical sensitization*;
2. to cause the grains to be able to use light in a region of the spectrum in which they would normally not absorb, i.e. *spectral sensitization*, which will be considered in Chapter 6.

Digestion

Many years ago it was discovered that when an emulsion in this insensitive condition was given a further heat treatment, the crystals became much more light sensitive. Long before the chemical processes occurring at this stage were properly understood, a number of names were given to this step and these included digestion, chemical ripening and after-ripening. All these terms are still used in the photographic literature but the nature of the process is defined unambiguously by the term chemical sensitization. In essence, this consists of a treatment, often after the addition of a chemical sensitizer, at an elevated temperature, from 40° to 70° C, which may vary in duration from a few minutes up to several hours, when speed and fog are increased, as shown in Figure 5.1.

The degree of change in the photographic response can vary and if the conditions used were not optimum in terms of pH, nature of the gelatin or the quantities of various additions, then the speed increase might be much smaller or the onset of fog might take place sooner (indicated by the dotted line). Thus, during the heating treatment a change takes place in the emulsion which greatly enhances the sensitivity, but as this reaches its maximum value the onset of fog occurs, that is some of the silver-halide crystals become developable without exposure.

Only a few years ago the behaviour of an emulsion in this digestion stage was always entirely controlled by the nature of the gelatin. Gelatins which produced a large increase in sensitivity in a conveniently short time were referred to as fast or active gelatins while those that produced little or no change were referred to as

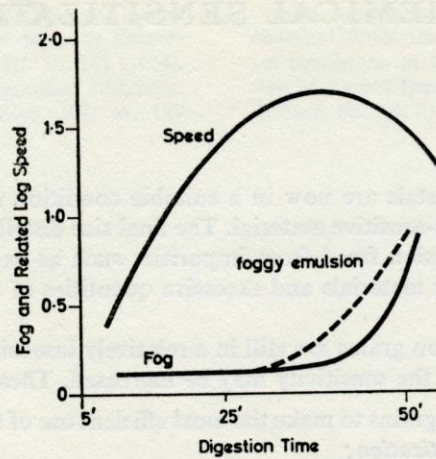


Fig. 5.1 Growth of speed and fog in digestion: iodobromide emulsion

slow or inert gelatins. Two very important changes, however, have occurred in more recent years, these are:

1. A fairly clear picture of the chemical impurities or micro-constituents of gelatin, which produce this increase in speed and fog, has emerged.
2. It is now more usual to add known amounts of these sensitizers, and other substances not normally found in gelatin, before the digestion stage in order to permit control of the process.

Three types of chemical sensitization are used in the digestion process of modern photographic emulsions

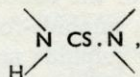
1. Sulphur sensitization
2. Reduction sensitization
3. Precious metal sensitization.

The first two types of sensitization may be produced by chemicals naturally present in gelatin, but it is necessary to add special compounds to the emulsion for the third type.

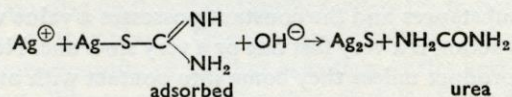
Sulphur Sensitization

Sulphur sensitization is the most widely-used method of conferring speed and contrast on a silver-halide emulsion. It was demonstrated many years ago that fast gelatins contain substances which formed small quantities of silver sulphide when emulsions containing such gelatins are digested. It was earlier believed that this substance was allylthiourea or some closely related material. The general formula

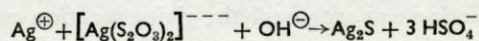
for these substances is



where the incompleted links carry a hydrogen atom or are the point of juncture of simple organic groups. Active compounds of this class usually possess the unsubstituted H atom, to make the formation of a silver-sulphur link possible. The fully substituted 1,1,3,3-tetramethylthiourea $(\text{CH}_3)_2\text{N} \cdot \text{CS} \cdot \text{N}(\text{CH}_3)_2$ is reported as being substantially inert. The complex so formed then reacts as



More recently, it has been made clear that although allylthiourea, or similar substances can sensitize an emulsion, the sensitizing substance of normal commercial gelatins is sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, possibly with sodium tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$. It is normal practice today to use a gelatin which is substantially free from this kind of additive and then to introduce it in the desired quantity. After addition to the silver-halide emulsion, the sulphur-containing compound is rapidly adsorbed to the crystal surface, this is a basic requirement for sulphur sensitization. Its adsorption may occur either by the reaction of silver ions present on the crystal surface with the sensitizer, e.g. thiosulphate, to form the complex ion in an adsorbed state or by the formation of the complex ion from the very low, but not negligible, concentration of silver ions existing in solution in the emulsion, followed by adsorption to the crystal surface. This adsorbed complex is then decomposed



to produce the sensitizing substance, silver sulphide, and by-products.

This equation illustrates two important points concerning sulphur sensitization, these are the dependence of the rate of the reaction on the pAg and pH. The rate of the reaction is directly proportional to the silver-ion concentration but the situation is not as simple with regard to pH. *James* and *Vanselow* found a dependence to a power greater than unity with allylthiourea, methylthiourea and other derivatives whereas *Sutherns* and *Loening* found the rate with allylthiourea to be proportional to the 0.7th power of the hydroxyl-ion concentration. Apart from pH and pAg, the rate of the digestion reaction is affected by the gelatin concentration, the temperature and the emulsion type, recent work has indicated very different rates on 100-faces, of silver bromide, relative to those of 111-faces.

This silver sulphide is part of the crystal surface, formed by the displacement of bromide ions and the replacement of every two of them by one doubly-charged sulphide ion and must not be confused with the massive quantities of brown precipitate formed by the precipitation of silver sulphide in a simple chemical reaction which is composed of massive three-dimensional crystals. Silver sulphide formed elsewhere, for example in the gelatin medium, usually gives yellow or

dichroic fog. By careful selection of the conditions it is possible to sensitize an emulsion by direct treatment with a sulphide-forming substance, such as hydrogen sulphide and in that case the silver sulphide must again be formed on the crystal surface.

Much attention has been given to studying the digestion reaction in order to obtain a clearer picture of the silver sulphide. The rate of a chemical reaction is proportional to the concentration of each of the reacting species, this is expressed mathematically in the Law of Mass Action.

Velocity = constant \times (concentration of A) \times (concentration of B), where A and B are the reacting substances and the constant possesses a value which is dependent upon whether the reaction is a very fast one or a very slow one. Now A and B cannot interact to form a product unless they come into contact with one another and the probability of their coming into contact would be dependent upon the concentration of each of them, the constant depends upon such things as how much energy is necessary to cause the molecules to interact on collision and so on. As the reaction proceeds the concentration of both the reacting substances will decrease and the velocity of the reaction will therefore decrease accordingly. This can be represented by the graph in Figure 5.2 which shows the completion of a normal reaction, involving two reacting substances, against time.

Many chemical reactions show a different type of behaviour known as *autocatalysis* in which one product, or less frequently both accelerate the reaction by catalysis. In this case, although the initiating process may be a very slow one, it rapidly becomes faster and then becomes slower as the reagents, or one of them, are consumed, the curve in Figure 5.3 shows this pattern of reaction.

Early work, carried out with much larger quantities of sulphur sensitizers, showed that the digestion reaction was autocatalytic, giving reaction curves similar to those in Figure 5.3. However, in recent years, the use of more refined methods, in partic-

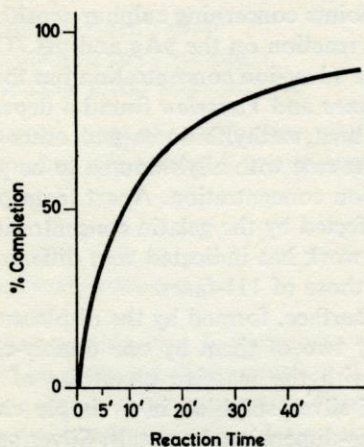


Fig. 5.2 Simple bimolecular reaction curve

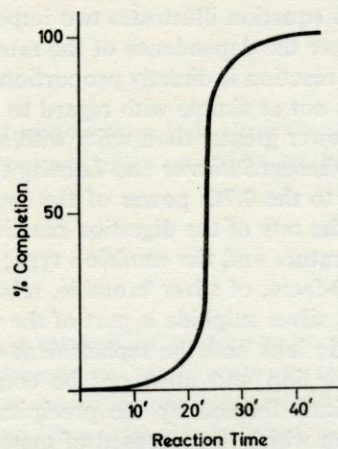


Fig. 5.3 Autocatalytic reaction curve

ular the application of radiotracer techniques which permit the reactions to be followed accurately with the small quantities normally used in emulsions, have shown a behaviour like that of the normal uncatyalsed reaction of Figure 5.2. *James* and *Vanselow* showed that silver sulphide, already formed on the grain, can accelerate the breakdown of further quantities of added sensitizer, thus supporting the earlier work, but *at normal emulsion quantities* there seems no evidence for autocatalysis. Indeed, *Sutherns* and *Loening* found that the initial stage of the breakdown of allylthiourea on silver-bromide sols is *more rapid* than that of the greater fraction of the reaction, this is shown in Figure 5.4. This important result suggests that reaction takes place at certain sites on the crystal surface where the initiation of the reaction is rather easier than at other places. One very surprising fact which concurs with this view is that optimum quantity of sulphur sensitizer varies very little with the grain size of the emulsion. When one considers that crystals of one micron diameter will possess roughly ten times the surface area of crystals of 0.1. micron diameter, then this is a very surprising fact indeed and points undeniably to the concept that only certain selected sites on each crystal need to collect their "coating" of silver sulphide.

Some emulsions do not require any distinct digestion treatment. These are silver-chloride emulsions made using fast gelatins, that is containing substantial quantities of sensitizing substance, and physically ripened in only a small excess (1-3 %) of chloride. The relatively low pAg of these emulsions, even before washing, enables the silver sulphide to be formed during physical ripening and in melting treatments so that the emulsion is fully sensitized by the time it is melted after washing.

It is, however, not certain that silver sulphide is the only sensitizing substance formed during sulphur sensitization. Although it is clear that silver sulphide is formed on the grain surface when an emulsion is digested, some of the Russian workers, notably *Chibisov*, are of the opinion that silver metal is the essential part of the sensi-

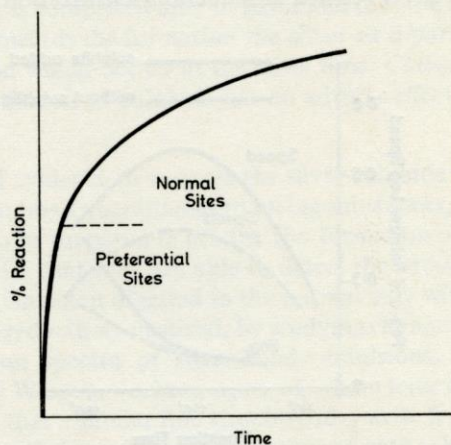


Fig. 5.4 Reaction curve showing initial rapid stage in formation of silver sulphide

tivity speck. They propose that the function of sulphur sensitizers is to encourage the formation of silver. This view of the sensitivity speck will be discussed after considering the next mode of sensitization.

Reduction Sensitization

The addition to the emulsion of very small quantities of reducing substances followed by a heat treatment, also produces an increase of emulsion speed similar to that obtained by sulphur sensitization, except that the contrast obtainable after treatment with a reducing agent is generally lower and there is a greater tendency to fog formation. Sodium sulphite and stannous chloride are examples of effective reducing agents and this kind of reduction sensitization may be carried out at the same kind of pAg and pH values as are used for sulphur sensitization. It is also possible to reduction-sensitize an emulsion by a heat treatment carried out in excess silver ions, bromide ions are then added to give the usual coating pAg. The reduction process has been shown to be autocatalytic. That is, the formation of further quantities of silver is accelerated, or catalysed, by silver formed early in the reaction. The type of reaction curve obtained in this case is shown in Figure 5.3.

After reduction sensitization, the sensitivity centres comprise silver atoms. These also reside on the grain surface but may not be an integral part of the surface (see Chapter 9) as are the silver sulphide entities. However, less attention has been given to this form of sensitization and therefore a detailed description is not possible. It is likely that a process in which a distribution of silver atoms is formed on the grain could easily give rise to fog, because when any one nucleus becomes as large as a latent-image speck it will be able to initiate development of the crystal. This conclusion agrees with the observed easy formation of fog by the reduction process. It has been shown that the silver formed in reduction-sensitization is only weakly associ-

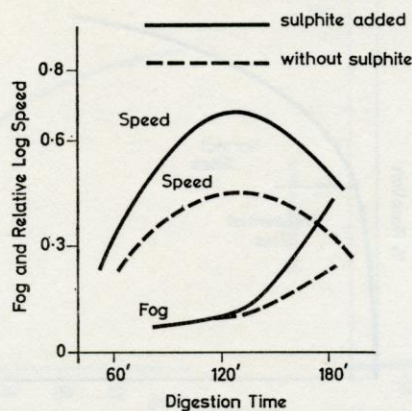


Fig. 5.5 Effect of sulphite on digestion

ated with the grain. This follows from the fact that stripping of the gelatin film from large silver-bromide crystals, which had been reduction sensitized, removed the bulk of the surface sensitivity. The same loss occurs with the adsorption of dyes in similarly sensitized emulsions. Also, although reduction-sensitization is prone to give fog, it is possible to confer considerable sensitivity without producing fog; this shows that the silver of the sensitivity speck must be different in some way from that of the latent-image, otherwise it would catalyse development. These facts suggested to *Mitchell* that the sensitizing substance was a small group of silver-atoms surrounded by gelatin molecules and therefore attached to, but slightly separate from, the grain. *Bekunov* has also drawn attention to the fact that the presence of sulphite can increase the sensitivity given by sulphur sensitization although no increase in the rate of growth of sensitivity was obtained. The rate of fog growth was found to be higher in the presence of sulphite, but only after maximum speed had been obtained, this is shown in Figure 5.5. The results of this and other similar experiments suggest that both silver sulphide and silver may be involved in sensitization, and therefore the nature of the sensitivity speck formed in commercial emulsion preparation will now be considered.

Nature of Sensitizing Substance from Sulphur Sensitization

Many different views have been expressed as to the exact nature of the surface speck on a silver-halide emulsion grain which is responsible for its photographic sensitivity. At the present time, the two most discussed views are

1. It is silver sulphide in a layer form, e.g. islands on the grain surface, as proposed by *James* and *Vanselow*, and that silver sulphide alone is able to explain the properties shown by the sensitizing speck.
2. The sensitivity speck is comprised only of silver and that the formation of silver sulphide is a step towards the formation of silver or a parallel, and possibly unnecessary, reaction which occurs at the same time. *Chibisov* and his colleagues even postulate that silver sulphide has an adverse effect on the properties of an emulsion.

There is a great deal of evidence to support the silver sulphide view, nevertheless there are present in gelatin small quantities of reducing substances, and since all commercial emulsions need to be prepared in gelatin the formation of silver is possible. The Russian workers claim that they are able to detect the presence of very small quantities of silver in an emulsion digested in the normal way with sulphur sensitizers, and not deliberately reduction sensitized, by studying changes in the fine structure of the light absorption spectra of silver-halide emulsions. This experimental work has been queried by Western workers, none of whom have been able to repeat it, and it has been shown that a similar fine structure may arise from an interference effect. Also, *Chibisov* himself showed that the presence of gold salts during digestion prevented the formation of non-halide silver. Since gold salts are usually added along

with the sulphur sensitizer (see later section of this chapter) and produce high sensitivity, this is strong evidence against the silver-speck theory.

If the quantities involved in these sensitization processes are considered the very great difficulty in carrying out analytical and other studies of the sensitization reactions will be appreciated. In an emulsion, such as the one mentioned above possessing 4×10^{14} silver-halide grains per gram mole of silver, there will be something like 10^9 silver ions per grain and, if all the sulphur sensitizer is reacted (which is unusual) only about one in 50,000 of these silver ions will be converted into silver sulphide. If it is assumed that as many as 100 silver atoms per grain are necessary in order to render the grain developable, then only one silver atom in every 10,000,000 would be involved in the conversion. It seems very likely that the quantities of silver concerned with the sensitizing process might even be less than this and therefore any method for checking the chemical nature of the sensitivity speck must be able to estimate quantities of silver far smaller than those of silver sulphide, and this is beyond the limit of ordinary chemical analysis.

Another view of the sensitizing entity has been proposed by *Sauvenier* and *Hautot*, who suggest that it is the silver-thiosulphate complex, adsorbed to the grain surface, which is the sensitivity speck and provides the site at which silver atoms are formed. As it is known that the sulphur sensitizer is very rapidly adsorbed to the surface and that, in the presence of gelatin, only a fairly slow reaction gives rise to the required sensitivity, these authors propose that an etching reaction, arising from the silver-halide solvent action of the thiosulphate, is necessary to create the correct surface condition for sensitization. The formation of silver sulphide in appreciable quantity is believed to produce fog.

The current position of the sensitivity speck theory would be best viewed as follows: the formation of silver sulphide by the breakdown of the silver-sensitizer complex on the grain surface at certain reactive sites results in the formation of small quantities of silver sulphide. If it is necessary that this must be accompanied by the formation of an even smaller quantity of another sensitizing substance, e.g. silver, then this occurs in a way which, at the moment, we cannot detect.

Nature of Digestion Fog

The question then arises as to what constitutes a centre which will produce fog. Examination of the diagram above (Fig. 5.1.) shows that in a normal emulsion, as maximum sensitivity is approached, some of the grains reach a state where they are fogged, that is develop without the action of light. These fog centres could consist of:

1. Aggregates of silver sulphide which are distinctly different in shape from the sensitizing form, for example, the formation of a three-dimensional lattice.
2. Specks of silver sulphide which are larger than are necessary for increasing sensitivity, but recent work has shown that even large quantities of silver sulphide are unlikely to render the grain developable.

3. Within or adjacent to a silver-sulphide speck there is a slower or more selective reaction proceeding, which could be the formation of silver, and that when this has proceeded beyond a certain point, for example, the formation of an aggregate of silver large enough to initiate development, then the grain becomes fogged.

Therefore it is likely that the sensitivity and fog specks, which it is assumed are of similar type, would not be pure silver sulphide or pure silver but would probably comprise both substances. Evidence has recently been produced to support this view. The digestion of emulsions containing only very small quantities of sensitizer, e.g. thiourea, for prolonged periods produces fog which can be almost completely bleached by dilute chromic-acid solutions while a similar level of fog, produced by a large quantity of sensitizer, is very resistant to bleaching. This result suggests that silver, which is easily oxidized by the bleach, is present to a pronounced extent in the fog produced by prolonged digestion with small quantities of thiourea while the use of large amounts of sulphur sensitizer give mainly silver sulphide. The action of a subsequent gold treatment on the fog is also interesting. That ascribed mainly to silver sulphide becomes lower in density which is in agreement with the finding that the presence of gold reduces physical development by silver-sulphide nuclei. On the other hand, the post treatment by gold enhances the fog believed to be due to silver centres.

The tendency for silver sulphide to collect silver ions, and thereafter assist in their reduction to silver atoms, to give fog centres, is commented on by a number of workers. Thiourea forms silver sulphide very slowly at pH 6.0 whereas at pH 8.0 it reacts very rapidly. It has further been shown that if the reaction of silver halide with thiourea has been started at pH 8.0 and, when the reaction is incomplete, the pH is dropped to 6.0, the formation of fog continues at a fair speed. These experiments suggest that this fog is due to silver or silver in combination with silver sulphide, again showing that the presence of some silver sulphide aids the formation or stabilization of silver.

In conclusion, it seems possible that fog is probably silver in many cases, certainly in commercial emulsion, and it is only with large quantities of sulphur sensitizers that silver-sulphide fog is really important.

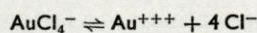
Gold Sensitization

About thirty years ago a further method of chemical sensitizing photographic emulsions was discovered by the *Agfa* workers, based upon treatment of the emulsion with a solution of a gold compound. The gold compound is used in amounts comparable to the sulphur sensitizer and is one of two types: potassium aurothiocyanate or potassium aurochloride. The complex potassium aurothiocyanate, the original gold sensitizer, is formed by treating gold chloride with an equivalent quantity of an alkali thiocyanate.

Gold sensitization alone gives a very poor effect characterized by a low contrast and is, therefore, always applied in conjunction with sulphur sensitizing. This is normally done by adding both sensitizing substances before the commencement of digestion although it has been stated that useful gold sensitizing effects can be obtained by the use of gold as a final addition. The results of combined gold and sulphur sensitization are shown in Figures 5.6 and 5.7, the first showing digestion curves with and without gold while the other shows a pair of characteristic curves at optimum effect.

The conditions for the use of gold are critical. there is always a tendency with gold sensitization to produce fog and the type of gelatin used both for ripening and digestion of the emulsion is very important. Under optimum conditions, the speed obtainable by the combination of gold and sulphur sensitization is 2 to 2½ times that obtainable by sulphur sensitizing alone. Gold sensitization is effective on both negative and positive emulsions but is used mainly with fast iodobromide materials, such as those for camera use, either black-and-white or colour, or X-ray emulsions. It is apparent from the literature that the effect of gold upon the rate of the digestion process is dependent upon the nature of the emulsion being studied gold salts may either accelerate digestion or retard it.

The mechanism of gold sensitization is uncertain. All the methods described in the literature involve the use of complex gold salts and since no sensitizing occurs if a very stable gold complex is used, it appears very likely that a fairly low concentration of gold ions are required which are then converted, probably at the same site on the crystal at which the other sensitizing reactions take place, into the sensitizing substance. The concentration of gold ions is not the same as that of the complex ions: in a solution containing the complex ion, e.g. that of the aurochloride, there is always an equilibrium



producing a certain concentration of free gold ions.

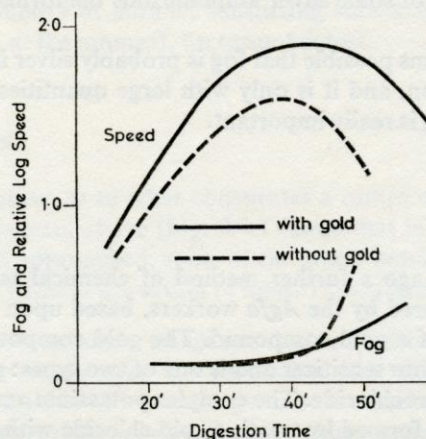


Fig. 5.6 Effect of gold on digestion: iodobromide emulsion

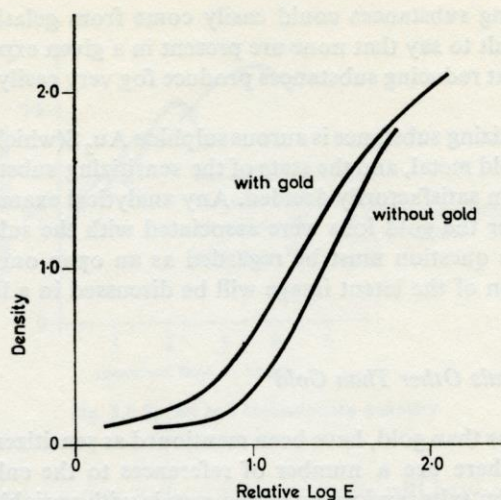
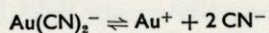
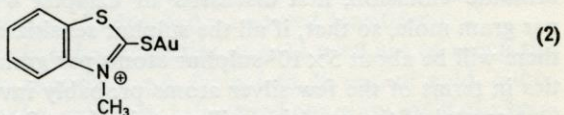
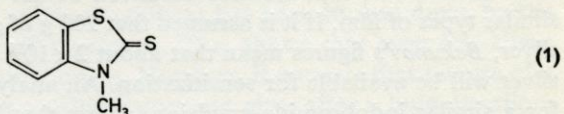


Fig. 5.7 Effect of gold on D-log E curve: iodobromide emulsion

The necessity of the concentration of gold ions being within certain limits is well illustrated by two facts. The first is that the very stable gold cyanide complex salt, $K Au (CN)_2$, does not sensitize at all. This is because the equilibrium, analogous to that given above



is very heavily displaced towards the left-hand side. The second is a patent claim that the use of certain organic agents complexed with gold salts, and supplying definite concentrations of soluble gold, are particularly effective in giving gold sensitization when added before digestion. Amongst these compounds is the N-methylbenzothiazole-2-thione (1) which gives the gold complex (2), the equilibrium giving just the optimum free gold-ion concentration.



Another observation is that gold-sensitized emulsions are very susceptible to the action of small quantities of reducing substances. It has been stated that in the absence of any reducing substance, gold sensitization is not possible although, of

course, such reducing substances could easily come from gelatin impurities and, therefore, it is difficult to say that none are present in a given experiment; there are many indications that reducing substances produce fog very easily in gold-sensitized emulsions.

Whether the sensitizing substance is aurous sulphide Au_2S (which has been claimed as a sensitizer) or gold metal, and the state of the sensitizing substance on the grain surface have not been satisfactorily decided. Any analytical examination would fail to determine whether the gold ions were associated with the sulphide ions and at the present time the question must be regarded as an open one. The function of gold in the formation of the latent image will be discussed in a later section.

Sensitization by Metals Other Than Gold

Many metals, other than gold, have been mentioned as sensitizers for photographic emulsions, e.g. there are a number of references to the enhanced sensitivity produced by cadmium salts, and many of the metals with variable valency, such as mercury, iron, palladium and platinum have been mentioned in the patent literature. At a conference in London in 1960 on the maximum sensitivity of photographic materials, reference was made to the use of palladium, in particular in the sensitization of the fastest emulsions.

Quantities of Sensitizer

The active sulphur quantity present in gelatin varies from 1 to 2 parts per million for the inert types to 100 parts per million for active gelatins. *Bekunov* gives quantities, similar to those of other authors, of between 25 and 150 parts per million of thiosulphate in a gelatin added to sensitize an iodobromide emulsion containing 3.1 molar per cent of iodide and mean grain size 1.2–1.4 μ^2 surface area; this would be a normal fast iodobromide emulsion of the type used for *Kodak Tri-X* and similar types of film. If it is assumed that 200 g of gelatin are used per gram mole of silver, *Bekunov's* figures mean that about 2×10^{19} sulphur atoms per gram mole of silver will be available for sensitization. An analysis of figures given by *Dickinson* for a similar iodobromide emulsion, shows that his range of quantities of added thiourea are greater than 0.6×10^{18} sulphur atoms per mole of silver. In the iodobromide emulsion, first discussed in Chapter 4 p. 66, there are 4×10^{14} grains per gram mole, so that, if all the sulphur sensitizer is converted into silver sulphide there will be about 5×10^4 sulphur atoms per grain. These are considerable quantities in terms of the few silver atoms probably involved in latent-image formation. One crystal of the emulsion will contain about 3×10^8 silver ions on the surface and therefore only about 3% of this silver (2 silver ions per sulphur atom) will be associated with sulphur, and the silver sulphide will tend to be formed in a small number of groups of atoms probably located at certain places on the surface. Finer grain

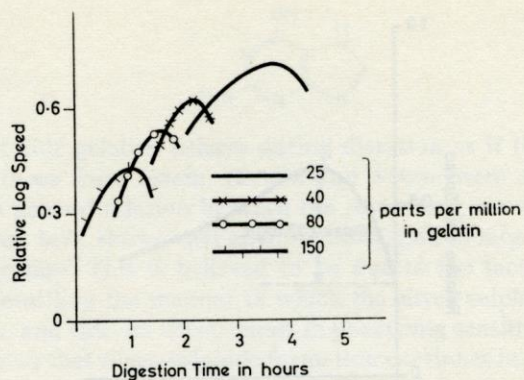


Fig. 5.8 Speed and thiosulphate quantity

emulsions, possessing a larger surface area per mole, will have a smaller percentage of their surface covered and, of course, fewer sulphur atoms per grain, there is no indication from the literature that such emulsions require more sensitizer per mole of silver.

The question arises as to whether these quantities of sensitizer are optimal. It is clear from many publications that quantities far larger than these produce no more speed and some of *Bekunov's* data, given in Figure 5.8, show that larger quantities produce lower maximum speed. With other gelatins, not specified, *Bekunov* obtained a constant maximum speed over a wide range of values of added thiosulphate. It might be expected however, that there was an optimum quantity but if there is a lower limit it has not yet been established. Since the rate of digestion is controlled by the content of both retrainer and sensitizer, it is likely that the use of very small quantities of sensitizer would result in the onset of fog before useful sensitivity is obtained. This may well be the controlling factor

Recent work has shown that, under widely differing circumstances, only a fraction, usually around 10%, of the sulphur sensitizer has been broken down by the time that the speed has reached its maximum. This shows that even less silver sulphide is required than previously thought. However, it appears that the use of a corresponding quantity of sulphur sensitizer does not give, after a long digestion, as high a photographic sensitivity; fog formation is increased. It seems likely that in addition to silver sulphide another agent is needed, *Sutherns* and *Loening* suggest the need for sufficient surface coverage of adsorbed unreacted sensitizer.

It appears from published data that the quantities of gold used are of much the same order as that of the sulphur sensitizer, e.g. from 1 to 30 mg. of gold, either as chloroauric acid or a more complex gold salt, being used per gram mole of silver. If a gold sensitizer is added at the completion of digestion, then larger quantities are needed. There is an optimum in the quantity of gold required in an emulsion and this is shown in Figure 5.9., where the quantity of gold added is plotted against

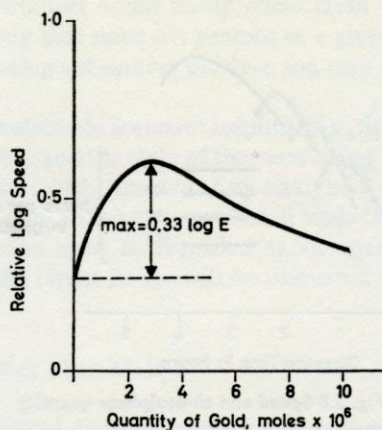


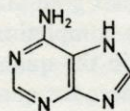
Fig. 5.9 Quantity of gold — sodium aurothiocyanate iodobromide emulsion

the speed increase produced, the maximum increase in this case over speed from sulphur sensitization alone is $0.33 \log E$ units.

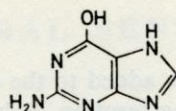
The amounts of other rare metals added for sensitization are of a similar order to those of gold.

Restrainers

This topic was mentioned earlier but will now be discussed in more detail. It is known that in the presence of the same quantity of sensitizing substance, whether the sensitization is carried out by fast gelatins or by added sensitizer introduced just before the digestion stage, the same emulsion will digest at quite different rates with different gelatins. This fact led to the view that there were substances present in gelatin which controlled the rate of sensitization, these were therefore called *restrainers*. The nature of these restrainers has been the subject of much speculation. Probably the closest approach to the answer of their identity to date lies in the work of *Gordon* and *Swann*. These workers demonstrated that gelatins from hide contained an average of 30–50 parts per million, sometimes even 200 p.p.m. of adenine (3), a heterocyclic substance related in structure to many of the stabilizers (guanine (4), was also present), but gelatins from ossein were found to contain only 4–6 p.p.m. of adenine.



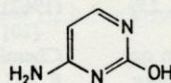
(3)



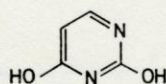
(4)

It is known that hide gelatins behave during digestion as if they contained more restrainer than those from ossein. *Gordon* and *Swann* were able to demonstrate that there was a general relation between the restraining activity and the adenine content, and it has been shown that adenine slows, and in large quantities curtails, chemical sensitization. This is believed to be due to the fact that the restrainer functions by controlling the manner in which the silver sulphide is laid down on the grain surface, and thus its effectiveness in producing sensitivity and fog. Analytical evidence shows that silver-sulphide formation continues in spite of the presence of the adenine and its effect on sensitization. The opinion has been expressed that the influence of the adenine may be to cause the silver sulphide to be located in the absorbed gelatin layer instead of on the grain surface.

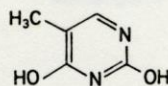
One important point must however be made: the method applied for the determination of the adenine uses drastic treatment which would break down any fragile molecule. There is, therefore, no real support for the assumption that adenine itself is the restraining substance, it is much more likely to be a derivative of adenine, probably of high molecular weight. The pyrimidine fragments from nucleic acids, cytosine (5), uracil (6) and thymine (7) are not generally referred to as frequently as adenine and guanine and have been shown to be far less active restrainers than the fused ring compounds.



(5)



(6)



(7)

Reference is frequently made to 'the addition of artificial restrainers' and it seems likely, therefore, that at least some manufacturers make such additions to their emulsions.

Digestion Accelerators

Some writers refer to substances added to the emulsion before digestion which influence the rate of the sensitizing reaction. Polyethylene oxides (see Chapter 8) were believed to be in this class at one time. The polyamines mentioned by *Kodak*, for example diethylene triamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ would seem to be the kind of agent likely to etch the grains and, therefore, accelerate digestion. Another substance mentioned is ammonium thiocyanate. However, as in the case of restrainers, these kinds of additions to commercial emulsions are closely-guarded secrets.

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VI SPECTRAL SENSITIZATION

Introduction

The foregoing chapters have described how photographic emulsion crystals may be prepared and their light-sensitivity improved. A very important law of photochemistry, the *Grotthus-Draper* law, states that only that light which is absorbed can be effective in producing a chemical change; the formation of a latent image is a chemical change. Silver chloride absorbs no appreciable light in the visible region whilst silver bromide alone or admixed with iodide absorbs light at the blue end of the spectrum only. Therefore, emulsions prepared from these halides will only be sensitive to blue or violet light and are described as non-colour sensitive; their spectral sensitivity is shown in Figure 6.1.

In order to confer sensitivity in other regions of the spectrum, light of different colour must be absorbed in some way and the absorbed energy transferred to the silver halide in order to produce a latent image. This is achieved by sensitizing the emulsion with a particular class of chemical compounds, dyestuffs, and is termed *spectral sensitization*. There are vast numbers of coloured substances and dyes, which absorb light in the long-wavelength region of the spectrum, such as those used for dyeing textiles, plastics, etc., but most of these are either completely without action in a photographic emulsion or have adverse effects.

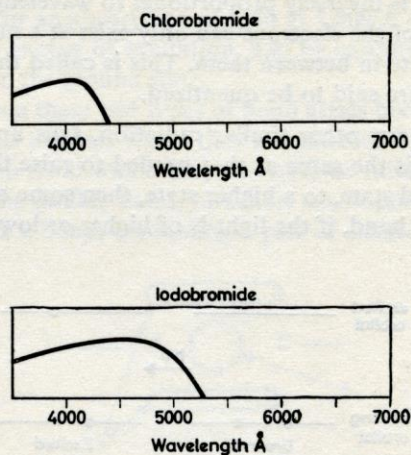


Fig. 6.1 Spectral sensitivity of undyed emulsions

Light Absorption by Molecules

BASIC PRINCIPLES. It is useful at this point to consider the absorption of light by a molecule. Every atom possesses a nucleus and electrons. The nucleus is a positively-charged entity in which the greater part of the mass resides, while the negatively-charged electrons lie outside it; in a molecule an important proportion of the electrons lie between the nuclei of the atoms and make up the bonds joining the nuclei together to form the molecule. These bonding electrons exist at certain energy levels and the most important level is the unexcited or *ground state* of a molecule; this can be thought of as the state of a molecule at rest and it may be assumed that almost all the molecules in a solid or solution at room temperature exist in this state.

When a molecule absorbs radiation, the energy contained within the radiation is transferred to the molecule. There are two important facts which must now be appreciated.

1. The energy of a particular beam of radiation is that of each individual photon of the radiation, and does not depend on the intensity of the radiation, which is merely governed by the number of photons. The value of this energy is given by the simple equation

$$E = h\nu,$$

where E is the energy, h is Planck's constant and ν is the frequency of the radiation, that is the number of vibrations per second. Now it is well known that every form of radiation consists of electromagnetic waves, which are propagated at the same speed, 3×10^{10} cm per second. Therefore: —

$$\text{wavelength} \times \text{frequency} = \text{velocity},$$

that is, the energy is inversely proportional to wavelength.

2. The energy states of the electrons can only exist at a number of distinct levels and not at any state in between them. This is called the quantum theory and the energy states are said to be quantized.

If therefore light, or any other similar radiation, falls upon molecules, and the energy of each photon is the same as that needed to raise the molecules from one state, usually the ground state, to a higher state, then some of these photons will be absorbed. On the other hand, if the light is of higher or lower energy it will not be absorbed.

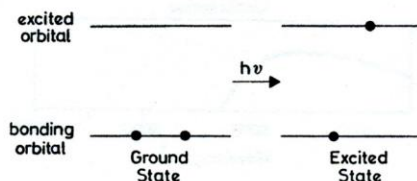


Fig. 6.2 Ground and excited states in molecules

Radiation from the U.V. and visible region (1,000–10,000 Å) is of appropriate energy to cause changes in the energy levels of the bonding electrons and is able to raise the molecule from the ground state to the first excited state. (Figure 6.2). It is worthwhile mentioning that infra-red light, just beyond the visible spectrum (20,000–150,000 Å), causes vibration of the molecule, that is stretching of the bonds, or rotation of the atoms in the molecule but these changes cannot be put to any photographic use in silver halide. However, the *Thermofax* document-copying process uses the absorption of infra-red rays by the original image to cause local heating which is then exploited in bringing about the chemical process in the copy sheet.

SINGLE AND DOUBLE BONDS. The types of molecules which show these changes will now be examined. Consider a very simple molecule, ethane (1)



which contains only very stable single bonds, and only absorbs the very high energy u.v. light at 1,300 Å. The only electronic changes which can occur in such a molecule will virtually break one of the bonds. Molecules containing double bonds, or triple bonds, behave in a more interesting manner. In a molecule where the double-bonded atoms are joined by two pairs of electrons, it is possible to elevate one of the electrons to an excited state, where it can no longer bond the molecule, and yet the two atoms are still kept together by the intact pair. In a substance such as ethylene (2) the electrons of the C=C double



bond are responsible for an absorption of light at 1,800 Å and the excited ethylene molecule then loses its energy of excitation, e.g. by causing changes in the environment, and drops back to the ground state.

The difference between these two types of bond arises because the electron pair of a single bond reside in σ orbitals where they are shielded by the nuclei and located in a very stable position from which they can only be raised to a higher level by a high energy photon. The double bond, however, is composed of a σ bond, with its pair of electrons, plus a π bond, containing a pair of electrons in π orbitals (Figure

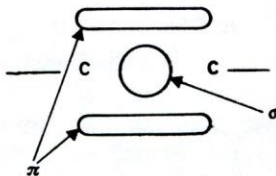
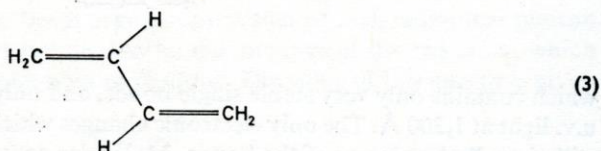


Fig. 6.3 Illustration of orbitals in double bond

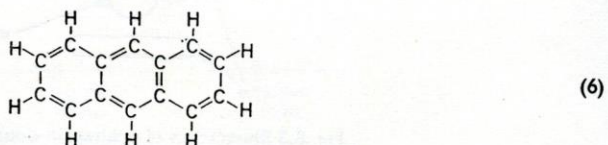
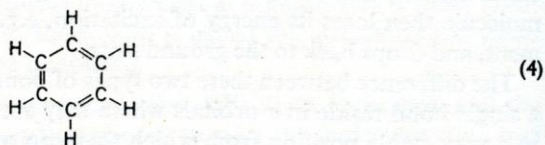
6.3). Unlike a σ bond, a π orbital is composed of two similar spaces situated outside the line joining the two nuclei and electrons in these π spaces are more easily raised to an excited state.

Conjugated Molecules

If a molecule contains a number of π orbitals so placed that they can interact with one another, that is the available electrons can be regarded as being spread over a larger volume, it is termed a *conjugated system*. In a conjugated system, there exist a multiplicity of excited states, and generally speaking, the *larger* the conjugated system, the *lower* will be the energy difference between the ground state of the molecule and its first excited state, the difference which controls the wavelength of the longest wave absorption band. For example, the simplest conjugated molecule is butadiene (3).



containing two ethylene units joined together. The π orbitals overlap at the middle of the molecule with the result that the longest wavelength of absorption moves from the 1,800 Å of ethylene to 2,100 Å. Another, and well known, example of conjugation is benzene (4) in which there are three double bonds, all in a position to permit the conjugation of their π orbitals, forming a closed ring of six π electrons and in which the



longest wavelength absorption occurs at 2,590 Å. The more complicated naphthalene (5) has its first maximum at 2,750 Å, while anthracene (6) absorbs at 3,700 Å, very near to the visible spectrum.

LONG-CHAIN MOLECULES. The absorption of a series of compounds (7) containing a chain of carbon atoms with alternate single and double bonds and bearing phenyl groups at each end is shown in Table 6.1.

TABLE 6.1
 $C_6H_5-(CH=CH)_n-C_6H_5$
 LIGHT ABSORPTION
 OF A SERIES OF DIPHENYLPOLYENES

<i>h</i>	Longest absorption maximum Å
0	2,520
1	3,180
2	3,520
3	3,770
4	4,040
5	4,340
6	4,580
7	4,740
11	5,300
15	5,700

These results show that there is no essential difference in structure between a coloured substance and a non-coloured one. Indeed, all substances will absorb light; some appear coloured because the transmitted or reflected light is deficient in some of those wavelengths comprising white light. In what has been called the "dyestuff era" of organic chemistry, between 1850 and 1910, many scientists believed there was an essential difference between coloured and colourless compounds, which led to the view that there were certain groups in the molecule conferring colour: *chromophores*; other groupings which generally enhanced colour were called *auxochromes*. However, it is far better to consider the whole of the conjugated part of the molecule and not isolated groups.

Conjugation with Atoms other than Carbon

Although it is possible to obtain compounds incorporating only carbon atoms in the conjugation system, which are able to absorb in various regions of the spectrum, for many reasons the photographically interesting dyes always contain other elements. One very important grouping which enables a molecule to have excited

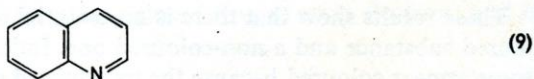
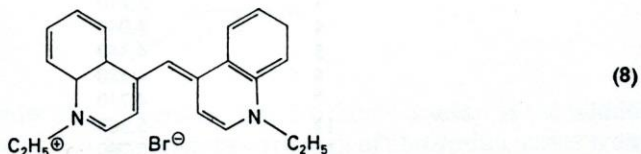
states at a fairly low energy level is the $-N=N-$ unit, called the azo link. Dyes containing this linkage are used in colour photography but no azo dyes act as spectral sensitizers.

Intensity of Light Absorption

Organic chemicals vary very widely in the strength or intensity of their light absorption. Clearly a spectral sensitizer is not going to be much use unless it absorbs the light very strongly and it is fortunate that the useful spectral sensitizers do possess a very high intensity of absorption, almost as high as is theoretically possible, although this absorption power is greatly influenced by the environment of the dyes.

Cyanine Dyes

HISTORY. The dyes used exclusively today for spectral sensitization are the *cyanine dyes*.



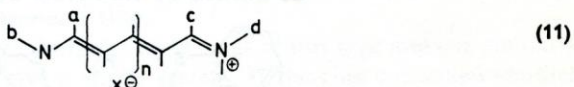
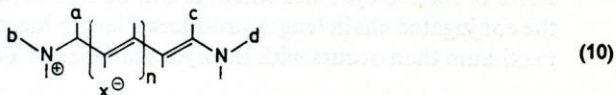
In 1873 *Vogel*, seeking to obtain a filtering effect by the use of dyes, discovered that silver-halide crystals could be spectrally sensitized. This was quickly exploited commercially and one of the early dyes which was suitable was Cyanine, which had been discovered by *Greville Williams*, as long ago as 1856, and whose structure is now known to be (8). A variety of dyes termed Isocyanines, Pseudocyanines, and so on, were produced. Later dyes containing rings other than the quinoline nucleus (9) were synthesized and from that time, the term cyanine has been applied in a generic sense to all materials of this class.

The methods used for preparing sensitizing dyes are outside the scope of this book and the reader is referred to the recommendations for further reading. The difficulties of synthesis and the "fragile" nature of the dye molecule has led to the devising of many elegant syntheses by *Pope, Mills, Koenig, Hamer, Kendall, Brooker* and many others. The cyanine dyes can be divided into two broad classes: *the true cyanines* and *the merocyanines*.

The True Cyanines

GENERAL FORMULAE. The true cyanines are compounds in which the ends of a conjugated carbon chain with an odd number of carbon atoms are occupied by nitrogen atoms, as shown in formula (10), one of which is the normal trivalent state and the other is quadrivalent, positively charged nitrogen, as occurs in ammonium salts, associated, of course, with

is an anion
= a integer



a negative ion to balance the molecule. This negative ion is most commonly a separate ion such as chloride, bromide, etc., but in some cases may be contained within the dye molecule as an ionized acid group such as —COO^{\ominus} or —SO_3^{\ominus} . It will be seen that merely by changing the arrangement of the bonds, the molecule (10) may be rewritten as (11). In fact in a symmetrical molecule, such as Cyanine itself, the charge will be distributed equally between the two nitrogen atoms. The free bonds in the general formula may be joined to a large variety of groups, may complete rings or be parts of longer chains and so on. The overall molecule may be quite unsymmetrical and in that case the charge will be located more on one side than the other. In the majority of dyes the bonds a and b form part of one ring and c and d another ring; the rings may contain only carbon atoms but the best dyes are those containing sulphur or oxygen in these rings as well as carbon.

One aspect of cyanine structure must be stressed: all the bonds must lie in one plane because conjugation through the whole π bonded system requires that all the chain atoms, including the nitrogen, must participate. Therefore, the nitrogen atoms must also be planar in their bond arrangements. Failure to achieve this overall planarity due to the geometry of the whole molecule, results in a decrease of light absorption and sensitization by the molecule.

POSITION OF ABSORPTION MAXIMUM. The absorption maximum of a cyanine dye depends on two factors: —

1. The basicity of the nitrogen atoms. Generally speaking the more basic the nitrogen, the longer is the wavelength of the first absorption band. This basicity is, however, rather specially defined and may not be simply equated with the simple basic strength in terms of the ease of salt formation by the ring com-

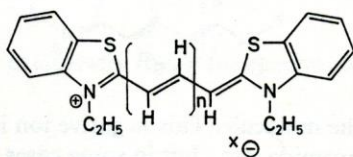
pounds incorporated in the dye. The detailed influence of this factor has been studied by *Brooker* but is outside the scope of this book.

- The length of the carbon chain which is the most important influence. It will be observed from Table 6.1 that, as the chain becomes longer, the wavelength increase produced by each successive increase is less. In cyanine dyes this is not the case and this is fortunate otherwise infra-red photography would not have been possible. Table 6.2 shows the wavelength of the absorption maxima of a series of related cyanines where it will be observed that the same increment in the conjugated chain length produces a larger increase in the wavelength of the maximum than occurs with the hydrocarbons of Table 6.1.

TABLE 6.2

General Formula

WAVELENGTH OF ABSORPTION MAXIMA
OF SERIES OF RELATED CYANINES



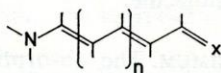
(12)

<i>n</i>	Wavelength Å
0	4230
1	5570
2	6500
3	7580

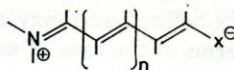
Merocyanines

The *merocyanines* (13) contain a chain of an odd number of carbon atoms with a ternary nitrogen atom at one end and the other end is double bonded to another hetero atom, usually oxygen but it may be sulphur or nitrogen, and the total molecule does not possess

$$x = \text{O}, \text{N or S}; \quad n = \text{an integer}$$



(13)



(14)

a charge. A bond rearrangement occurs in a manner similar to that shown by the cyanines to give a dipolar form as indicated in (14); the actual state of the molecule is again intermediate between the two possible formulae. The polarity of the environment can have an important effect on the electronic structure of the molecule and on its sensitizing effect because it is adsorbed to a highly polar surface when present in a silver-halide emulsion. Again, the uncompleted bonds may be, and usually are, incorporated in rings.

Heterocyclic Rings

The stability and the reactivity of the benzene ring (15) are related to the arrangement of three single and three double bonds in the ring, or each of the six carbon atoms in benzene has a π -orbital electron and all the orbitals overlap to form a stable system; this system is called an *aromatic* ring.

Elements other than carbon can be included in rings of this type and can similarly contribute their π electrons to give a stable system. If the ring contained another atom, e.g. trivalent nitrogen, instead of one of the $-\text{CH}=\text{}$ groups, it would be termed

a *heterocyclic* ring, e.g. pyridine (16).



(15)



(16)

Five-membered heterocyclic rings, (17), (18), (19), are also valuable in photographic chemistry and it is important that both the six-membered



(17)



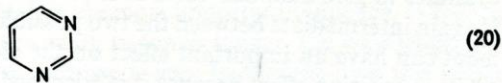
(18)



(19)

pyridine ring and these five-membered rings possess the aromatic stability and reactivity of benzene. Heterocyclic rings containing two hetero atoms are very important,

e.g. pyrimidine (20) present

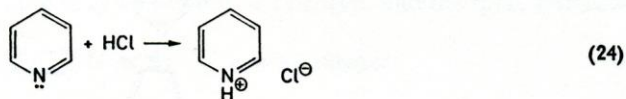


in so many stabilizers (see Chapter 7), thiazole (21) and the pyrazole ring (22), present in almost all magenta colour couplers.

However, not all heterocyclic rings possess aromatic character. If, for instance, the carbon – carbon double bond in thiazole (21) is converted to a single bond, by the introduction of extra atoms or groups, the thiazoline ring (23) is obtained which, although not possessing the stability of an aromatic ring, is easily introduced into sensitizing dyes, and many thiazoline cyanines are mentioned in the literature.

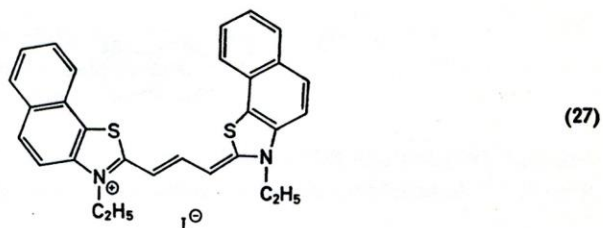
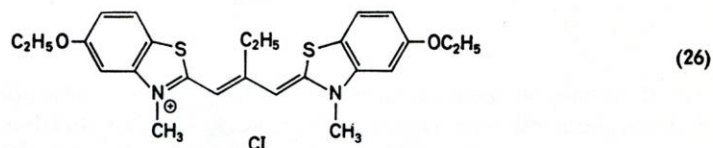
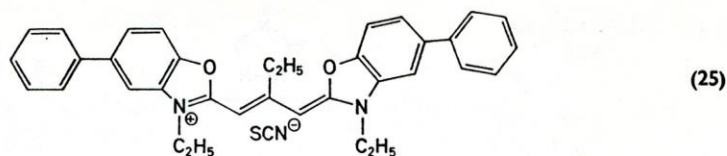


Brief mention should also be made of the substituents attached to many nuclei. Oxygen and sulphur in a ring cannot carry a substituent because no available bond remains, but nitrogen in the form –NH– can have the hydrogen replaced by an organic radical such as a methyl CH_3 – , ethyl C_2H_5 – or phenyl C_6H_5 – grouping. The trivalent –N= many carry a fourth substituent by virtue of the nitrogen carrying a positive charge. The simplest case of this is the salt (24) formed from pyridine and an acid such as hydrochloric acid:

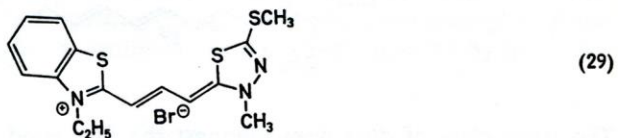
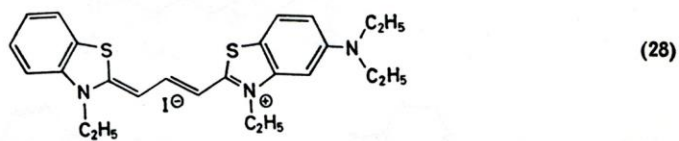


In the same way as the uncharged –NH– group, this charged nitrogen may carry a hydrocarbon unit, e.g., as in Cyanine (8) itself.

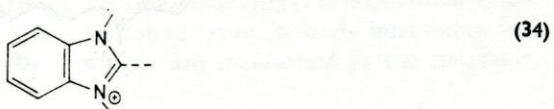
The carbon atoms in all these rings, bearing only a hydrogen in the parent substance, may be substituted by a vast range of atoms or groups and this influences the light absorption of the dyes. Some of the common substituents are illustrated by the well-known 5,5'-diphenylbenzoxazole dye (25), the 5,5' diethoxybenzothiazole dye (26) and dye (27).



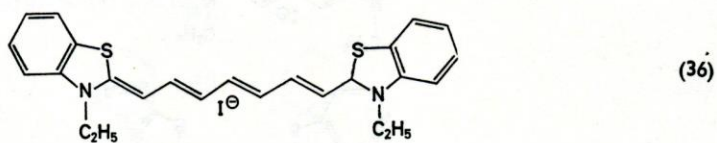
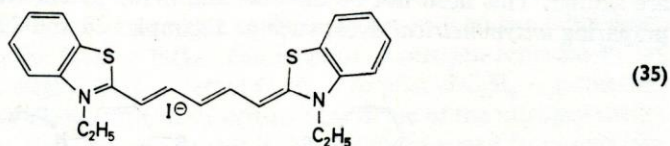
It will be observed that in two of these examples the middle carbon atom carried a substituent; in many dyes this is an important factor which can greatly modify the sensitizing properties. Examples 25–27 are *symmetrical* dyes, that is both rings are similar. This need not be the case and many patents relate to the methods of preparing *unsymmetrical* dyes; such as Examples 28 and 29.



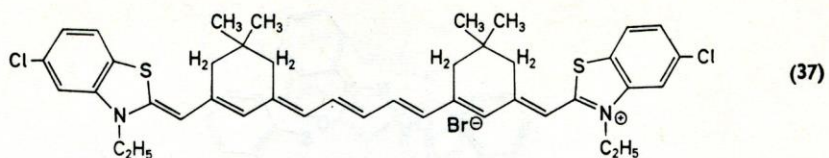
A wide variety of heterocyclic rings, not all of them of aromatic type, have been used in cyanines; these include thiazoline (23), triazole (30), pyrroline (31), indole-nine (32), benzoselenazole (33), and benzimidazole (34), the dotted lines showing the point of attachment of the polymethine chain.



The polymethine chain may be extended considerably, for example dyes with five (35) and seven (36) carbon atoms in the chain.



The latter class of dyes were amongst the first good sensitizers to the infra-red. This process cannot be continued indefinitely, partly because it becomes increasingly difficult to devise convenient syntheses for obtaining pure dye but more because dyes with very long chains are unstable although a cyanine dye (37) with thirteen carbon atoms between the two rings has been prepared, which has an absorption maximum at 11,000 Å in solution, and sensitizes in the far infra-red at 11,800 Å.

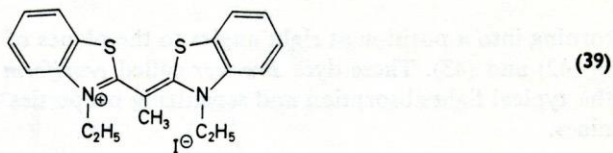
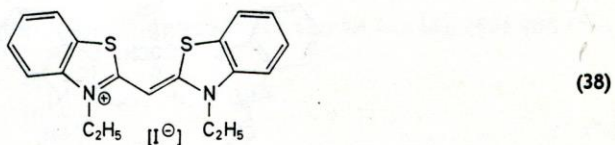


Distorted Cyanines

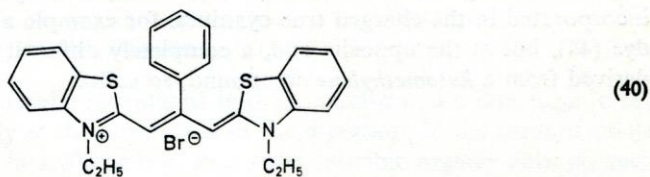
In a cyanine dye the whole central part of the molecule must be planar. If the various parts of the molecule are such that crowding occurs, then the molecule will be unable to remain planar and usually three effects will be observed.

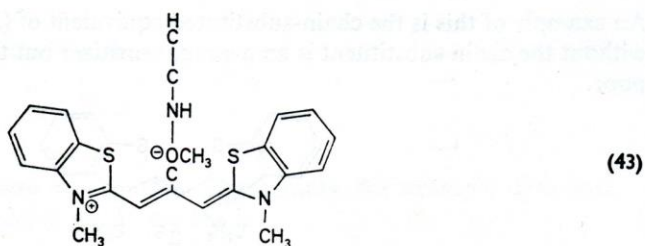
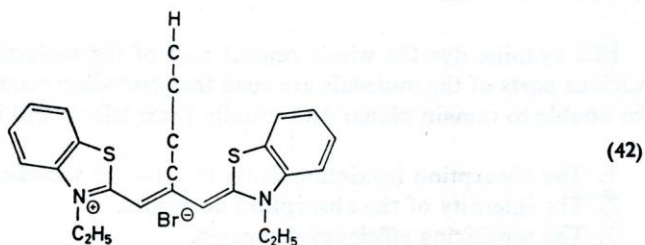
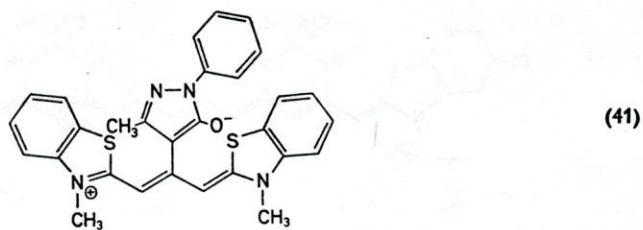
1. The absorption maximum shifts to a longer wavelength.
2. The intensity of the absorption decreases.
3. The sensitizing efficiency decreases.

An example of this is the chain-substituted equivalent of (38), the dye (39). The dye without the chain substituent is an average sensitizer but the substituted dye is very poor.



Certain cases of dye molecules which might be expected to show extreme crowding do, in fact, relieve this by a surprising change. Two very good examples of this are the dyes (40) and (41) where the strain can be completely relieved by the bulky middle substituent

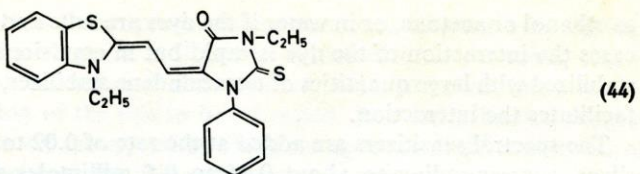




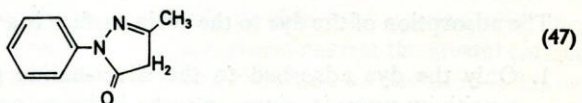
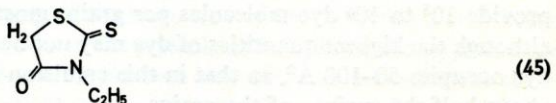
turning into a position at right angles to the planes of the rest of the dye as shown in (42) and (43). These dyes *Brooker* called *cruciform* molecules and they possess the typical light absorption and sensitizing properties of the simple trimethincyanines.

Examples of Merocyanines

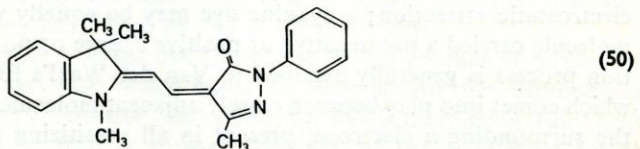
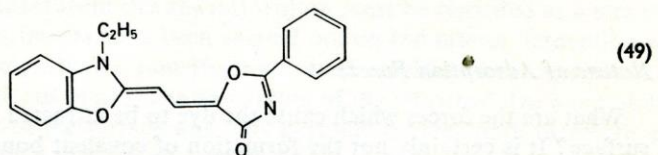
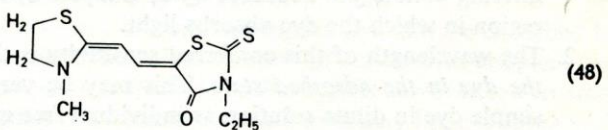
In a merocyanine dye, the rings at either end of the chain are of different types. The commonest merocyanines are those with a two-carbon chain, referred to as dimethin merocyanines. At one end of the chain, the ring is of a similar type to that incorporated in the charged true cyanines, for example a benzothiazole ring as in dye (44), but at the opposite end, a completely different ring is present, which is derived from a *ketomethylene* compound, so called



because it contains a $-\text{CO}-\text{CH}_2-$ grouping. Examples of this are N-ethylrhodanine (45), 2-phenyl-5-oxazolone (46) and 1-phenyl-3-methyl-5-pyrazolone (47).



Examples of dyes derived from these compounds are shown in (48), (49) and (50).



Incorporation of Cyanine Dyes in Emulsions

The cyanine dyes are usually introduced into the emulsion at a late stage in the making process, normally at the conclusion of the digestion, in the form of dilute solutions, normally of 1 in 1,000 or less, in a water-miscible organic solvent, such

as ethanol or acetone, or in water if the dyes are salts and therefore soluble. In most cases the interaction of the dye is rapid but in emulsions which have already been stabilized with large quantities of tetrazindene stabilizer, a period of heat treatment facilitates the interaction.

The spectral sensitizers are added at the rate of 0.02 to 0.2 g of dye per g mole of silver, corresponding to about 0.05 to 0.5 millimoles per mole or 1 : 20,000 to 1 : 2,000 relative to the silver halide, which are larger quantities than those of the chemical sensitizing substances usually used. In the case of the emulsion considered earlier, with 4×10^{14} grains of silver halide per gram mole, these concentrations provide 10^5 to 10^6 dye molecules per grain, mostly adsorbed on the grain surface although the highest quantities of dye may not be adsorbed completely. An average dye occupies $50\text{--}100 \text{ \AA}^2$, so that in this emulsion the higher quantities would cover about half the surface of the grains.

Dye Adsorption

The adsorption of the dye to the grain surface is a very important step because: —

1. Only the dye adsorbed to the silver-halide grain is effective in conferring sensitivity upon it, since only the intimate contact of an adsorbed molecule can transfer the effect of the light. Dye in the gelatin phase will only cause a filtering action (see acutance dyes, Chapter 8) and thus reduce speed in the region in which the dye absorbs light.
2. The wavelength of this conferred sensitivity is that of the *light absorption of the dye in the adsorbed state*. This may be very different from that of the simple dye in dilute solution as individual free molecules.

Nature of Adsorption Forces

What are the forces which cause the dye to be attracted so strongly to the crystal surface? It is certainly not the formation of covalent bonds, neither is it primarily electrostatic attraction; a cyanine dye may be equally well adsorbed whether the molecule carried a net negative or positive charge or no charge at all. The adsorption process is generally ascribed to Van der Waal's forces, a force of attraction which comes into play between closely adjacent molecules. It seems most likely that the surrounding π electrons, present in all sensitizing dyes, do interact with the surface of the silver halide thus forming a weak linkage.

An important measure of the strength of a bond, of any kind, is its heat formation. To date, no direct measurement of the heat produced by the dye-adsorption process has been reported; the quantities involved will be very small indeed because the bulk of the emulsion, water and silver halide, remain unaffected and would therefore dilute the heat evolution and only a very small temperature rise would occur.

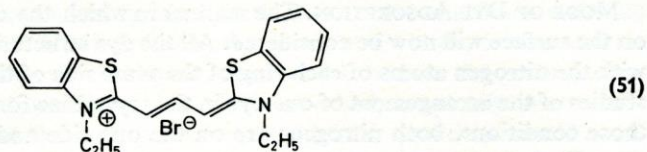
Indirect methods, based on adsorption measurements at different temperatures, indicate that the heat of adsorption is 10,000 to 12,000 calories per mole, that is, less than half the heats of formation of conventional chemical bonds, but it may be higher for the first fraction of the dye to be adsorbed. This latter finding suggests that there are special sites on the crystal at which the dyes are preferentially adsorbed and where the link between the dye and the crystal is stronger.

MODE OF DYE ADSORPTION. The manner in which the dye molecule is adsorbed on the surface will now be considered. All the dye structures have been drawn so far with the nitrogen atoms of each ring of the same side of the molecule. Fairly recent studies of the arrangement of one dye in the crystalline form have shown that under those conditions, both nitrogens are on the one side and this arrangement seems most likely but there is no theoretical reason why this must be so. The presence of the nitrogen substituent, the first bond of which must be coplanar with the ring and with the whole of the conjugated part of the molecule, will prevent close contact between the two nitrogens and the crystal surface. Also many good dyes contain N-ethyl substituents and in these the nitrogen atoms must be further removed. The most likely orientation for the dye molecule is, therefore, upright, with their long sides on the grain, possibly with the nitrogen atoms nearest the crystal surface, and measurements of the total amount of dye adsorbable on an emulsion of known surface area support this. However, *Carroll* has stated that this may not necessarily be the case and that for only partial surface coverage, the situation existing in most commercial emulsions, the position is very unclear at present.

The adsorption process is also one of equilibrium, the dye may be desorbed by powerful agents, for example the cyan colour coupler of substantive couplers (see Chapter 10) can strip off the sensitizer from the surface and remove the red sensitivity. The high water insolubility of so many common dyes may impose some limit on the desorption but apart from this the adsorption must be regarded as a strictly reversible process. Experiments have been carried out on the rate of desorption of a dye from silver-halide grains by centrifuging a dyed emulsion and then placing the grains in a fresh aqueous phase. The desorption of the adsorbed dye was a slow process, particularly when the surface was only partially covered and, therefore, it has been generally assumed that the adsorption of a dye under practical conditions in a photographic emulsion has a high degree of irreversibility.

Gelatin, also has an influence on the dye adsorption. In the absence of gelatin, the adsorption of the dye is very fast indeed but it has been shown that, although an adsorbed gelatin layer may retard dye adsorption, the dye is more powerfully held. Measurements, by direct analysis of nitrogen content, of the amount of gelatin remaining on dyed emulsions, have shown clearly that gelatin is readily displaced from the grains. At sufficiently high dye concentrations, higher than those used commercially, the gelatin may be completely removed. The heat of adsorption of a dye is higher with emulsions of low gelatin content. This suggests that the measured heat of adsorption, around 7,000 calories per gram-mole in the case of an emulsion with 7% gelatin, is the difference between that of the dye and that of the gelatin.

EFFECT OF ADSORPTION ON LIGHT ABSORPTION. When a spectral sensitizer is adsorbed to the silver-halide crystal a shift in the absorption maximum usually occurs which is often attributed to some change in the dye molecules. In a large number of cyanines, this shift is about 200–400 Å towards longer wavelengths. Thus the *N,N'*-diethyl benzothiazole dye (51) absorbs at 5,590 Å in solution but sensitizes at 5,820 Å. Merocyanine dyes are different in their behaviour. The



absorption maximum of many of these dyes in solution is very dependent upon solvent polarity and no general rule can be given of the changes that occur, the exact direction of the change being controlled by the nature of the rings at either end of the chain. It is not surprising therefore that the highly polar silver-halide crystal has a great influence on the wavelength of the absorption.

Dye Aggregation

M-BANDS. The light absorption of a dye in dilute solution and the corresponding sensitization of an emulsion at low dye concentrations, when only a few per cent of the crystal surface is covered, are spectrally very similar which indicates that sensitization is due to the effect of individual molecules separately adsorbed to the

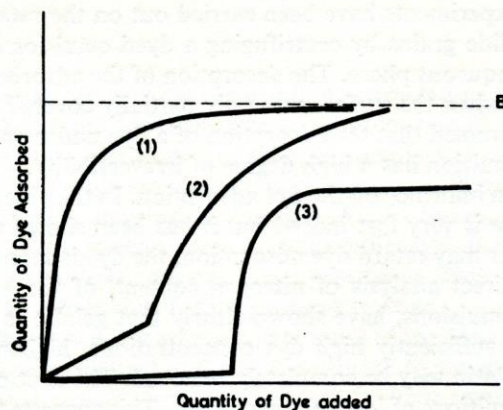
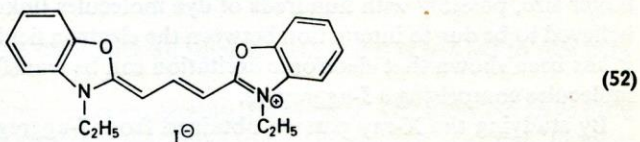


Fig. 6.4 Adsorption isotherm for cyanine dyes. (1) Langmuir isotherm, merocyanine (48). (2) Benzoxazole trimethincyanine (52). (3) Pyrazolone merocyanine (50)

crystal and not coupled with other dye molecules. This absorption band is called the molecular or *M-band*.

J-BANDS. However, a large number of dyes, including many important cyanines and merocyanines, show another type of adsorption behaviour which affects their sensitization. The adsorption of a dye, such as the merocyanine (48), is shown in curve 1 of Figure 6.4 which is a typical simple adsorption curve, a *Langmuir isotherm*; the dotted line B shows saturation level of adsorption. Very different results are obtained with other dyes, e.g. curve (2) shows the behaviour of the N,N'-diethyl dye (52) while the merocyanine (50) gives the curve (3). In these cases, the adsorption is slow until a certain dye concentration is reached when a rapid increase occurs and the amount quickly approaches the saturation limit.



A study of the sensitization by these dyes shows an even more interesting effect. At low concentrations, most dyes giving adsorption curves like curve (2) in Figure 6.4 confer spectral sensitization at a longer wavelength, usually 200–300 Å longer, than the maximum of light absorption in dilute solution. Larger additions of dye

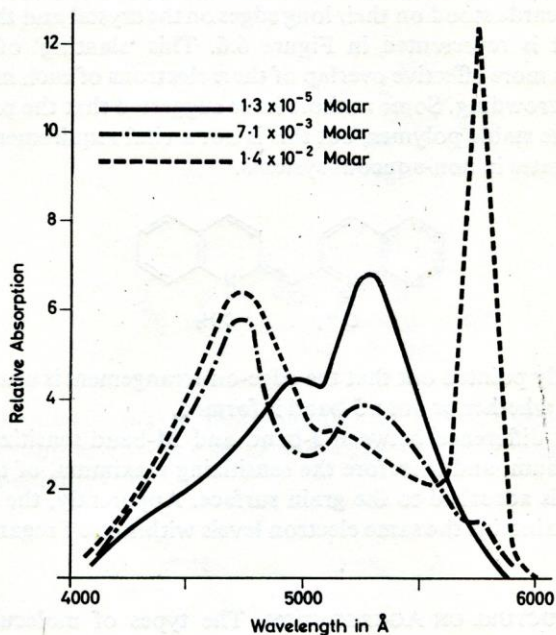
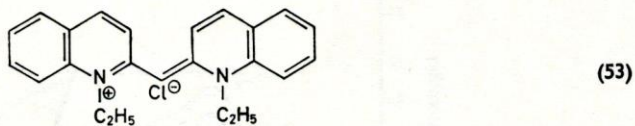


Fig. 6.5 Absorption of quinoline dye (53) in aqueous solution

introduce another sensitizing peak at longer wavelengths which is enhanced as the quantity increases.

It is known that these two effects are due to the formation of aggregates of dye molecules, in a special relation one to another, on the grain surface. This long wave band is called a *J-band*, and the associated molecules J-aggregates. The formation of a J-aggregate can occur quite easily in aqueous solution with some dyes. For example, aqueous solutions of the quinoline cyanine (53) show the characteristic maximum at 5,250 Å, the usual maximum in ethanol, but more concentrated solutions exhibit first a change in the relative heights of the 5,250 Å and 4,900 Å bands and then the appearance of a totally new and very intense band at 5,700 Å (Figure 6.5). Physical measurements show that solutions of this dye possessing this long wavelength absorption band no longer contain individual molecules, but molecular units of much larger size, possibly with hundreds of dye molecules linked together. This linking is believed to be due to interaction between the electron fields of each molecule because it has been shown that electronic excitation can be transferred through the group of molecules comprising a J-aggregate.

By studying the X-ray pattern obtained from J-aggregates, and by other less direct methods of analysis, a clearer idea has been obtained of the structure of the polymer formed by 2,2'-quinoline cyanine (53). The dye molecules are stacked edge-on, the nitrogen atoms being nearest the plane of adsorption, about 4–5 Å apart, which accords with other physical measurements and is within the range of Van der Waal's forces, the stacking being at an angle of about 30° from the vertical; the molecules are like a pack of cards stood on their long edges on the crystal and then tilted slightly. This arrangement is represented in Figure 6.6. This 'slanting' of the polymer is believed to permit more effective overlap of the π electrons of each molecule with the next by avoiding crowding. Some authors have suggested that the presence of water is necessary for the stable polymer, but this is not a vital requirement because many dyes give J-aggregates in non-aqueous systems.



Carroll has recently pointed out that the edge-on arrangement is usual for all adsorbed dye molecules, whether or not a J-band is formed.

One important difference between J-band and M-band sensitization is that the absorption maximum, and therefore the sensitizing maximum, of the J-band is *not* changed when it is adsorbed to the grain surface. Apparently, the high stability of the J-aggregate maintains the same electron levels within itself regardless of the substrate.

EFFECT OF STRUCTURE ON AGGREGATION. The types of molecules which show this important J-band formation have been much discussed. It is clear that the abil-

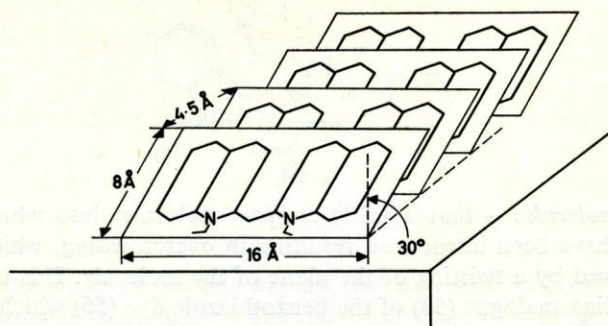
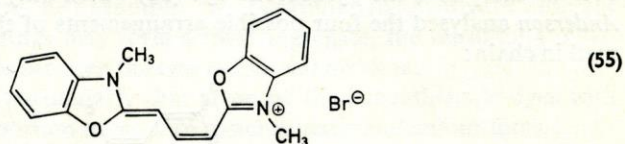
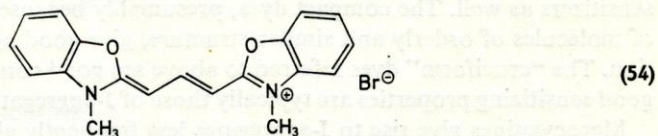


Fig. 6.6 Stacking of dye molecules in J-band aggregate

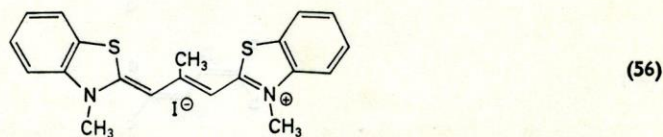
ity of each molecule to align itself with another is vital and this has led to two concepts.

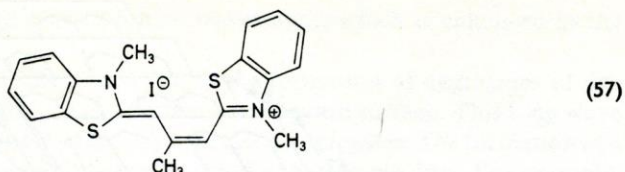
If the dye formulae are replaced by projection drawings in which the effective radii of influence are shown, it is apparent that three types of structure can exist. *Brooker* classified these types as: —

1. *loose molecules* — that is, those in which there is still a fair degree of empty space within the overall molecule permitting it to exist in two different geometrical arrangements, e.g. the 3,3'-dimethyl benzoxazole dye which may be represented as (54) or (55).

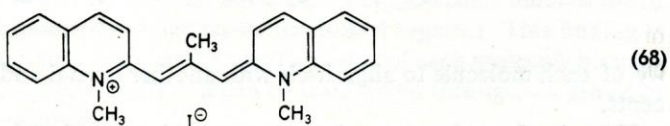


2. *compact molecules* — that is, molecules like the benzothiazole dye (56) which, possesses no appreciable free space and prefers that particular arrangement to the other possibility (57).





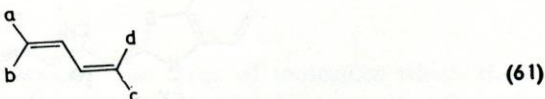
3. *crowded molecules* — that is, fairly compact molecules into which further substituents have been introduced resulting in overcrowding, which is normally only relieved by a twisting of the plane of the molecule. This is illustrated by the quinoline analogue (58) of the benzothiazole dye (56) which is crowded in either form and must be distorted.

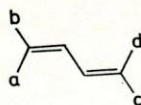


The size of the anion plays no part at all in the shape of the dye molecule. The link between the anion and the dye is purely an electrostatic one and, therefore, the appropriate ion is located at any convenient point in the dye crystal, in the solution or adjacent to the silver halide. The nature of this anion has no spectral effect either on the light absorption or the spectral sensitization of the dye.

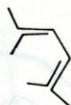
Brooker was able generally to show that loose dyes possessed poor properties of association, and the same was true of crowded dyes which usually were very poor sensitizers as well. The compact dyes, presumably because of the ready association of molecules of orderly and similar structure, give good aggregation and sensitization. The "cruciform" dyes referred to above are good compact molecules and their good sensitizing properties are typically those of J-aggregates.

Merocyanines give rise to J-aggregates less frequently although there is one very notable exception, the pyrazolone dye (50) which only shows J-band sensitization. *Anderson* analysed the four possible arrangements of the end groups about the dimethine chain:



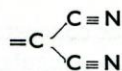


(62)



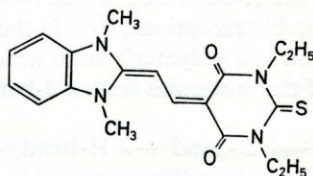
(63)

(59) represents the basic nucleus one way up, (60) the other, and (61) and (62) similarly for the keto-methylene nucleus. The chain could also be arranged as in (63) but the crowding in this case with the usual end groups is so enormous as to make the form impossible. However, he suggested that if one end or the other, or better still both ends, consisted of symmetrical groups then the dyes which would then be composed of only one form of the molecule should show better aggregation. This is the case; dyes with the group (64) at the keto-enol



(64)

end are better at giving J-bands than other similar dyes with the customary unsymmetrical group e.g. rhodanine (45), while the dye (65) can exist in only one form and



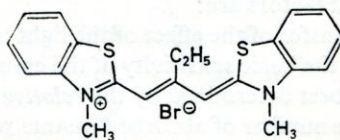
(65)

exhibits powerful J-band sensitizing.

J-aggregates may also be formed from mixtures of two different dyes which must be of closely-related structure. For example, two benzothiazole dyes with different substituents in the benzene rings may form a joint aggregate, the sensitizing maximum of which is intermediate between the two individual maxima.

The J-band sensitization, particularly that given by the benzothiazole dyes with a trimethine chain, is very important in modern panchromatic and colour films.

OTHER AGGREGATED STATES. There are a number of other aggregation states of cyanines. The two best-defined of these give rise to light absorptions on the *short* wavelength side of the dilute-solution molecular-band. These are illustrated particularly well by the benzothiazole dye (66), the behaviour of which is shown in Figure



(66)

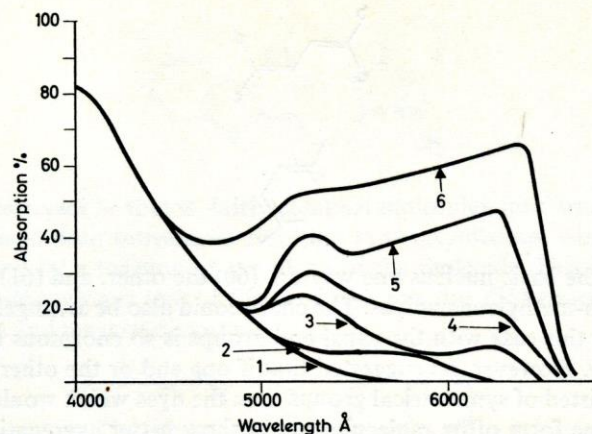
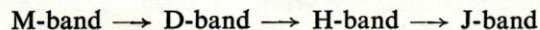


Fig. 6.7 Absorption of dye (66) when adsorbed in an emulsion

6.7. The first alteration to appear as the concentration is increased, is the building-up of the short wavelength shoulder into a regular peak, called the dimer or D-band, believed to be due to the formation of a dimer, a pair of molecules. At higher concentrations a shorter wavelength band of fairly high intensity is formed, shown in Figure 6.8, which is called the H-band and is due to a further aggregation of dye. Although there are some notable exceptions, dyes in the H-aggregate form are rather poor sensitizers. The H-band is a polymeric state which may be different either in size or in the orientation of the molecules from a J-band aggregate, e.g. it has been suggested that



is one of increasing size of aggregation.

Efficiency of Sensitization

So far only the wavelength of the dye sensitization has been considered but, of course, of equal importance is the photographic sensitivity obtained from this sensitization.

The first factor in deciding this effectiveness is the intensity of the light absorption. This varies little within a family of dyes, and, except for non-planar crowded dyes, where it can drop to as low as a third of the value of a closely related non-crowded dye, is very high and generally increases with chain length. This is shown in Figure 6.8.

By far the most important factors are:

1. the efficiency of the transfer of the effect of the light to the silver halide;
2. the effect of the dye on the basic sensitivity of the emulsion.

The first of these factors is best determined by the *relative quantum yield*. This is defined as the ratio between the number of absorbed quanta required to produce a given

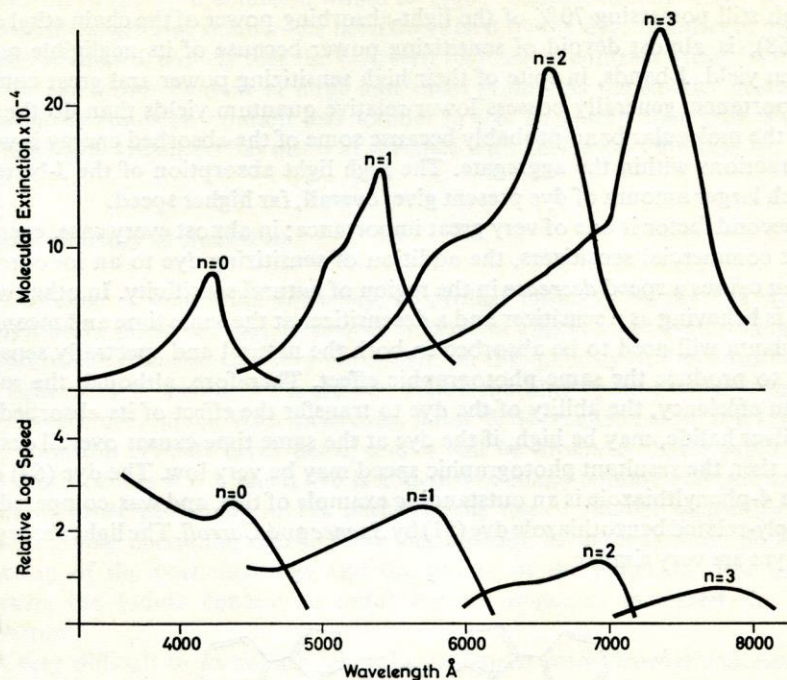
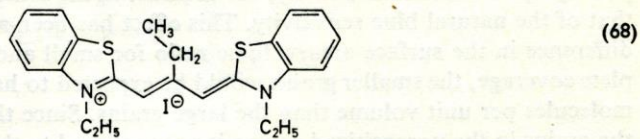
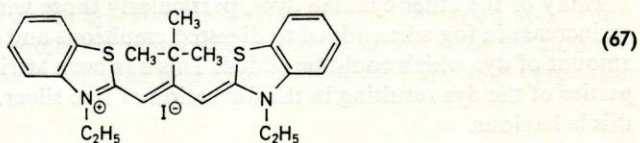


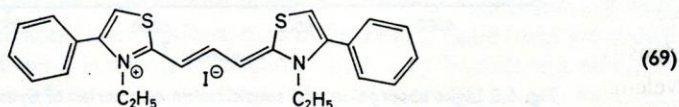
Fig. 6.8 Light absorption and sensitization of a series of dyes, formula (12)

density at 4,000 Å divided by the number of quanta similarly required at the wavelength of sensitization. It will be observed that this definition takes account of the light-absorbing differences between dyes; the wavelength of 4,000 Å is chosen because the sensitivity at that point is due entirely to the silver halide. The value of the relative quantum yield can never exceed 1.0 and is only brought near to that value by the very best dyes. This factor is very low for crowded dyes, e.g. the crowded tertiary-butyl cyanine (67),



although still possessing 70% of the light-absorbing power of the chain ethyl derivative (68), is almost devoid of sensitizing power because of its negligible relative quantum yield. J-bands, in spite of their high sensitizing power and great commercial importance, generally possess lower relative quantum yields than do the same dyes in the molecular band probably because some of the absorbed energy is wasted by interactions within the aggregate. The high light absorption of the J-band and the much larger amount of dye present give, overall, far higher speed.

The second factor is one of very great importance; in almost every case, even with the best commercial sensitizers, the addition of sensitizing dye to an iodobromide emulsion causes a speed *decrease* in the region of natural sensitivity. In other words, the dye is behaving as a sensitizer and a desensitizer at the same time and means that more quanta will need to be absorbed in both the natural and spectrally sensitized regions to produce the same photographic effect. Therefore, although the relative quantum efficiency, the ability of the dye to transfer the effect of its absorbed light to the silver halide, may be high, if the dye at the same time causes overall desensitization, then the resultant photographic speed may be very low. The dye (69) derived from 4-phenylthiazole is an outstanding example of this, and was compared with the closely-related benzothiazole dye (51) by *Spence and Carroll*. The light absorptions of the dyes are very similar



and the relative quantum efficiency of the thiazole dye is slightly *higher* than that of the other. However, the thiazole dye is a very powerful desensitizer and reduces the emulsion sensitivity at 4,000 Å so greatly that in effective sensitizing power the benzothiazole dye would be classified as good but the thiazole dye as very poor. On the other hand, good sensitizers such as (25) and (48) combine high relative quantum yield with slight desensitizing action.

Many of the older cyanine dyes, particularly those with a quinoline ring, caused an increase in fog when added to digested emulsions and this imposed a limit on the amount of dye which could be added. This has been attributed to the reducing properties of the dye resulting in the formation of free silver. Modern dyes rarely show this behaviour.

In addition to affecting the speed, a sensitizing dye also influences the contrast of a photographic emulsion. Usually, the contrast in the sensitized region is higher than that of the natural blue sensitivity. This effect has been analysed and related to the difference in the surface area/volume ratio for small and large grains. At incomplete coverage, the smaller grains would be expected to have a larger number of dye molecules per unit volume than the large grains. Since the basic light sensitivity of the grains in the unsensitized region is proportional to their volume, it is likely that

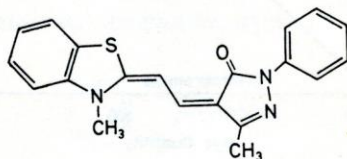
the contrast of the dyed emulsion would be higher because the sensitivity difference between the larger and smaller has been decreased by the dye. Another explanation has been advanced, namely that the observed increase in contrast arises from differences in the iodide content of large and small grains; as the smaller grains of an iodobromide emulsion contain less iodide, it was suggested that they would be more efficiently sensitized but this is at variance with *Dickinson's* findings.

Optimum Quantity of Sensitizer

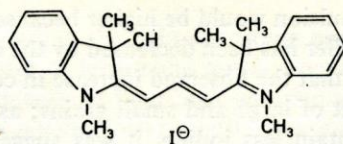
The balance of sensitizing efficiency, controlled basically by the dye structure, although other additives may have very important effects and desensitizing power in iodobromide emulsions, is very dependent on the quantity of dye adsorbed. The usual behaviour is shown in Figure 6.9, where the blue speed and the spectrally-induced speed are shown. With most dyes, point 'X' is reached before total coverage of the emulsion crystals takes place, and it will be observed that a rapid loss of useful speed occurs if too much dye is added. For many commercial purposes, the balance of other properties makes desirable the use of smaller quantities of dye than that giving maximum speed. The exact position of the maximum point 'X' is a function of the particular dye and the nature of the emulsion. For instance, increasing the iodide content in iodobromide emulsions increased the J-band sensitisation.

It is very difficult to formulate general rules, apart from *Brooker's* classes, as to whether a dye will be a good sensitizer or not. The nature of the rings is of paramount importance. Many nuclei, such as benzothiazole, consistently give good sensitizing power but many others give only a few useful sensitizers and, of course, where the rings at either end of the chain are different they must both be taken into account. Substituents present in hetero or carbocyclic rings have a powerful influence on sensitizing ability, affecting factors (1) or (2) above. *Brooker* mentions that, although introduced where they can cause no crowding, many groups such as nitro, cyano, acetyl or propargyl depress the sensitizing power to a marked extent.

Exactly the same consideration applies to merocyanines where the overall molecule must be taken into account to an even greater extent. The good sensitizing ability of the pyrazolone indolenine merocyanine (50) is an example because the pyrazolone dye (70) and the indolenine trimethin cyanine (71) are both very poor sensitizers.



(70)



(71)

The length of the carbon chain is another factor. Cyanines possessing chains of one or three carbon atoms are frequently good sensitizers, assuming the other factors outlined above are favourable. The five-carbon and seven-carbon members

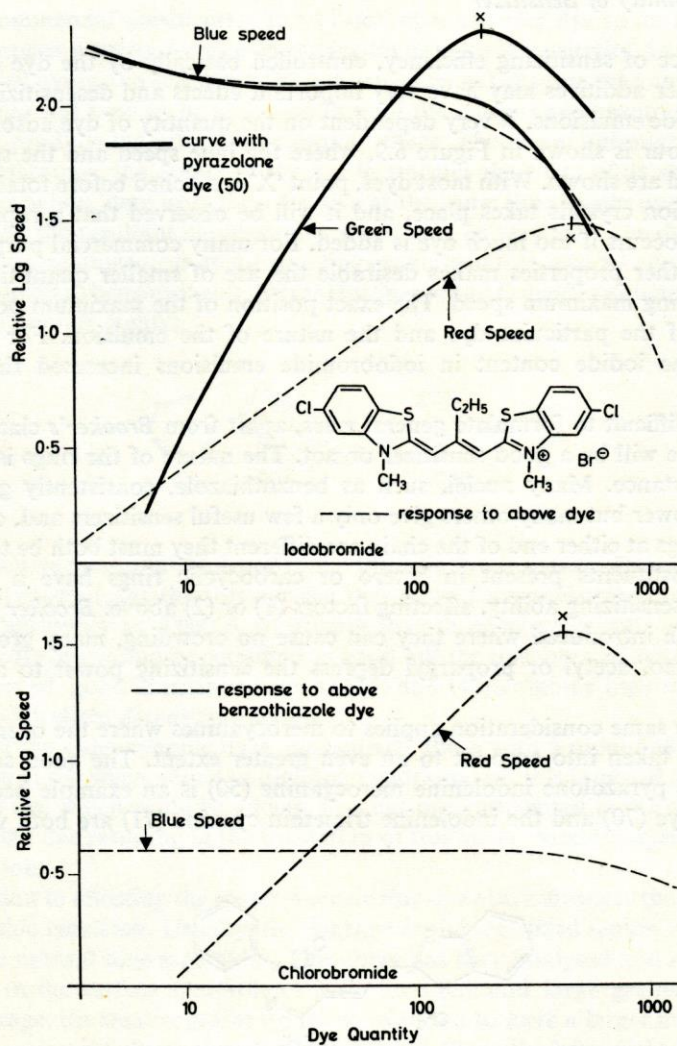


Fig. 6.9 Speed and the quantity of sensitizer

of the benzothiazole series, shown in Figure (6.8), are poorer sensitizers in spite of their higher light-absorbing power. This is because of their desensitizing influence and is generally true of all long-chain dyes where the point 'X' in Figure 6.9 occurs at a low dye concentration. In order to obtain the best use of such dyes, therefore, they are added in much smaller amounts than customary for their shorter-chain analogues.

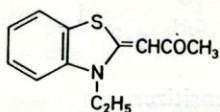
Sensitization of Chloride Emulsions

Very little has been published on the spectral sensitization of silver-chloride or chlorobromide emulsions, although this is of technological importance. Although these emulsions and iodobromide emulsions respond in a comparable manner to the action of similar types of dyes, there is one outstanding difference. The addition of a spectral sensitizer to an iodobromide emulsion rarely confers an increased total sensitivity because the natural sensitivity of the silver halide is high and the blue speed decreases as the spectrally-sensitized speed rises; this is shown in Figure 6.9. On the other hand, a powerful sensitizer can increase the total speed of a chloride or chlorobromide emulsion by as much as thirty times, probably because of the low light-absorbing power of silver chloride and also because very little desensitization occurs in the region of natural sensitivity.

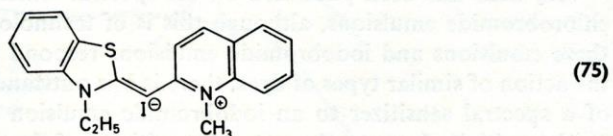
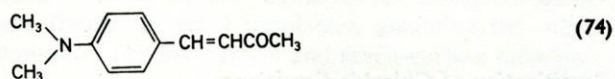
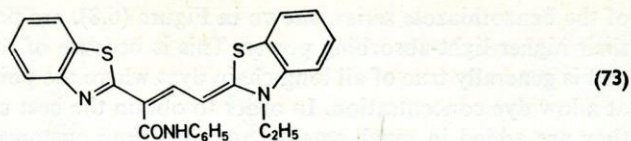
Supersensitization

One important property of sensitizing dyes is that of *supersensitization*, that is the enhancement of the sensitizing power of a dye by adding a small quantity, frequently 1% of the dye quantity, of another substance; in some cases an increase in sensitized speed of as much as twenty times is produced.

Only dyes which show polymer, usually J-band, type sensitization, e.g. dye (53), are capable of supersensitization. A vast range of supersensitising compounds has been described in the patent literature; many of these compounds are cyanines, or bear some structural resemblance to cyanines, but many are colourless and clearly the position of the absorption maximum of the supersensitizer is not important. Among compounds active as supersensitizers are acylmethylene derivatives of heterocyclic bases, of type (72), the cyanine dye bases (73), possessing trivalent nitrogen atoms in both rings and therefore not capable of conventional cyanine mesomerism, and ketone derivatives such as p-dimethylaminobenzalacetone (74). Apart from being supersensitized themselves, dyes



(72)

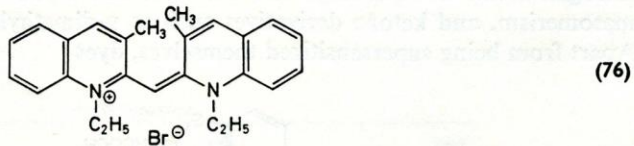


similar to the 2,2'-quinoline dyes (53), such as dye (75) may act as supersensitizers for trimethine dyes; for example, dye (66) is supersensitized in this way. Many patents claim supersensitizing combinations of two dyes of similar type.

Supersensitizing appears to operate by affecting either the relative quantum yield of the desensitizing power of the dye. Measurement of the light absorption and dye adsorption show that neither of these is increased although in some cases the wavelength of the sensitisation maximum is changed slightly.

Antisensitization

Exactly opposite to supersensitization is the phenomenon of *antisensitization* in which the addition of similar quantities of a foreign substance causes a great reduction in spectral sensitization by a dye; this is not desensitization because the blue speed of the emulsion remains unaffected. Only J-band sensitizers show this phenomenon and there is a fairly specific connection between the structure of the dye and the antisensitizing agent. The often-quoted example is of the 2,2'-quinoline dye (53) and the closely-related dye (76) containing two rings with methyl groups, which cause it to be crowded and therefore twisted out of planarity. The crowded dye (76) is itself quite useless as a



sensitizer but is a powerful antisensitizer.

There must be a fairly close relation between the absorption maximum of the dye and the antisensitizing agent; if a non-planar, crowded dye absorbs at a much *shorter* wavelength (more than 700 Å difference) than the sensitizing dye, then it can act as a slight supersensitizer but is an antisensitizer for another dye where no such difference exists.

Mechanism of Dye Sensitization

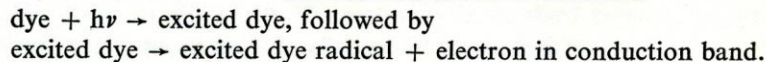
The first stage of dye sensitization is the lifting of a dye molecule from its ground state to the first excited state; the evidence for this is the direct correlation between the wavelength of the light absorption and the wavelength of the spectral sensitization. Also, light of the wavelength of the absorption maximum of the adsorbed dye will cause the dyed silver halide to show increased conductivity. This is due to the silver halide and not the dye itself because of the very low conductivity of dyes adsorbed to a non-photosensitive halide, such as lead bromide.

The result of an exposure in the dye sensitized region appears to be the same as that produced by exposure in the region of natural sensitivity of the silver halide; chemical sensitization also has a similar effect in the two regions. Clearly therefore the dye is involved in the primary step of the latent-image formation, that is, the energy of the excited state of the dye has caused an electron to be raised from the valence band to the conduction band; this electron is at a higher energy and is now able to conduct electricity. After the formation of this conduction-band electron, the subsequent steps in latent-image formation are similar in both regions.

Two important points arise:

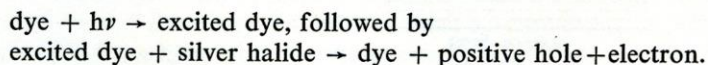
1. Does the conduction electron come directly from the dye, i.e. *electron transfer*, or is it formed by the dye bringing about an excitation of the silver halide, i.e. *energy transfer*, causing the bromide ion to part with an electron?
2. How does the dye-sensitized latent-image process compensate for the apparent energy deficiency.

Electron transfer requires the following stages:



A radical is a molecular species in which there is an unpaired electron; the loss of an electron from one of the many pairs of bonding electrons in the dye leaves one unpaired electron.

The stages in an energy transfer system are:



Thus the first mechanism gives a dye radical and the second a positive hole.

The time during which these processes take place should be mentioned. The excited states of molecules can only exist for very short times (with the exception of phosphorescence) and *West* has shown that only a very short-lived excited state is responsible for spectral sensitization. The transfer from dye to substrate is achieved in a period of no more than 10^{-11} sec, which in terms of all normal photographic exposures is instantaneous.

Electron Transfer

When the dye has lost an electron, the charge on the molecule is changed; a positively-charged dye, as are most cyanines, becomes doubly positive, merocyanines become positive ions and negatively-charged dyes become neutral. It is difficult to confer a double positive charge on a cyanine dye, but there are no indications that neutral or negatively-charged dyes are more efficient sensitizers. Some variation of this kind would be expected if the ease of parting-up with an electron was important and the lack of any relationship has been used as an argument against the loss of an electron. Furthermore, it is possible to detect the existence of radicals by electron spin resonance where the unpaired electron can be detected, and this has been done successfully in a dye-sensitized emulsion at low temperatures. However, analysis showed that the detected radicals were formed by the reaction of photolytic bromine with the sensitizer; that is, the radicals were a secondary and not a primary product of photolysis.

Measurements on sensitizing dyes have shown that the excited state of a dye molecule is at a sufficiently high electronic level to permit the transfer of an electron directly to the conduction band of the dye. This is shown in Figure 6.10 where the energy levels of a dye and the silver halides are shown. A study by *West* of a range of related cyanines and merocyanines with different chain lengths has indicated that they all have an excited state at very similar electron levels which means that as the wavelength of absorption increases, i.e. the energy between ground and excited states decreases, the energy of the ground state must increase.

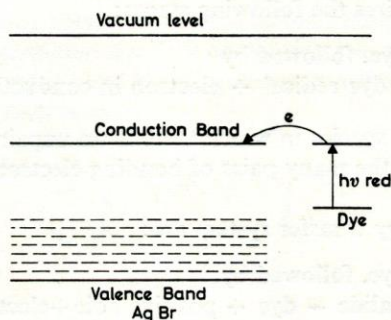


Fig. 6.10 Electron transfer diagram for spectral sensitization

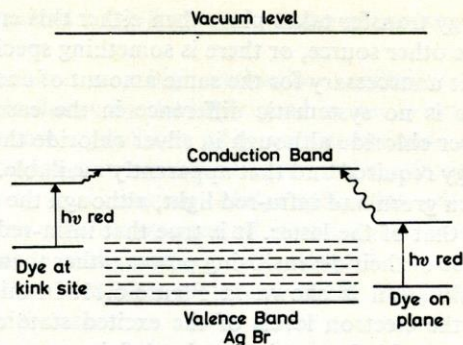


Fig. 6.11 Energy transfer diagram for spectral sensitization

The question arises as to whether a dye molecule can be used more than once. Experiments carried out in the presence of an agent to trap the bromine from the photolysis, and thus prevent its degradation of the dye, have shown that during print-out exposures the dye is used many times. It is therefore assumed that a dye is similarly used many times during latent-image exposures, although the formation of the small number of silver atoms, e.g. 4–25, in a latent-image speck would not require this in a grain containing 10^5 – 10^6 dye molecules on its surface. The valence band of the silver halide, as shown in Figure 6.11, is too low to supply an electron to the dye radical in order that it may revert to its original state.

Some authors have suggested that in the immediate vicinity of the adsorbed dye molecule, there is a downward displacement of the electron level of the conduction band. In this case it might be possible for an electron to be placed in this band, although the excited state of the dye is not as high a level as the normal conduction band of the halide. The objection to this view is that an electron in this condition would have to remain in the area of the grain surface and it is then difficult to see why spectral sensitization is as efficient for internal as surface latent-image formation. In fact, photoelectrons induced by light absorbed by sensitizing dyes have been shown to diffuse 40–50 microns in large sheet crystals, i.e. as far as photoelectrons produced by light absorption by the halide.

Energy Transfer

As mentioned earlier, there is a direct relationship between the wavelength of a radiation and its energy. In order to form a latent image by absorption of light by the crystal, the light must possess an energy equivalent to $5,000 \text{ \AA}$ in silver bromide, corresponding to 57,000 cal per g mole, whereas in dye sensitization the energy of the light, apparently producing the same effects, can be less than half of this. This

means that if an energy transfer takes place then either this energy will have to be augmented from some other source, or there is something special about dye sensitization which makes it unnecessary for the same amount of energy to be used.

Furthermore, there is no systematic difference in the ease of sensitization of silver bromide or silver chloride although in silver chloride there is an even bigger difference in the energy required and that apparently available. Neither is there any real difference between green and infra-red light, although the energy of the former is much greater than that of the latter. It is true that infra-red sensitizers are poor dyes but this is because of their desensitizing power rather than their low sensitizing power. The energy situation is shown in Figure 6.11. In this scheme, no restrictions are placed on the electron levels of the excited state of the dye but some mechanism has to be provided to make up the deficiency.

In any system, except at absolute zero, there are molecules which are not at their lowest energy level. It might therefore be supposed that this energy might provide the extra energy required to make up the deficiency. This is not the whole answer because it has been shown that dye sensitization is still quite measurable at liquid-air temperatures, -196°C where the contribution from thermal energy will be very much less than at room temperature. However, the loss in sensitivity at this temperature is much greater in the dye-sensitized region than in the region of natural sensitivity so there must be some influence of temperature. Also, this loss in sensitivity is no greater with red sensitizers than with blue, so there is no dependency of the effect of low temperatures on wavelength. These results show that no thermal activation of the surface state of the silver halide or of the dye can be important and *West* suggests that temperature affects the *transfer* of energy or of an electron from the dye to the silver halide.

Only an incomplete picture of the light absorption of silver halide has been considered so far. On the long-wavelength side of the region of strong absorption there is a long sensitivity "tail" which decreases in efficiency as the wavelength increases. This is particularly true of chemically-sensitized emulsions but is apparently the case with even the purest crystals. The existence of this phenomenon means that there are levels within the crystal where less than the usual amount of energy is needed to cause a photographic change. These may be the silver sulphide or silver formed in chemical sensitization (which are known to produce appreciable long-wavelength sensitivity), silver oxide or, as suggested by *Mitchell*, energy-rich surface bromide ions. Whatever their nature, it has been suggested that these entities are responsible for the ability of dyes to sensitize using quanta with apparently insufficient energy. These sites must occur in sufficient numbers even in undigested emulsion otherwise a greater effect of dye sensitization would be obtained after chemical sensitization; also there must be enough of them to use most of the dye molecules to the same degree because the relative quantum yield remains constant over wide ranges of dye quantity, unless there is a change in the state of aggregation. *Mitchell* considered that the electron from the special surface ion passes to the vacant ground level of the excited dye molecule with simultaneous passage of an electron from the excited dye to a surface silver ion at conduction band level, or

near enough to it to permit a small amount of thermal energy to raise it to conduction level.

The dye molecules have very high extinction coefficients relative to the silver-halide crystals. This is shown by the high speed in the dye region obtained by less than monomolecular coverage of dye, while a silver-bromide crystal 0.2–0.3 μ thick will give no greater response in the region of natural sensitivity. It is not surprising therefore that relatively small numbers of dye molecules, adsorbed at special sites, might make those sites effective by spectral sensitization. Since one thousandth of the normal dye quantity still corresponds to 10^3 – 10^4 dye molecules per grain, it will be appreciated that these dye molecules could make use of and swamp the same number of special sites.

Therefore, the existence of special sites, in large numbers even in undigested crystals, could explain the action of sensitizing dyes by the utilization of intermediate energy levels at those points in the crystal.

The good evidence for both energy and electron transfer mechanisms for spectral sensitization seems to point to the possibility that they both can function; one dye may sensitize by both mechanisms simultaneously or under different conditions.

Polymer Sensitization

Whether the transfer mechanism is electron or energetic, a J-band polymer must absorb the light, raising an electron to its excited state, which can now move freely through the whole polymer chain and is responsible for the transference of the effect to a suitable site on the silver-halide crystal. This will lead, because of the high light-absorbing power, a combination of high extinction coefficient and high dye density, to high speed. In fact, the relative quantum yield may be lower than for many monomolecularly-adsorbed dyes because the transfer from molecule to molecule may proceed so easily that the out-of-polymer movement to the silver halide may be less efficient. Any probability of degradation, for example by vibrational changes is also bound to be increased by this ready transfer from molecule to molecule.

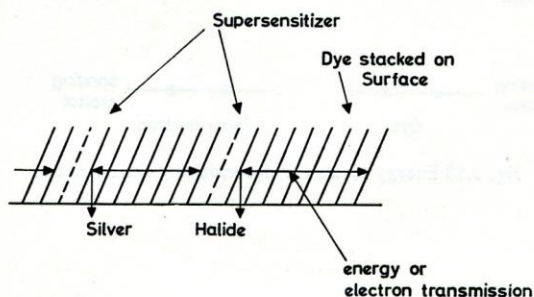


Fig. 6.12 Action of supersensitizer

Supersensitization and anti-sensitization can also be considered in this context. There seems little doubt that the supersensitizer molecule is incorporated into the polymer where it could form an irregularity in the aggregate as shown in Figure 6.12 and this could provide a point at which the energy transfer to the crystal takes place. Energy transfer cannot proceed via the excited state of a supersensitizer because most of them absorb at shorter wavelengths than the dyes they supersensitize which means that insufficient energy is available to bring about the first electronic change in the supersensitizer. Another possibility is that the supersensitizer provides a block, preventing further energy transfer within the polymer, and reduces the useless degradation of energy within the polymer; it can be regarded as chopping the polymer into smaller, more efficient pieces (Figure 6.12).

Antisensitization is rather different. The wavelength limit, mentioned above, suggests that the excited state of the antisensitizer *is* involved by causing the absorbed energy to be trapped; being a non-sensitizer it cannot hand this energy to the silver halide, and the sensitization is therefore reduced.

Desensitization

To complete the picture, reference must be made to desensitization of emulsions by sensitizing dyes. This is not a property of the excited state of the dye, there being no dependence on the wavelength of the light. The ground state of the dye desensitizes by accepting an electron, which can be the product of silver-halide light absorption or come from an excited molecule, and the dye molecule becomes a free radical, the levels of which (Figure 6.13) will be very different from either the ground or excited state of the original dye. There may be cases in which an excited molecule accepts an electron more easily than the molecule in the ground state (see Chapter 11) but this does not apply to normal spectral sensitizers. It has recently been pointed out that this so-called desensitization may be due to interference with development rather than lower efficiency in latent image formation.

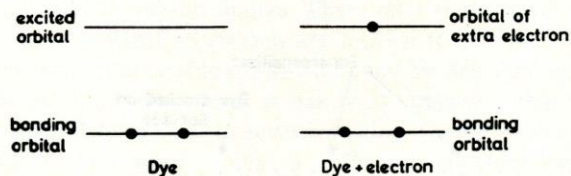


Fig. 6.13 Energy levels for desensitizing action of dye

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DEPARTMENT OF CHEMISTRY
CHICAGO, ILLINOIS

MEMORANDUM FOR THE RECORD
DATE: [illegible]
TO: [illegible]
FROM: [illegible]
SUBJECT: [illegible]

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