VII STABILIZERS AND ANTI-FOGGANTS

Introduction

At the conclusion of the digestion process, the photographic emulsion is at optimum sensitivity, that is, the required speed, contrast and fog will have been reached, and it is now suitable for coating on the appropriate support. The condition of optimum sensitivity is, however, a metastable one, in other words there is a tendency for changes; either a continuation of the digestion process or its regression will cause the properties of the material to become less acceptable and generally steps are taken to prevent this occurring.

There are two circumstances under which changes of the emulsion properties can take place. The first of these may occur during the handling of the emulsion by the manufacturer prior to coating; practically every emulsion has to be kept in a molten state, at a temperature which is not so different from that commonly used for digestion, for a period of up to some hours before it is coated upon the film or paper. The second type of change is that which occurs during storage of the coated material. Modern photographic materials are expected to keep for at least two years, in many cases under adverse storage conditions of high temperature and humidity, although many commercial films are not normally stored for as long as this. Therefore, the sensitometric properties of both the liquid emulsion and the dry coated layer must be rendered stable.

There is one fairly obvious method whereby the stability can be improved. Since the rate of the digestion process is dependent upon the silver ion-concentration, some stabilization may be achieved by decreasing the silver-ion concentration in the emulsion and for this purpose it is customary to add excess halide at the end of the digestion process. This addition would normally be chloride in chlorobromide emulsions or bromide in iodobromide emulsions. Another means, and for many years the only other way, of conferring the desired stability was by the action of a carefully selected gelatin. It is customary, although not so usual nowdays, to add further quantities of gelatin at the end of digestion in order to bring its concentration up to a suitable level for coating the emulsion. By selecting a gelatin which contains larger than usual quantities of restrainer, the continuation of the digestion process can be retarded. Even today, the selection of the gelatin used at this point can be important with gold-sensitized emulsions, where the use of highly-restrained gelatin can aid the keeping properties.

These two methods are, however, only of secondary importance.

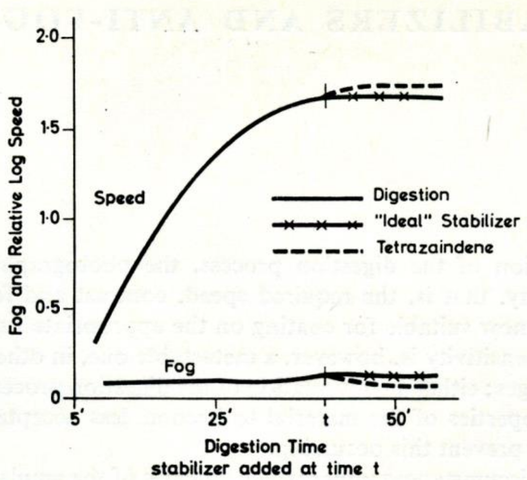
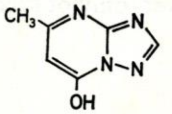


Fig. 7.1 Effect of adding stabilizer to an iodobromide emulsion

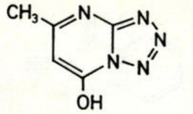
Organic Stabilizers

Some thirty years ago, it was discovered that by the addition of certain classes of organic compounds, usually containing a heterocyclic ring or rings possessing not only carbon atoms but also nitrogen and sometimes sulphur atoms, a very high order of stability could be conferred upon the emulsion. It is generally true that stabilizers which are effective in the liquid emulsion are also effective, but may be less so, in the coated and dried layer. However, the exact conditions, for the storage of emulsion prior to coating may be critical and frequently different from those required after the coating stage. An ideal case of stabilization is illustrated in Figure 7.1, where it will be seen that from the time t when the stabilizer is added, further photographic changes are arrested and the emulsion properties remain constant.

The class of compounds which comes nearest to this ideal are the tetrazaindenes, or triazaindolizines to use the older style name, the parent member of which was discovered to be a stabilizer by *Birr* in 1935. This first member was 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (1), and constant reference is still made to it in the photographic literature. Since the original discovery, a vast range of these materials has been prepared. The position of the nitrogen atoms has been varied, and different groups introduced into the two rings; also the number of nitrogen atoms has been changed. Two of the analogues are the compounds (2) and (3).



(1)



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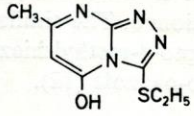
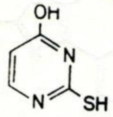


(3)

The outstanding advantage of this class of compounds is that as well as conferring great stability upon emulsions of many kinds, particularly those of high speed, no speed loss occurs when they are added; on the contrary a slight speed increase is frequently detectable, as shown by the dotted line in Fig. 7.1. This may be produced either on the addition of the stabilizer or after a short heat treatment.

Apart from the tetrazaindenes, very many other heterocyclic ring compounds have been described as photographic stabilizers, indeed there can be few heterocyclic rings that have not been incorporated in a stabilizer. One much used ring is the pyrimidine nucleus; this was present in the earliest heterocyclic stabilizers to be discovered. Among the substituted pyrimidines mentioned are the mercapto compounds, such as 2-mercapto-4-hydroxypyrimidine (4), 2-amino-4-hydroxypyrimidine (5) and 2-mercapto-4-methylpyrimidine (6).



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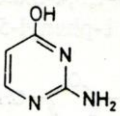

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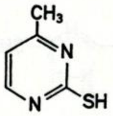
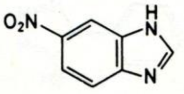


(6)

Benziminazole is another widely-used nucleus and is represented by the well-known 5-nitro compound (7) and its 2-mercapto derivative (8).



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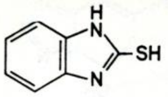
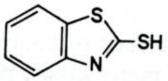


(8)

Closely related to benziminazole is benzothiazole, where again the 2-mercapto compound (9) is frequently mentioned. The similar thiazole, oxazole and benzoxazole rings are present in 2-mercapto-4-methylthiazole (10), 2-mercaptobenzoxazole (11) and 4,5-diphenyl-2 mercapto-oxazole (12).



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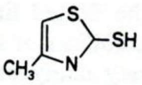

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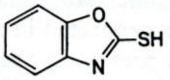

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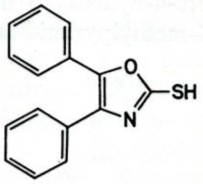
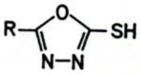


(12)

Stabilizers containing five membered rings containing two or more nitrogen atoms linked together include 2-mercapto-1,3,4-oxadiazoles (13), 2-mercapto-1,2,4-triazoles (14) and the very well-known 1-phenyl-5-mercaptotetrazole (15).



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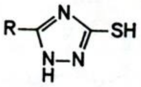
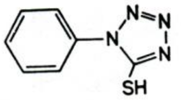


(14)

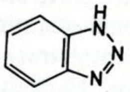
R = hydrocarbon or similar group e.g. methyl,

phenyl or heterocyclic residue.



(15)

Active materials derived from similar multi-nitrogen ring compounds include the commonly-used benzotriazole (16) and its 6-nitro derivative (17). A recently described stabilizer is 3,3′-dipyrazolyl (18) containing two linked rings each with two nitrogen atoms.



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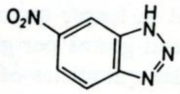

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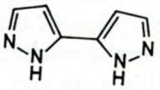
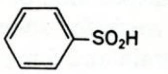


(18)

Many of these mercapto derivatives, 1-phenyl-5-mercaptotetrazole is a well-known example, cause a marked speed loss particularly in iodobromide emulsions. This means that although they function satisfactorily in arresting the digestion process, they are quite useless in many high-speed commercial emulsions. On the other hand, 1-phenyl-5-mercaptotetrazole has far less effect on the speed of chloride and chlorobromide emulsions, at the quantities found to be effective, and is therefore commonly used in paper emulsions.

Apart from these many heterocyclic compounds, which all possess common structural features, there are other active agents, to which reference must be made, and which are very different in structure. One class is the sulphinic acids, benzene sulphinic acid (19) being the commonest example.



(19)

Some authors mention that this is useful as an anti-oxidant in emulsions and this is precisely what one would expect from its chemical behaviour, but oxidation is not usually regarded as a common cause of fog; reduction is much more likely to produce fog. Oxidation would more likely cause loss of sensitivity and it is in preventing this that these sulphinic acids could be effective although they are referred to as anti-foggants.

Mode and Quantity of Stabilizer Addition

At the conclusion of the digestion therefore, tests on the emulsion having shown it to possess the desired speed, fog and contrast, a solution of a stabilizer and usually bromide, or chloride, depending on the emulsion, are added to arrest the digestion process. The organic agent may be added as an aqueous solution, in alkali solution, if it is a water-insoluble alkali-soluble compound, or in a photographically inert organic solvent such as ethanol or acetone. In practice, the optimum quantity of stabilizer is always determined by experiment but a few generalisations may be made from the quantities referred to, particularly in patents. The organic mercapto compounds are effective in very small quantities. Frequently, with the most active materials, such as 1-phenyl-5-mercaptotetrazole, 1–10 mg of the organic compound per gram mole of silver is effective. The other older types of derivative, such as 5-nitrobenziminazole, usually require up to 100 mg per gram mole. It is, however, the tetrazaindenes which are used in larger quantities than the other heterocyclic compounds; quantities up to several grams per gram mole of silver are mentioned in the literature. The use of similar quantities of the other heterocyclic stabilizers would desensitize an emulsion completely, largely by making it undevelopable. This big difference may be because of the difference in the solubility of the silver salts of the stabilizers or in the adsorption of the stabilizer to the grain; these two aspects are discussed in the section on the mechanism of stabilizer action.

A clearer picture of the grain at this stage may help in understanding the process. In the iodobromide emulsion, first introduced in Chapter 4 and used to illustrate the growth of a typical silver-halide emulsion, there are 4×10^{14} grains per gram mole of silver and if 5 mg of 1-phenyl-5-mercaptotetrazole per gram mole of silver are added, the emulsion will contain approximately

$$6\times10^{23}\times\frac{5}{178\times1000}\simeq2\times10^{19}\text{ molecules of}$$

stabilizer, where 178 is its molecular weight, which is equivalent to 0.5×10^5 molecules per grain. This figure of 50,000 may seem enormous until the space available for these molecules is considered. Each stabilizer molecule has an area of about 60 Å^2, or $0.60/10^6\ \mu^2$ while the surface area of a triangular grain in this emulsion is about 2 μ^2. Therefore there is room for about 3×10^6 phenyl-mercaptotetrazole molecules on the surface of one grain and 5 mg of this compound only gives about 1 % surface coverage. A fine-grain emulsion for example of 0.2 μ side, will possess an even higher surface area per gram molecule of silver and the coverage will be still lower. Other stabilizers are used in larger quantities but it will be seen that a selective function is demanded rather than blanket action.

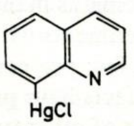
Notably different from all other stabilizers is benzenesulphinic acid which is apparently not adsorbed to the crystal surface and most probably functions in the bulk of the emulsion; this is added in quantities up to 10 g per gram mole of silver. The tetrazaindenes are adsorbed to the crystal surface in very similar quantities to the other types, although they are added to the emulsion in larger amounts (see below).

Stabilization by Metal Compounds

Although organic stabilizers are most frequently used to achieve emulsion stability, other compounds are available. A large number of compounds of metals, most of which are divalent, are described in the patent literature as being effective stabilizers of photographic emulsions. Mercury, cadmium, zinc and manganese salts are among these and greatest attention has been paid to the first two.

Cadmium has already been referred to in connection with emulsification, but the addition of large quantities, 5 to 25 g, of a water-soluble cadmium salt, such as the chloride or the nitrate, imparts good stability on chlorobromide emulsions, where it may increase the speed, and on iodobromide emulsions. Many modern lithographic emulsions, all chlorobromides, contain large quantities of cadmium salts.

There have been many patents for mercury stabilizers including organomercury compounds where mercury is linked covalently. Compounds claimed include mercuric chloride, $HgCl_2$, and substances such as 8-chloromercuriquinoline (20) and bis(2-amino-5-iodopyridine hydroiodide)mercuric iodide (21).



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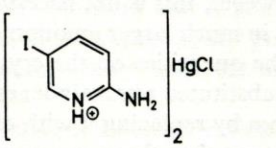


(21)

Contrary to cadmium salts, these mercury compounds are effective in very small quantities indeed, e.g. from 0.02 to 0.25 mg of mercuric chloride per gm mole have been described as effective in iodobromide emulsions. The more complex derivatives are needed in larger quantities, up to 25 mg being specified for some.

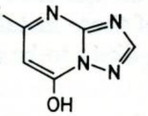
No information is available on the quantities of the inorganic stabilizer adsorbed to the grain surface. In the case of those metal compounds present in large quantities, only very small fractions are likely to be adsorbed, the remainder presumably remains in the gelatin medium.

Mechanism of Stabilization

Although it is many years now since the very high stability conferred upon photographic emulsions by the action of organic stabilizers, of the type discussed above, was discovered, our understanding of the mechanism of action of these substances is very vague indeed. It is clear that the action of the stabilizer must do one of two things,

1. prevent the continued formation of the sensitizing entity from excess chemical sensitizer still present, or
2. prevent further quantities of the sensitizing entity, formed on storage, becoming effective photographically.

All theories of the action of added sensitizing substances in emulsions are based upon the assumption that these are effective at the crystal surface and it would seem most likely that the stabilizer material also acts there. It is known that stabilizers are adsorbed to the silver-halide crystal. In the case of substances such as phenyl mercaptotetrazole, and other closely-related mainly mercapto derivatives, the stabilizer is completely and rapidly taken up from the solution and deposited on the surface of the crystals. This can be demonstrated quite simply by adding such a compound to a silver-halide emulsion, centrifuging out the silver-halide grains, and determining the concentration of the stabilizer in the supernatant solution by U.V. absorption measurement, chemical analysis or by measuring the radioactivity if the stabilizer has been synthesized to contain radio-carbon. It will be found that none of the mercapto compound remains in the aqueous phase. This is not true of the tetrazaindene class; similar experiments with these materials show that they are adsorbed only to the extent of a few per cent and also that the adsorption process is not such a rapid one. These facts have promoted the view that the action of these stabilizers is different from that of other types in which complete and rapid adsorption takes place. However, this is not necessarily the case because tetrazaindenes are commonly added in much larger amounts and therefore even though only 5–10% may be adsorbed the quantities on the crystal surface will be similar. *Birr* has studied a variety of 6-substituted tetrazaindenes (22) in which the group R was varied from a hydrogen atom by replacing it with carbon groups of increasing size, from 1 to 17 atoms. He found that there was a general relationship between the amount adsorbed to the crystal surface and the stabilizing efficiency, which dropped as the carbon chain became longer and the quantity adsorbed increased; the photographic effects of these compounds are given in Table (7.1). These results suggested to *Birr* that the tetrazaindenes are different in their action from that of many other stabilizers; his views are discussed below.


(22)

One of the early theories of the action of stabilizers was that they all acted in a similar manner to the bromide addition, namely to reduce the silver-ion concentration. The silver salts of the older stabilizers are exceedingly insoluble, commonly approaching the insolubility of silver iodide, and therefore the pAg is increased by the addition of these substances. This is not the case with the tetrazaindenes which

TABLE 7.1

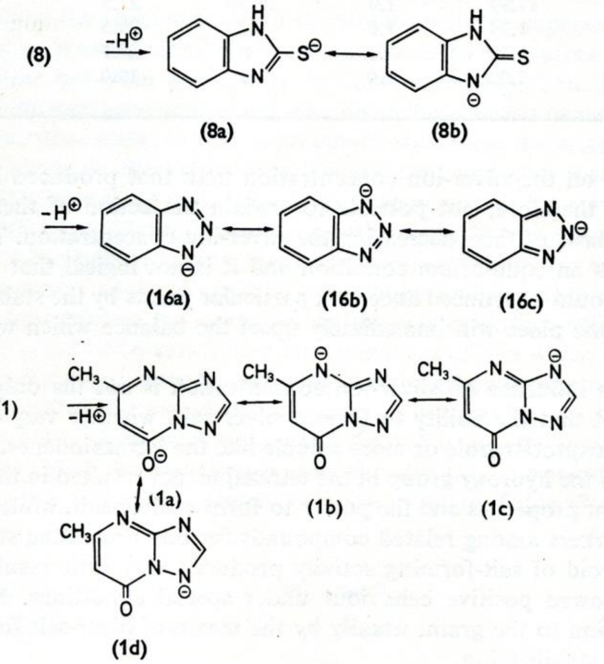
EFFECT ON SENSITIVITY AND STABILIZATION OF A SERIES OF COMPOUNDS

Number of carbon atoms in side-chain R	*Quantity added*	*Quantity adsorbed*	*Quantity in gelatin*	*Sensitivity*	*Fog increase after five days incubation**
—	none	—	—	21.5	1.66
0	2.18	1.0	1.18	21.5	1.42
1	15.65	1.0	14.65	21.5	0.05
2	2.63	1.0	1.63	21.5	0.59
3	17.89	1.0	16.89	21.5	0.0
4	1.34	1.0	0.34	20.5	1.32
7	1.00	1.0	0	20.5	0.28
11	1.00	1.0	0	19.0	0.06

have less effect on the silver-ion concentration than that produced by the added bromide. It is, therefore, not possible to explain the action of these substances merely on the basis of their decreasing the silver-ion concentration. The silver-ion concentration is an equilibrium condition and it is not logical that the silver-ion concentration could be reduced at certain particular points by the stabilizer because any action at one place will immediately upset the balance which will rapidly be re-established.

Although the influence on silver-ion concentration is not the only effect, there seems no doubt that the ability to form a silver salt, whether very insoluble like 1-phenyl-5-mercaptotetrazole or more soluble like the tetrazaindenes, is important. The removal of the hydroxy group in the tetrazaindenes resulted in the loss of both their antifoggant properties and the power to form a silver salt, while a long search by Russian workers among related compounds for one possessing stabilizing properties but devoid of salt-forming activity produced very little result: only a few compounds showed positive behaviour under special conditions. Many authors regard adsorption to the grain, usually by the means of silver-salt formation, as a prerequisite of stabilization.

It may not be obvious why all the kinds of compounds discussed so far should form stable silver salts. This is best illustrated by reference to some examples: consider 2-mercaptobenziminazole (8), benzotriazole (16) and the original Birr compound (1). In all these compounds the removal of a hydrogen ion or proton gives a negatively-charged ion, an anion which could be represented as (8a), (16a) and (1a). However, these ions can also be written in other forms (8b), (16b and c) and (1b, c, and d) in which the only differences are the arrangements of the electrons forming the bonds although the position of the atoms remains the same. Now, a compound which may be represented in a number of different electron structures is said to possess *resonance*, and the actual state of the molecule is not any of the individual possibilities but an intermediate form called a hybrid. Also, the molecule is at a lower energy level than would be the case if there were only one form, which increases its stability. A simple comparison of formulae (8), (16) and (1) with their anions shows the latter to possess more resonance so that their formation is an easier process, that is the separation of the proton is easier than in related compounds in which resonance is not increased by its ejection. A compound giving rise to a proton in aqueous solution, is called an acid and, therefore, compounds (8), (16) and (1) are fairly strong acids and able to form stable salts, such as the one with silver. This is an important property of this type of heterocyclic compound, used so widely in photographic technology.



The ability of these compounds to form silver salts will obviously depend on pH and in the case of the tetrazaindenes is very important.

Two other explanations have been advanced. (1) The effect of the stabilizer upon the hydroxyl-ion concentration; experiments carried out at different pH values show that this is not significant. (2) The stabilizer surrounds the emulsion grain to prevent further chemical reaction. If this is the case, then only discrete sites in the crystal are involved because stabilizers are effective in quantities not large enough to produce a complete surface layer one very grain. Since the concept that certain sites on the crystal have particular functions is the basis of many theories of photographic action, it is also possible that stabilizers only act at certain specific sites.

Our incomplete understanding of the chemistry of the digestion process, including the uncertainty of the nature of the sensitizing substance or of the fog, is a further difficulty in attempting to arrive at a mechanism of stabilization.

The fact that some tetrazaindenes, which are more completely adsorbed to the crystal than the original compound, are less effective as stabilizers led to the view that these compounds are active in the gelatin phase rather than on the grain surface. As already mentioned, adsorption measurements show that about 10% of the tetrazaindene (1) is adsorbed to the grain under normal emulsion conditions.

Birr believes that the tetrazaindenes function by a mechanism different from that of other stabilizers. He proposes that the tetrazindene *in the gelatin phase* "liberates" and recomplexes silver ions from the silver gelatinate by forming a more stable complex which is not adsorbed to the silver halide. This may then give silver, by reduction of this complex, or alternatively silver sulphide, by reaction of the complex with sulphur compounds, which are formed away from the grain surface and in the gelatin, although there seems to be no real evidence for either of these reactions. Silver and silver sulphide in these positions are supposed not to alter sensitivity or produce fog and there is no tendency for emulsions stabilized by these agents to give the yellow stain associated with the physical development of such centres, even if drastically over-sensitized. More important, however, is the fact that *Birr*'s picture implies that the stabilizer, at one point in the system, produces the complete unbalancing of the equilibrium concentration of silver ions which appears to be a contradiction of the laws of equilibrium which require that the concentration of silver ions must be constant throughout a single phase of a system.

Birr's original finding, of the action of a series of tetrazaindenes could, equally be attributable to the different activities of the stabilizers; such drastic changes in molecular shape could be the reason for the variations observed and the amount adsorbed could be incidental, except perhaps with the higher members of the series in which marked loss in speed occurs. The same relation between desensitizing action and the size of the alkyl substituent has been confirmed by Russian workers. Therefore, *Birr*'s work does not contradict the widely-accepted view that the stabilizer functions on the grain surface.

The rate of formation of silver sulphide from thiourea on silver bromide, unprotected by gelatin, in the presence of compound (1) has been investigated. It was found that (1) the stabilizer inhibits the reaction at high pH values, about 8.0, but at 5.85 actually accelerates it. This is surprising because 5.85 is quite a normal digestion pH and is one at which the tetrazaindene (1) is very effective as a stabilizer. (2) The ratio of stabilizer to sensitizer affects the efficiency of the inhibition, larger quantities of stabilizer being required with more thiourea to achieve the same control on the reaction.

From these results it appears unlikely that the stabilizer functions merely by preventing the formation of silver sulphide. This is also the deduction of some of

Birr's experiments in which he showed that benzotriazole retarded the digestion rate but that tetrazaindene (1) accelerated it.

Two possibilities of stabilizer mechanism are most likely:

1. That the silver sulphide is formed at a different site in the presence of the stabilizer.
2. That the quantity of silver sulphide has very little to do with speed or fog and that the stabilizer is functioning at a different site. An extreme case of this kind of action is the power of large amounts of 1-phenyl-5-mercaptotetrazole to stop development of the exposed emulsion.

No work has been published on the function of inorganic stabilizers, such as cadmium and mercury salts. A recent paper from *Brady* and *Hamilton* studied the effect of cadmium ions on the electrical characteristics of emulsion grains and showed that cadmium salts greatly decreased the concentration of interstitial silver ions (see Chapter 1); they suggested that there was a considerable parallel between the function of organic stabilizers and cadmium ions.

One further point must be made. It has already been observed that organic compounds differ in stabilizing efficiency in the molten emulsion and in the coated layer. When an emulsion is dried after coating, about 85–90% of the water is lost and this means that the condition of the coated layer is quite different from that of the liquid one. The pAg rises, by about one unit, while the effective concentration of the stabilizer also increases about ten-fold. Thus, the chemical reactions occurring in coated films on storage may be quite different from those of the liquid emulsion: even the tetrazaindenes may be almost completely adsorbed after coating and drying and the high pAg of the layer must play a large part in modifying the condition at the grain surface.

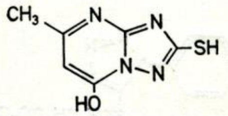
Anti-foggants

In the foregoing section, the term 'fog' has been used in a very general sense when really it should have been defined. Basically a fog grain is one which will develop without light exposure but this implies that the nature of the development influences the fog. While considering stabilization and the means of combating changes in the liquid emulsion and the coated layer, it was assumed that the emulsion would be subjected to "normal" development. When a commercial photographic emulsion is prepared, the sensitometric testing in order to ascertain contrast, speed and fog, must be carried out under the conditions in which the emulsion will be subsequently used, i.e. normal processing. After digestion, the properties are stabilized and the emulsion will then remain fog free for its prescribed life, provided it is processed normally. With many other types of emulsion including those subjected to vigorous and lengthy processing cycles, or those that are commonly mishandled by the user, further precautions are necessary. Therefore, it is possible for an emulsion to have an acceptable low fog value, both when fresh and after a lapse of time, in a conventional developer, but in a developer of very high activity the aged emulsion might contain centres which would be sufficiently active to initiate development without exposure and the emulsion would then be foggy.

Fog produced under these conditions may not result in the formation of a neutral overall density; sulphide contamination of films, which may arise from accidental exposure to sulphide-containing substances or from sulphide present in the processing solutions, can cause the formation of yellow fog.

It is convenient to consider anti-foggants as a separate class, and to define them as substances which combat fog formation under vigorous conditions of processing. It may be felt that this division between stabilizers and anti-foggants is rather an artificial one. However, this is commonly done in the scientific and patent literature although the types of compounds used are frequently very similar in structure and activity.

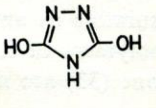
Two very good examples of anti-foggants are benzotriazole (16) and 5-nitrobenziminazole (7) which possess low restraining activity for the digestion processes but which are effective in both black-and-white and colour developers in preventing for formation. The mercapto derivative (23) of the tetrazaindene stabilizer and similar compounds are very active anti-foggants.



(23)

One important class of anti-foggants, which are frequently claimed in the patent literature, are those effective against fog produced on keeping emulsions containing long-chain polyethylene-oxide derivatives (see Chapter 8 for a discussion of their uses). This tendency appears to be particularly pronounced with gold-sensitized emulsions because gold and polyethylene oxides are frequently used together. Perhaps this is because it is only with emulsions already chemically sensitized to the maximum that recourse is made to this type of additive as a means of obtaining further speed increases.

A number of classes are worthy of mention here. Foremost are the inorganic stabilizers; cadmium and mercury. The latter in particular is mentioned in many patent specifications in the form of simple salts and complexes, very much as with classical digestion stabilization; all three mercury compounds referred to in the earlier section are active with polyethylene oxides. A variety of heterocyclic compounds possessing acidic groups including 3,5-dihydroxy-1,2,4-triazole (24) 2-guanidobenziminazole (25) 4,5-diphenyl-2-mercapto-oxazole (12) and 5-mercapto-3-methyl-1,2,4-thiadiazole (26) have been claimed,



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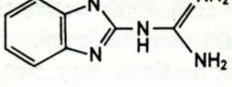

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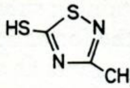
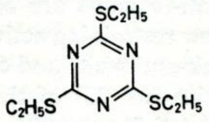


(26)

to quote a few representative samples. It is interesting that heterocyclic compounds unable to form silver salts are also claimed, including 2,4,6-triethylthio-1,3,5-triazine (27) and the ester (28) derived from 1-phenyl-5-mercaptotetrazole.



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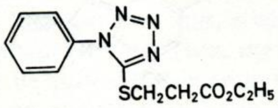
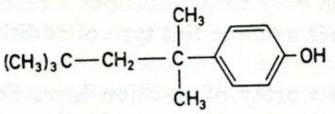


(28)

Two other classes of compounds are also reported to be powerful anti-foggants against polyethylene-oxide-induced fog and these are noteworthy because they are markedly different from the usual stabilizing structures. The first are phenols, including p-substituted phenols (29), or for example the bis phenol (30),



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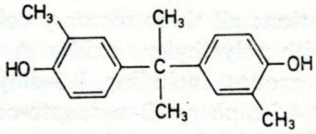
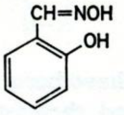


(30)

and phenolic aldoximes such as salicylaldoxime (31).

The final class of derivatives suitable as anti-foggants are polymers, of which polyvinylpyrrolidone (32) or copolymers of it with vinyl acetate and the iodine complexes of polyvinyl oxazolidone (33) are notable examples. Probably because of their fairly recent introduction, there is no published work on how these substances function but their structures suggest a very different mode of action from that of the conventional stabilizer.



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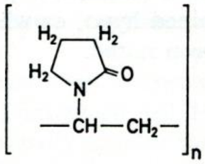

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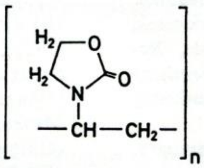

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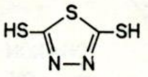
Image Toning and Anti-bronzing

In addition to their fog-combating activity, the addition of heterocyclic compounds can have another very important effect on positive materials, namely chloride or chlorobromide papers. The addition of these compounds changes the image colour on development, probably by modifying the surface nature of the developed grain, and this can be used to produce a more blue or colder image.

In a black-and-white print material the 'colour' of the developed silver is of very great commercial importance. By their nature, the chlorobromide emulsions used in modern 'bromide papers' give warm-toned images. Organic stabilizer-type molecules, in particular benzotriazole and related substances, when added to the emulsion, usually in addition to a modern stabilizer, change the physical form of the developed image, giving a colder toned image.

Many photographic papers are subjected to hot glazing, when the developed silver in the layer is raised to a temperature near to 100° C and this can produce very drastic changes in the image. This usually consists of a marked diminution of density and a change of the image colour from the good black obtained by the development procedure to a rather dullish brown; in many cases this may be accompanied by a metallic sheen. This process is called bronzing or plumming and is totally unacceptable. In order to overcome this behaviour a further type of stabilizer-like molecule is added to the emulsion or to the supercoat. Among the substances which have been recommended for this purpose are 4,5-disubstituted-

2-mercapto oxazoles, such as compound (12) and 2,5-dimercapto-1,3,4,-thiadiazole (34).



(34)

Of the types of compound which have been suggested in the patents, many form very sparingly soluble silver salts and, therefore, are strongly adsorbed to the image silver. Whether the action of these substances prevents the formation of image-toning silver sulphide from retained hypo, or whether they prevent some change in the image structure has not been stated.

References for Further Reading

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[2] GLAFKIDES, P., *Photographic Chemistry*, Vol. 1, Chapter 21, Fountain Press (London) 1963.

[3] BIRR, E. J., *Z. wiss Phot.* **47**, 2 (1952); **48**, 103 (1953); **49**, 1 and 161 (1954); **50**, 107 (1955). (All are in German, there is no account of Birr's ideas in English.)

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VIII COATING

The last stage in the preparation of a light-sensitive material is the coating of the stabilized emulsion, which has the desired speed, contrast and spectral range. It is very important that this is carried out under the correct conditions because the quality of the final photographic result is dependent upon the evenness, cleanliness and thickness of the coated layer.

The thickness of an emulsion layer, which varies widely with the type of material, between 30–600 μ at the coating point which will then be 2–40 μ thick after drying. Supercoats and filter layers are usually thinner than this, being 1–3 μ in the dry state. Colour materials frequently contain a large number of layers, all of them 1–3 μ thick in the dry state and correspondingly thicker when wet.

Emulsion Concentration

The first important factor to be adjusted is that of emulsion concentration. In earlier years, as was mentioned previously the principal consideration was that of gelatin concentration and it was customary always to add sufficient gelatin to achieve the desired concentration. Satisfactory performance of modern silver-halide materials stems from the correct silver/gelatin ratio and therefore the emulsion chemist is not free to vary this at will.

Trough Coating

It is useful to consider briefly the available methods of coating because these do have an effect upon the emulsion requirements. In many cases the emulsion is coated by passing the support, which may be film or paper, around a roller so placed that the support comes into contact with the surface of the emulsion at a closely-controlled temperature, usually between 36° and 40° C, in a specially designed trough. The temperature range is chosen so that it is above the setting point of the gelatin but is sufficiently near to it to permit ready setting of the layer soon after coating. The support may run through the trough so that the roller and, therefore, the base is actually immersed in the liquid emulsion or the emulsion may be picked up by "kissing" the surface of the support; this is represented in Figure 8.1. It either of these methods the level of the emulsion in the trough is carefully maintained by a suitable pumping system. The emulsion "picked-up" by this process is controlled by the viscosity of the solution which will be dependent upon the gelatin concentration and the temperature, and by the amount of "run-back" into the

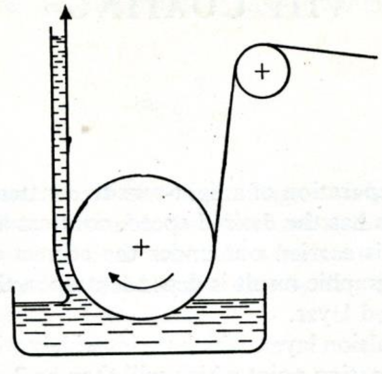


Fig. 8.1 Trough coating

trough which occurs as the emulsion is drawn away by the moving support. The amount of this run-back is inversely proportional to the coating speed; the faster the movement of the support the greater is the amount of emulsion picked up by the base. After coating, the emulsion is chilled to a set gel and is then dried.

An important consideration is that of the total water load which is being applied. If this is higher than a certain level it will not be possible to remove it in a satisfactory time or in an acceptable fashion; too rapid drying can cause physical defects in the coated layer while it is clearly uneconomical to apply large quantities of water, which has a very high latent heat, and therefore may only be removed at considerable cost in terms of fuel.

The factors controlling this type of coating, which is called dip or trough coating, areas follows:

1. The amount of pick-up is controlled by the physical properties of the system, which in turn depends upon its chemical composition. Of these properties, viscosity is of paramount importance. This is partly an inherent property of the gelatin but is also influenced by the presence of other emulsion constituents, for example substantive couplers (see Chapter 10) which increase viscosity, and temperature.
2. The gelatin in the coated layer must be concentrated enough to set the gel form in the time available for this change.
3. The water content must be as low as possible because of the disastrous increase in the drying time and expense with dilute emulsions.

These restrictions may be illustrated by reference to examples. If the emulsion is a very dilute one, pick-up will be low and this would appear to permit the use of a high coating speed, because run-back will be high. It might appear possible, therefore, to obtain a given coating weight from such a dilute emulsion at much higher coating speeds than could be obtained from a concentrated emulsion. However, although there is some variation in the setting rates of otherwise similar photographic gelatins, it is likely that dilute emulsions will not set sufficiently quickly, particularly as they will then spend less time in the chill zone because of the higher speed. Even if these difficulties were overcome, the very dilute emulsion would probably not dry in a short transit through the drying zones. The requirements of (2) and (3) could be met by using more concentrated emulsions. This would result in a higher volume of pick-up because of the increased viscosity and, on account of the higher emulsion concentration, would result in a much higher silver coating weight. One way to offset this would be to run at a lower coating speed in order to permit increased run-back, but then the whole object of working with more concentrated emulsions would be nullified. The whole system, however, restricts the manufacturer to the use of gelatins with only moderate viscosity but which give high jelly strength on setting.

The gelatin concentration used in dip coating is usually between 5% and 8% for film emulsions although it may be lower for paper emulsions because of the absorption of water by the paper and the fact that these emulsion are virtually drying from both sides.

In order to obtain these gelatin concentrations, particularly if the emulsion has not been concentrated during its manufacture, frequently it is necessary to add further quantities of gelatin. The physical properties of this final gelatin are important, and chemically it is usually designed to be as inert as possible because clearly the minimum change of the emulsion properties is required after coating.

Coating speeds are nevertheless limited and it is exceptional to exceed twenty-five feet per minute, and in many cases not more than half this is obtained.

Other Coating Methods

A more satisfactory method of coating is to "doctor" the still liquid emulsion coating at a short distance above the coating position with either an accurately placed metal knife or with a blade of compressed air, shown diagrammatically in Figure 8.2. This method permits the use of more concentrated emulsions, the pre-

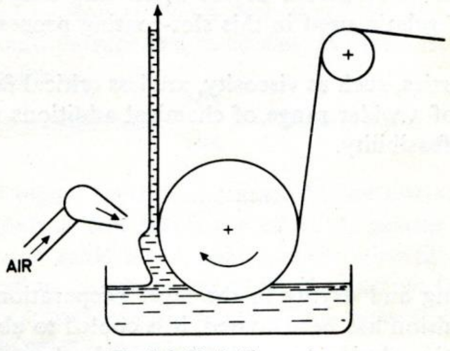


Fig. 8.2 Air knife coating

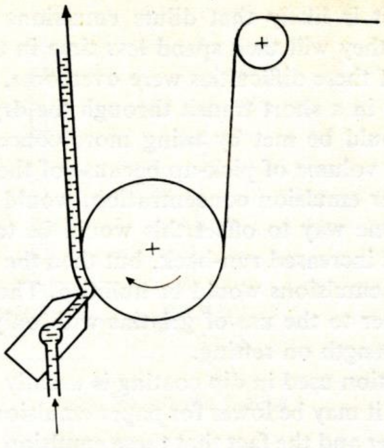


Fig. 8.3 Slot applicator coating

paration of which is made possible by modern methods of precipitation and washing, and the thick layer of emulsion automatically picked-up from this concentrated solution is reduced by this artificial increase in the run-back. This doctoring method is best carried out with gelatin percentages between 8% and 13% and this is frequently achieved in modern emulsions without the addition of further final gelatin.

Another commonly-used method of coating emulsions is by the controlled pumping of liquid emulsion through a very accurately machined slot, placed at a critical distance from the moving base. Figure 8.3. shows such an arrangement. In this procedure the coating weight is controlled, with a high degree of flexibility, by the volume of emulsion which is pumped onto a given area of support. In practice it seems likely that there are upper and lower limits to the attainable coating weight and speed but, nevertheless, this is a more satisfactory way of applying an emulsion than either the trough method, where no direction control is possible, or the air-blade procedure, where a restricted degree of coating weight control is possible. The concentration of gelatin used in this slot-coating process is between 6% and 10%.

The physical properties, such as viscosity, are less critical factors in this method; this permits the use of a wider range of chemical additions without drastic interference with coating feasibility.

Setting and Drying

The stages of setting and drying in the layer preparation are very important indeed. After the emulsion has been coated, it is cooled to about 10–15° C to convert the aqueous gelatin solution to a gel. This may be done by two methods:

1. passing the coated film over cooled rollers
2. blowing cold air, in a carefully controlled manner, onto the surface of the layer.

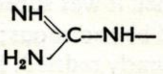
Whichever method is used, the rate of chilling must be sufficient to give a gel of sufficient rigidity before the film enters the warm drying zone of the machine.

There has been much discussion of the nature of the processes taking place during the setting of this gel. The gelatin molecules probably exist in random coils in the sol state, that is when the gelatin solution is fluid, although even this has not been conclusively proved. When the temperature is lowered the gelatin forms itself into regular patterns and some form of linking must occur between adjacent molecules. This is not ordinary chemical bonding: it seems most likely that it is a weaker form of bonding called *hydrogen bonding*. In this type of link, a hydrogen atom, already covalently linked by its only valency to another atom, is attracted, in a specific direction (hence its similarity to a bond) to another atom to give a hydrogen bond (1); see Chapter 2 for further discussion.

$$>\mathrm{N{-}H}\cdots\cdots\mathrm{O{=}C}< \qquad (1)$$

This bond is of less energy than a fully covalent link, when atoms share electrons, and will therefore easily be broken by the application of energy, e.g. from a moderate temperature rise.

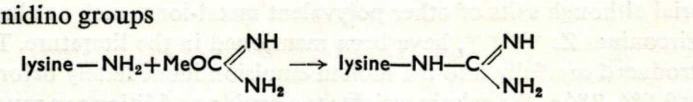
Which part of the gelatin molecule is is involved in this setting? *Janus* believes that the guanidino (2) groups in arginine play the predominant role in this process.



$$\begin{matrix}\mathrm{NH} \\ \mathrm{H_2N}\end{matrix}\!\!>\mathrm{C{-}NH{-}} \qquad (2)$$

This view is based upon experimental work in which he showed that:

1. the action of hypobromite, NaOBr, which is known to destroy guanidino groups in gelatin under very mild conditions, produces a gelatin which no longer forms gels;
2. the action of O-methylisourea (3) on normal gelatin, also under very mild conditions, which would be expected to convert the terminal amino groups of lysine into guanidino groups



$$\mathrm{lysine{-}NH_2 + MeOC}\!\begin{matrix}\mathrm{NH} \\ \mathrm{NH_2}\end{matrix} \longrightarrow \mathrm{lysine{-}NH{-}C}\!\begin{matrix}\mathrm{NH} \\ \mathrm{NH_2}\end{matrix} \qquad (3)$$

gives a gelatin of higher rigidity and much higher setting rate. It seems likely that these treatments do not drastically affect the gelatin in other ways, e.g. by lowering or raising its molecular weight, and therefore the evidence on the function of the guanidino groups seems quite convincing. Certainly the multiple hydrogen bonding capacity of the group would make it effective in linking adjacent molecules of gelatin together.

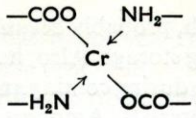
Drying will now be considered; this was found to have an important influence on the properties of the emulsion. This is carried out by passing the set layer through a series of drying zones at controlled temperature and humidity, which are designed to remove the moisture at the desired rate as warm air impinges on the layer. During drying, the water content will go from about 85%, only 15% being assumed to be gelatin, silver halide and other minor additives, to about 5%, because the gelatin will retain 10–12% of its weight of water. The conditions of drying vary greatly but are normally increased in successive zones in the drying chamber before the film enters a final zone designed to bring it back to room conditions for reeling up.

As the water is drawn off, the gelatin molecules initially held by the hydrogen bonds, produced in setting, will be drawn closer together and form a closer-packed array. Generally speaking the more slowly drying is carried out, the more orderly will be the array of the gelatin molecules. Recent work has indicated that in a normal set gelatin gel a substantial amount of gelatin is still present in free form, while it has been shown from the optical activity of gelatin gels, that maximum order is obtained by drying at room temperature; this is economically impossible and may not be desirable anyway.

Hardening

If an emulsion prepared in the manner described in the previous chapters, was coated and dried, it would remain in a very soft state making it susceptible to abrasion and the action of dust, etc. in during and after the processing. The swelling of an emulsion layer, left in this state, when it was subsequently placed in water, or worse still in an alkaline developer, would be enormous; this could cause reticulation when the greatly swollen layer is subsequently redried. It is frequently customary today to process films at elevated temperatures, for instance in the rapid-processing methods used for quick access recording materials and the automatic processing machinery available for X-ray films. These conditions require very robust layers and rapid removal of all the water after processing and, therefore, *hardeners* are added to the emulsion before coating.

Hardening agents can be divided into two broad types. The first are inorganic salts of which *chrome alum*, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, is the most commonly-used material although salts of other polyvalent metal-ions, such as aluminium Al^{+++} and zirconium Zr^{++++}, have been mentioned in the literature. The chrome alum is introduced carefully into the molten emulsion immediately before coating and at about 0,5%–2% of the gelatin weight; too rapid an addition can cause coagulation of the emulsion if there is a temporary excessive local concentration of the hardener. As soon as drying occurs the hardening reaction takes place, which is a rapid one involving ionic changes. In common with all types of hardening, the result is achieved by the linking together of different chains of gelatin molecules. The action of chromium is probably to form ionic links (4) between the carboxyl, $-CO_2H$ groups of different chains



(4)

with co-ordinate contribution from the amino groups. As might be expected, the action of chrome alum is dependent on pH, and is effective at the usual emulsion coating pH values, about 6.0, but is far less effective at higher pH values.

The other type of hardening is completely different. In this case, an organic aldehyde, or more rarely a ketone, is used to form a link between amino groups in different gelatin chains. The simplest compound of this class is formaldehyde, CH_2O, and this is still commonly used, particularly for paper emulsions. The commercially-available formaldehyde solution, formalin, is about 40% strength and 1–3 grams of formaldehyde per 100 grams of gelatin is a suitable quantity to obtain satisfactory hardening. It is clear that the link formed depends on whether two amino groups (5) or an amino group and a hydroxy group (6) are involved,

$$\text{—NH—CH}_2\text{—O—CH}_2\text{—NH—} \qquad (5)$$

$$\text{—NH—CH}_2\text{—O—CH}_2\text{—O—} \qquad (6)$$

and this implies two differences between the function of formaldehyde and that of chrome alum. The first is that the hardening reaction will be of an organic type, in other words it will be slow, and secondly, there is not the same pH dependence as occurs with the polyvalent inorganic ions. The kinetics of hardening with formaldehyde have been derived by a study of the viscosity increase, relative to the concentration of the reactants and pH. The relationship is shown in the following equation:

$$\text{cross linking rate proportional to } \frac{[\text{gelatin concentration}]^2\,[\text{hardener concentration}]^n}{\text{H}^+\text{ concentration}}$$

where n is 2 for formaldehyde, showing that two molecules of formaldehyde are involved in the rate-determining process; this accords with the type of link in (5) and (6). The initial stage is probably the reaction

$$\text{gel—NH}_3^+ + \text{CH}_2\text{O} \longrightarrow \text{gel—NH—CH}_2\text{OH} + \text{H}^+$$

followed by

$$\text{gel—XH} + \text{CH}_2\text{O} \longrightarrow \text{gel—X—CH}_2\text{OH}$$

where $X=O$ or N,
and finally

$$\text{gel—NH—CH}_2\text{OH} + \text{gel—X—CH}_2\text{OH} \longrightarrow \text{gel—NH—CH}_2\text{O—CH}_2\text{—X gel.}$$

The formaldehyde is added at the coating stage but it is not until a considerable time has elapsed after the completion of drying, usually two or three weeks, that the full hardening effect of the formaldehyde is complete. This presents no difficulties in commercial practice because a delay of this kind of order always occurs between coating and dispatch.

A large variety of other compounds of closely-related structure, which must therefore function by a similar mechanism, have been suggested to overcome the disadvantages of formaldehyde, which, probably because of its strong reducing action, is very prone to produce fog during storage. Also, its high volatility makes it difficult to prevent the loss of formaldehyde during coating and in extreme cases this can result in the contamination of other materials. Amongst the substances suggested is bis-hydroxymethylurea (7),

$$\mathrm{HOCH_2NHCONHCH_2OH} \qquad (7)$$

which is easily formed by the direct interaction of formaldehyde and urea and behaves as if it contained free formaldehyde, although the active agent is producedslowly during the drying process, and the volatility disadvantage of formaldehyde is completely absent. It seems likely that the reaction occurs as represented by the following equation:

$$\mathrm{gel\ NH_2 + HO{-}CH_2{-}NH{-}CO{-}NH{-}CH_2{-}OH \longrightarrow gel{-}NH{-}CH_2{-}NH{-}CO{-}NH{-}CH_2{-}OH}$$

$$\mathrm{2\ gel{-}NH{-}CH_2{-}NH{-}CO{-}NH{-}CH_2{-}OH \longrightarrow 2\ NH_2{-}CO{-}NH{-}CH_2{-}OH + H_2O +}$$

$$\mathrm{gel{-}NH{-}CH_2{-}O{-}CH_2{-}NH{-}gel.}$$

As the equation suggests, the mono hydroxymethylurea is also effective as a hardener because this can undergo the same sequence of reactions.

Many substituted aldehydes have been described as active in hardening emulsion layers although it is clear that aldehydes containing large hydrocarbon groups are ineffective. The simplest

$$\mathrm{CHO{-}CHO} \qquad (8)$$

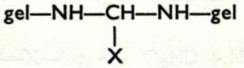
dialdehyde, glyoxal (8) is very active and so are glutyraldehyde (9)

$$\mathrm{CHOCH_2CH_2CH_2CHO} \qquad (9)$$

and mucochloric acid (10),

$$\mathrm{OHC.CCl{=}CCl.\ CO_2H} \qquad (10)$$

which may even behave as a dialdehyde by losing its acid grouping. This change, which occurs during hardening, causes an appreciable drop in pH and thus sometimes in sensitivity; this must be allowed for in manufacture. The quantities of the agent added are the same molecular proportions as for formaldehyde. With these more complicated aldehydes the link between the two gelatin amino groups is either of type (11),



$$\mathrm{gel{-}NH{-}\underset{\underset{X}{|}}{CH}{-}NH{-}gel} \qquad (11)$$

where x represents the other part of the molecule joined to the aldehyde function, or in a dialdehyde there is most probably grouping (12)

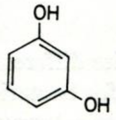
$$\mathrm{gel{-}N{=}CH{-}X{-}CH{=}N{-}gel} \qquad (12)$$

uniting the two parts of the chain.

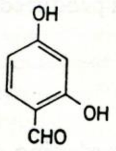
Kinetic studies on glyoxal show that Equation 8.1 is balanced when $n=1$ indicating that only one glyoxal molecule is involved per two gelatin units. The nature of the linkage between adjacent gelatin chains is radically different from that formed by formaldehyde. This changes the balance of properties, for example, hardness, toughness (these two properties may not necessarily be the same), and factors such as developer penetrability and the influence of the hardened gelatin on the developed state of the image and thus its covering power. The choice of hardener depends on an assessment of its effect on all these properties.

References to particular hardeners frequently include such phrases as "reduces contrast" but these can only be regarded as generalisations because the influence of one agent is very dependent on the overall make-up of the system in which it is being used; clearly excessive hardening of the layers will interfere with developer penetration. Many hardening agents have been reported to give fog, particularly in fast emulsions, but this again is related to the chemical make-up of the emulsion. All the aldehyde hardeners are reducing agents and will naturally be prone to give fog so the emulsion must be balanced to reduce this tendency. Active stabilizing substances can greatly assist with the control of these adverse influences, while avoiding the use of excess chemical sensitizers, particularly metal salts, will help in overcoming any deleterious effects.

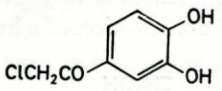
One interesting, and apparently important, action is that of hardening accelerators. These are compounds which are added to photographic emulsions and which do not themselves bring about the cross-linking between gelatin chains but accelerate the action of aldehyde hardeners such as formaldehyde. All the compounds possessing this kind of action are phenols or phenolic aldehydes, such as resorcinol (13) and resorcylaldehyde (14). A recent *Agfa* publication draws particular attention to 4-chloroacetyl catechol (15).



(13)



(13)

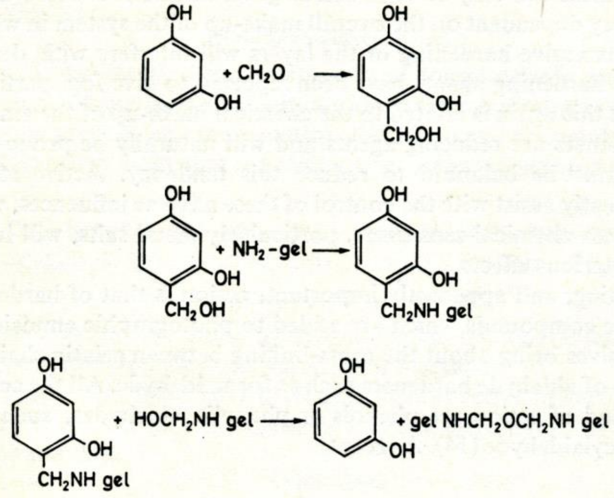


(15)

Quantities of the order of 0.1 to 1.0 g per 100 g of gelatin are effective, the optimum amount depending very much on the accelerator chosen.

The inclusion of these compounds in an emulsion enables the time of hardening to be reduced, and this can be important in avoiding a long interval between coating and the dispatch of the film. In extreme cases the quantity of hardener can be reduced, thus avoiding untoward side effects and permitting adequate hardening to be produced which could not be obtained by the action of the hardeners alone.

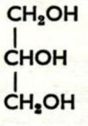
It is very probable that the accelerators, all of which condense easily with formaldehyde, react with that reagent to give a product which then condenses with the gelatin:



These phenols are added for quite different purposes from those put in at earlier stages in the emulsion preparation for bacteriocidal effects. However, the two classes of additives are very similar in chemical structure and it is likely that frequently accelerated hardening must have been produced unwittingly in the past.

Plasticizers

Almost complementary to the hardening agent is the plasticizer. Gelatin, when dry, is a very brittle substance and it is important that the gelatin layer of the emulsion is able to bend as easily as the film or paper support on which it is coated. The simplest way of achieving this suppleness is to prevent the moisture content from becoming too low, for example by the addition of a humectant, such as glycerol (16).



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \qquad (16)$$

Glycerol is not without its shortcomings because it tends to make the coated layer tacky under conditions of high humidity, and this can cause sticking and marking of the surface by the layers adjacent to it. This was a very common fault at one time but is rarely seen in present-day films. Many compounds, most of them fairly closely related to glycerol, have been described as plasticizers; derivatives of ethylene glycol, $HOCH_2CH_2OH$, containing ester and ether linkages have been referred to in the patent literature.

Wetting Agents

By the time all the above additives have been included, the emulsion is almost ready to be coated on the support and it is very necessary that this coating process takes place evenly. However, the 'water-liking' or hydrophilic parts of the gelatin molecules are those containing the $-CO-NH-$ and similar groups while the other parts of the gelatin molecules, namely the carbon chains and rings, tend to be water-repelling or hydrophobic groups. There is, therefore, a tendency for the hydrophilic groups to point inwards to the bulk of the aqueous solution and for the hydrophobic groups to point outwards during the drying process. This occurs in the subbing layer and in the emulsion layer. When therefore the dilute aqueous emulsion is applied to the subbed base, or alternatively one emulsion or a supercoating layer is coated on top of an emulsion layer already dried, the aqueous solution meets a hydrophobic layer. This would result not in the desired even thin layer but in the formation of globules, utterly preventing the coating process. Even coating can therefore be achieved only by the addition of a wetting-agent surfactant or spreader. The main function of this agent is to reduce the *surface tension* of the liquid, that is, to lower the force which holds the surface of the liquid together and prevents spreading. The magnitude of this force on the surface depends on the nature of the liquid and becomes lower with increasing temperature.

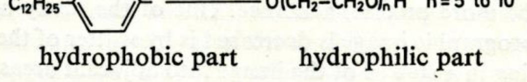
Suitable wetting agents are compounds containing a hydrophilic part and a hydrophobic part, for example, a soap molecule, but this type is not suitable in a photographic emulsion because of their fairly low activity compared with modern synthetic wetting agents. Those used today include

1. anionic wetting agents which may be sodium alkylsulphates such as sodium lauryl sulphate

$$CH_3(CH_2)_{10}CH_2 \text{ ——— } OSO_3^{\ominus}Na^{\oplus}$$

hydrophobic part hydrophilic part

2. non-ionic wetting agents, such as dodecylphenol polyethylene oxide ether



hydrophobic part hydrophilic part

3. cationic wetting agents, such as hexadecyltrimethylammonium bromide

$$C_{16}H_{33}{-}N{\equiv\equiv}(CH_3)_3^{\oplus}Br^{\ominus}$$

hydrophobic part hydrophilic part

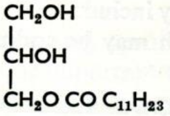
It will be noted that the naming of wetting agents is derived from the polarity of the hydrophobic part. These agents are added to the emulsion or supercoat as an aqueous solution at 20 mg–1.0 g of pure wetting agent per 100 g of gelatin although it is common practice, particularly in multilayer coatings, to use mixtures of compounds of different types.

One very common wetting agent, of a non-ionic type, is the natural product saponin. In a pure form, which must of course be ascertained by photographic testing, it is a widely-used material even today, while at one time it was almost the only known product for this purpose.

One further function of these wetting agents must be mentioned: this is the wetting action on the film during processing and drying. Although wetting agents may be added to the final rinse water to obviate drying marks, the evenness of the spread of the developer, which in certain types of treatment such as rapid processing and other critical developer formulae may be important in producing even development, is wholly controlled by wetting agents added to the emulsion coating. Frequently such compounds are added deliberately for this purpose alone.

Anti-foaming Agents

One of the many hazards of handling emulsions is their tendency to froth. This is a natural behaviour of gelatin solutions which is enhanced by the addition of wetting agents. As well as mechanical solutions to the problem, such as withdrawing emulsion from below the surface of the liquid emulsion and taking all precautions to avoid introducing bubbles at the later stages, it is customary to add an anti-foaming agent. Aliphatic alcohols of intermediate chain length such as amyl (C_5) and nonyl (C_9) are used for this purpose while glycerol monolaurate (17) is also mentioned as being effective.

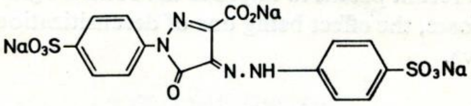


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2O\,CO\,C_{11}H_{23} \end{array}$$

(17)

Acutance Dyes

Many modern emulsions are specifically designed to provide the highest possible definition or, to be more precise, acutance. One of the many means whereby the sharpness of a photographic image is decreased is by scatter of the light by the emulsion grains, resulting in a spread of the image into adjacent areas. The scattering of light is much higher at the blue end of the spectrum than at the red end, and is proportional to the fourth power of the wavelength. This is illustrated by the fact that the sky is blue, the colour coming from the light scattered by fine dust in the atmosphere. Frequently, therefore, a dye, particularly a yellow dye which absorbs blue light, tartrazine (18) for example, is added to the emulsion to reduce the effects of this scatter.


(18)

Some speed loss must inevitably result from the light absorbed by this addition, apart from any chemical desensitization which is always likely to occur. Nevertheless, many emulsions, such as those used for aerial photography, contain acutance dyes.

Polyethylene Oxides

Related to the wetting agents discussed above, but added for quite different purposes, are the long-chain polyethylene oxides. Unlike those non-ionic wetting agents which may contain 6–8 polyethylene-oxide units linked to a hydrophobic group, apparently the only essential requirement is a long polyethylene-oxide chain containing upwards of 20 individual units. This may terminate in an aromatic or aliphatic group, such as phenyl or cetyl, as with the wetting agents (19) or may just end with a hydroxyl group (20); both classes are equally active.

$$R\text{—}(OCH_2CH_2)_nOH \qquad (19)$$

$$H(OCH_2CH_2)_nOH \qquad (20)$$

Among the known compounds are *Texofor A1P* (19, $R=C_{16}H_{33}$, $n=23$ approx) and *Carbowax 4000* (20, $n=90$ approx). It must be stressed that these compounds are prepared by polymerization processes in which a range of molecular sizes is produced, and the values of n will be average figures only. There will be substantial proportions containing lower and higher values of n present as impurities in the materials.

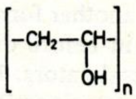
These compounds produce an increase in speed in fast iodobromide emulsions, in which they are mainly used, giving up to twice the speed under optimum conditions. This is a fairly recent introduction to photographic technology and has played a part in the outstanding fast films of the present day. Initially it was believed that these compounds brought about yet another form of chemical sensitizing and for that reason they were frequently put in before digestion, but it seems most likely that they function as development accelerators. *Wood* has shown that they do not desorb gelatin from the grain surface, one possible mode of action, although they are themselves adsorbed quite strongly to the grain, and it seems most likely that they function by reducing the charge of the double layer surrounding the grain, and thus facilitate the approach of the negatively-charged developing agents.

A speed increase is only produced with the usual superadditive developers such as metol-hydroquinone or Phenidone-hydroquinone systems. Development by hydroquinone developers is inhibited and *Wood* has suggested that this is because of interaction in the bulk of the developer between polyethylene oxide and the semiquinone, the half-way oxidation product of hydroquinone. This behaviour has been applied by *Perutz* in a recent patent to improve the contrast given by emulsions used for lithographic purposes, the effect being one of desensitization in the toe region of the characteristic curve.

Supercoating

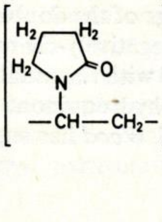
The emulsion coating, after drying, is very sensitive to physical abrasion. After processing, a simple emulsion layer would show finger marks and scratches as developed silver, presumably because of the effect of physical stress upon the surface of the grains, but this can be prevented by the application of a protective layer or supercoat. With the modern tendency to use less gelatin, leaving the grains more unprotected, and to subject so many films to rough usage, such as in the automatic processing machinery used for X-ray and graphic-arts films, the requirement to provide a protective layer on top of the uppermost silver-halide layer has become even more imperative. The supercoat usually consists of a thin gelatin layer, containing 10% or less of the amount of gelatin in the emulsion, coated either subsequently to the emulsion layer application point or from an additional slot during the emulsion coating. As with the coating of additional emulsion layers, the wetting agents used in the supercoat are important and must be balanced with those in the emulsion. The gelatin must be strongly hardened and it is normal to use a gelatin of high physical characteristics. It is also important to avoid coating it from too dilute a solution because this will cause the final strength of the dry supercoat to be low. Quite commonly the bulk of the emulsion hardener is added via the supercoat, the diffusion into the emulsion layer being relied upon to produce a sufficiently high hardening level there.

The main reason for using gelatin in the supercoat is its reliable compatability with the lower emulsion layer. More recently, however, patents and literature references have described the use of agents other than gelatin for the supercoat. Amongst agents mentioned are polyvinyl alcohol (21) and partial esters of it, polyvinylpyrrolidone (22), polyamide-acid mixtures such as acrylamide/maleic acid (23) and acrylamide/acrylic acid (24) copolymers, but the amount of commercial usage of these agents is not known.

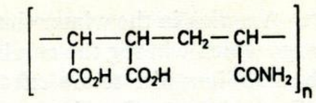


$$\left[-CH_2-\underset{OH}{\underset{|}{CH}}-\right]_n$$

(21)

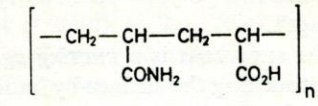


(22)



$$\left[-\underset{\mathrm{CO_2H}}{\mathrm{CH}}-\underset{\mathrm{CO_2H}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\right]_n$$

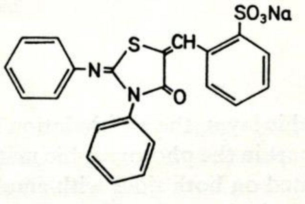
(23)



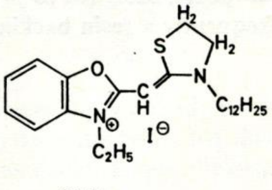
$$\left[-\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{CO_2H}}{\mathrm{CH}}-\right]_n$$

(24)

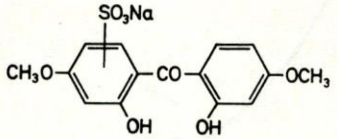
In the case of colour images, particularly in prints, the supercoat can also contain a compound able to absorb ultra-violet light. Ultra-violet is the most active radiation fading of colour materials and some protection is therefore given by a u.r. absorber which prevents some of the incident u.v. light from reaching the dye image. Many u.v. absorbers suitable for colour prints bear considerable structural resemblance to sensitizing dyes; two of the compounds claimed in patents are the thiazolidone (25), related to the merocyanines, and the colourless true cyanine (26),



(25)



(26)



(27)

while the water-soluble compound (27) is similar to the u.v. protecting agents used in plastics.

Two further constituents of the supercoat should be mentioned. The first is the *antistatic* agent which, although included in the film base, is vital to prevent the build-up of electric charge on the surface of the final coating. This may occur at the reeling-up stage (another reason why humidity is not kept low at this point but is at a higher value than exists in the final drying stage), when the coated film is unreeled for cutting into sheets or small rolls, or at a much later stage, the withdrawal of sheets of film from their boxes which can produce static electricity if it occurs in a very dry atmosphere, e.g. North America in the winter time. The build-up of charge can lead to an electrical discharge which will fog the emulsion, frequently rendering it useless. Inorganic salts such as sodium nitrate are effective in preventing this although more recent patents refer to the use of a wide range of polymers to achieve this end. These materials all contain a polymer chain carrying an ionizable group at frequent intervals along its length.

The other constituent of the supercoat is a *matting agent*. In most graphic-arts products, it is desirable that retouching the surface by hand is possible. Also the formation of Newton's rings* during exposure must be avoided. These may both be achieved by coating with a suspension of fine particles of a substantially transparent substance, e.g. starch or colloidal silica. More recently the addition of polymer to the supercoat has been claimed to prevent the formation of Newton's rings; the addition of an alkali-soluble methylacrylic acid — methyl methacrylate copolymer or the precipitation of ethylcellulose in the gelatin solution are two of the methods mentionped. Incompatibility between the polymer and the dried gelatin of the finished suercoat is probably the mode of action of these additions.

Backing Dyes

Although not a photographic layer, the anti-halation layer must be mentioned because it plays an important part in the photographic material.

Every film, unless it is coated on both sides with emulsion as X-ray film, carries a backing layer of gelatin, or a substitute, designed to prevent curl of the film. In colour film for example, this is frequently a resin backing designed to be removed in

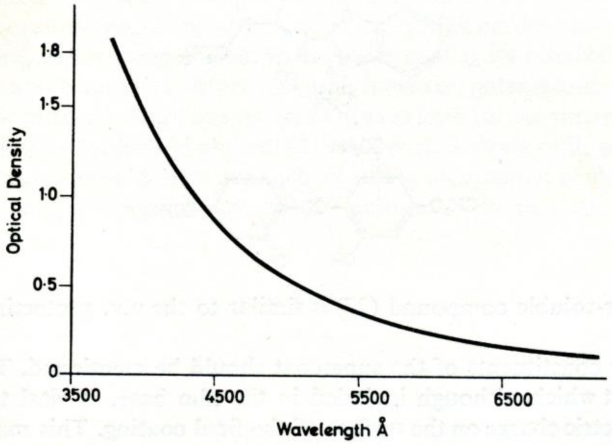


Fig. 8.4 Absorption of manganese dioxide backing

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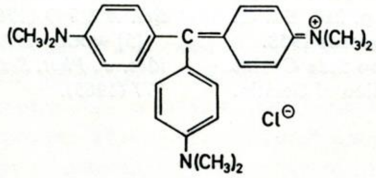
* These are concentric rings, not usually perfect circles, produced when one plane surface is held in contact with another, by interference between directly transmitted light and that transmitted after being reflected back and forwards between the layers imperfectly in contact.

processing. Incorporated in this layer is a pigment or dye designed to absorb light in those regions of the spectrum to which the emulsion is sensitive. In microfilms, where complete absorption of the light transmitted through the emulsion layer is desired for maximum sharpness, the back coating is a black-dyed resin.

One commonly-used substance is colloidal manganese dioxide, which is brown in colour and absorbing quite strongly at the violet end of the spectrum, dropping with increasing wavelength as shown in Figure 8. 4.

This is prepared by reducing potassium permanganate with a suitable material, e.g. glucose, in the presence of a suspending colloid, such as gelatin. The commonest dyes, used for backing layers, are the triphenylmethane dyes, for example crystal violet (28), acid fuchsine (29) and similar dyes. It is important that the dyes should reduce easily and that the products wash out of the gelatin backing layer; dye (30) with its solubilizing groups has been suggested for this. In addition, many cyanine-type dyes have been claimed as backing dyes of which (31) and (32) are examples.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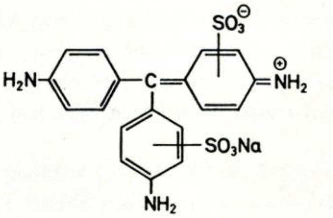
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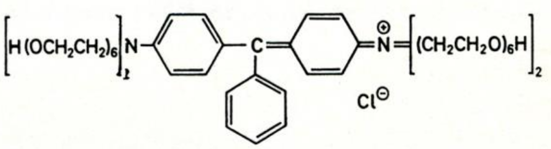
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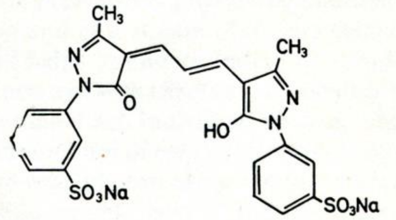
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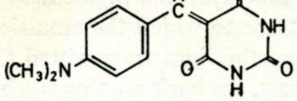

(32)

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IX LATENT IMAGE

Introduction

The changes which take place when the crystal of silver halide is struck by light will now be considered as well as the effect of the chemical conditions, produced by the preceding manufacturing stages, on the result of this action.

The first thing to appreciate is the nature of the difference that exists between exposed and unexposed grains: exposed grains are more readily reduced to silver metal. That is, there is a difference in the speed of the same chemical reaction which occurs more rapidly on some grains than on others. This difference in rate of development occurs because a centre able to catalyse development of a grain has been formed as a result of the exposure. This centre is termed a *latent image*.

Secondly, the only way of detecting the presence of the latent image is by development. An analysis by chemical means, other than development, of the action of light on silver halide is only possible after very heavy print-out exposures where really massive changes have been produced. More recently, electron spin resonance, which detects the presence of radicals, has been used to detect metallic silver in exposed silver-halide crystals but exposures were much heavier than those needed for photography.

Another simple but vital point is that the whole latent-image forming process can be considered as taking place within individual crystals; there is no evidence that any real interaction takes place between crystals during the latent-image formation stage. It is, therefore, necessary to consider the behaviour of only a single crystal during this stage. This may not be the case at the development stage, for example, in an infectious developer where a latent-image-bearing grain will initiate development and cause the reduction of those crystals near to it by chemical influence.

Light Exposure

NATURE OF LIGHT. The silver-halide emulsion is exposed to light. Light can be regarded in two ways, in fact present-day physics requires that light must be described as both a wave motion and as a stream of quanta called *photons*. The concept of the wave nature of light helps in understanding its propagation, reflection, refraction, etc., but when concerned with effects at atomic sizes then light must be considered as a stream of photons. Each individual photon, which has no mass in the ordinary sense, has a specific amount of energy associated with it, this energy depending on the wavelength, and each photon can bring about one individual photochemical change. In a silver-halide crystal, most of the quanta go straight through without achieving anything; there is a lot of empty space in a silver-halide crystal, or in any apparently solid substance. Those quanta which are absorbed by the crystal will give up their energy to produce one photochemical occurence.

NUMBER OF QUANTA. The next question is how many quanta must be absorbed by one crystal to render it developable. This is a very difficult question to answer but fairly recent painstaking work has given an answer to this question. By measuring the light sensitivity, in terms of light absorbed, on each of a number of size classes of grains of a single-grain layer, which adhered to a glass support when an unhardened emulsion layer was otherwise washed off with warm water, *Farnell* was able to calculate how many light quanta had to be absorbed to render a grain developable. He found that there was a wide range of requirements, some grains needing 50 or 100 quanta, even in a sensitive emulsion, but that *four seems to be the minimum number*.

Japanese workers have also studied the size of latent-image specks by two techniques. One was to deform the silver-halide crystal by physical stress, created by ultrasonics; the relation of the dimensions of the distortion to the grain dislocations pesent in the crystal before the physical treatment, enabled them to determine the size of a latent-image speck (see next section) able to initiate development. The second technique was the nearest to direct measurement carried out to date, namely a determination of the movement of the speck by ultracentrifugal force, produced by 40,000 r.p.m. at a radius of 65 mm, which was found to be only 3 microns in 10 minutes. Both these determinations gave an answer of 3–4 atoms of silver, similar to *Farnell's* conclusions. However, these workers did not report the detection of larger specks than these.

This is important in considering the mechanism of latent-image formation because, clearly, if a minimum of 3–4 quanta are required in the most efficient grains, then a reasonably small number of processes in a definite sequence must be taking place; that is, a multi-stage process is involved.

It must be stressed here that photons will arrive at the crystal over the interval of time covered by the exposure: they do not need to be absorbed at the same instant. The physical analysis of the system will assume a purely random distribution of photons, that is, the illumination is falling evenly on a crystal throughout the exposure. Therefore, during the exposure a succession of photons are being usefully absorbed and four of these will render the grain developable. During an exposure, say between 1/50th and 1 sec, the usual range for normal photographic materials, a lot of time is available for many atomic processes, each needing 10^{-9} secs or less, to take place. However, the time interval over which the absorption of the four photons, or the minimum needed to make a grain developable, is very important; if these photons arrive too quickly or too slowly then they are less effectively used. This will be discussed later.

Nature of Latent Image

Chemical Identity. There seems no doubt that the latent image is *silver metal*, that is it is composed of silver atoms, not ions. This does not resolve the question of whether the silver atoms are all closely adjacent, somehow sticking out of the silver-halide lattice, but it seems vital that they must be fairly near to one another; perhaps each silver atom is in a lattice site on the crystal surface. ***Berg*** feels that we can go no further than "a place with a stoichiometric surplus of Ag^+ ions and electrons". Certainly its chemical properties are similar to those of finely-divided silver, such as the oxidation (usually called bleaching) by, for example, dilute chromic-acid solutions.

Now there is a general connection between the number of photons and the number of silver atoms. In the more efficient crystals, that is those in which none of the effect of any of the photons is lost, four photons produce four silver atoms. In photochemistry this relationship is called the quantum yield and the greatest yield for a basic photochemical process is one photon giving a change in one atomic or molecular species; a quantum yield of one.

Critical Size. A corollary follows from these conclusions, namely that less than four photons do not form a latent image. This may mean that less than four photons do not produce a permanent entity in the grain or alternatively that the permanent result of the smaller number of quanta is insufficiently active to initiate development. When considering processes taking place at the atomic level, it is necessary to remember that the difference between say, two atoms and three or four atoms can be very large and therefore the arrival at a threshold level, able to bring about development, may occur at a very distinct point.

Function of Latent Image

Amplification. The silver-halide emulsion-grain is a very efficient amplifying device; this is one of the factors which explains the high sensitivity of modern materials. It will be seen that the capture of a small number, frequently only four, photons can result in a permanent record of four silver atoms. By the development step, these can be converted (see the emulsion examples in Chapter 4) into 10^9 to 10^{10} silver atoms. The form of this final silver-image is also important and can consist of compact or bulky filamentary silver-metal; the latter gives the higher covering power and is therefore beneficial in terms of speed, contrast and maximum density.

Kinetics of Development. The effect of the latent image is to render the grain more easily reducible by a reducing agent of appropriate activity. This is due to the catalysis of the reduction of silver ions, from the crystal or from solution (these two types of development are called *chemical* and *physical* respectively) by the silver of the latent image.

A clearer picture of this may be obtained by examining a generalized chemical process. When two molecular species, which will be called A and B, react together to give a product C, the first, and obvious, requirement is that they come enough together to interact with one another. However, all colliding molecules do not react automatically unless they possess sufficient energy to form an activated complex, represented as AB*. The energy required for this normally comes from thermal energy; at higher temperatures a larger proportion of molecules will possess this energy, hence the faster reaction rates which occur at higher temperatures. This activation energy, which may be determined from the change of rate with temperature, is a measure of the ease of a reaction. *Levenson* provides a useful compilation, given in Table 9.1. It will be seen that the presence of a latent image reduces, by around 10,000 Kcals per mole, the energy required to bring about the reduction of the silver halide. At normal development temperatures this can make the latent-image-catalysed process about 1,000,000 times as fast as the fog growth.

TABLE 9.1

ENERGIES OF ACTIVATION DURING DEVELOPMENT

Energy of activation KCal per mole	*Reaction*
4–7	Diffusion processes
10–20	Development of silver halide from latent image centre
20–30	Fog development; reduction without latent image

Mechanism of Development

The question now arises as to why a silver-speck should catalyse development. There are many theories on this, three of which will be considered briefly; a more detailed discussion is given by *Levenson* (see references for further reading). The first of these is the *electrode theory* in which the silver functions as the anode (positively-charged pole) of a silver/silver-halide couple and it is at that point therefore that the electron-donating developer will discharge and then reduce the silver-ion of the halide. This can be demonstrated by fairly satisfactory models and it is interesting to note that a highly crystalline silver-speck was inefficient in this capacity while a loose cluster was very effective. In this theory, the silver-ion concentration is maintained by diffusion through the crystal but it is doubtful if this could sustain the very high rates of development known to occur in certain cases. Nevertheless, this theory receives the greatest support today.

The second theory is based simply on the *adsorption* of the developer-molecule at the silver-halide. The silver-nuclei of the latent image would then deform the ions of the silver-halide lattice and provide an area where the adsorption of gelatin and protective ions is weakened. This breakdown may be additionally catalysed by silver ions adsorbed to this nucleus.

The importance of the barrier to the approach of a developer molecule is stressed in the third theory. It is well known that gelatin has a powerful effect in controlling the ease of reduction by developers and also that the negative charge barrier (see Fig. 1.5) of unexposed emulsion crystals. The *charge theory* which has been fully investigated by *James*, proposes that the silver latent-image provides a break in this charge barrier and this idea was supported by the fact that the higher number of negative charges on the developer molecule, the longer was the induction period before development became rapid; uncharged developers such as diethyl-p-phenylene diamine (see Chapter 10) have no induction period. It is very likely that all these three types of development are important.

Photolysis of Silver Halide

FIRST EFFECT. When a photon is absorbed by silver halide, or by any similar lattice, the energy annihilation produces two entities. These are an *electron* and a *positive hole* or defect electron; a positive hole is best defined as a negative ion from which one electron is deficient, hence the term defect electron. For silver-bromide, therefore, a positive hole may be thought of as a bromine atom, as long as this concept is not applied too rigidly. For example, the movement of a positive hole, an important factor in this discussion, must not be seen as the movement of a bromine atom but rather as the movement of a defect electron by a handing-on procedure between a series of bromine ions. Only when a positive hole reaches the grain surface does it really become a bromine atom.

POINT OF FIRST ACTION. Light absorption may occur at any bromide ion in the crystal. This is represented by

$$\mathrm{Br}^- + h\nu \longrightarrow \boxed{\mathrm{Br}} + e$$

where $\boxed{\mathrm{Br}}$ is the positive hole and e is an electron. This is true over the main wavelength range of sensitivity. There is purely random absorption of the light and no question of the photon being absorbed, and the electron and positive hole being preferentially released, at the surface; this may take place anywhere with equal probability. On the other hand, the absorption of light of longer wavelength will take place in chemical impurities rather than in the bulk of the crystal but this is usually a much lower order of absorption. Therefore, the *volume* of the crystal, not merely its surface area facing the incident light, is the important property in assessing the light-trapping capacity of a crystal. This accounts, for example, for the high speed to blue light of the thick grains of the modern high-speed x-ray emulsions.

What happens next is one of the many topics of photographic theory about which argument is still taking place, and there have been many hypotheses.

Gurney-Mott Theory

OUTLINE. The first theory which came anywhere near explaining the facts, on a modern solid-state basis, is that due to *Gurney* and *Mott* in 1938. In the succeeding years, this theory has undergone many minor modifications but the original authorship is still given to the more recent versions. According to their picture the process occurs as follows: —

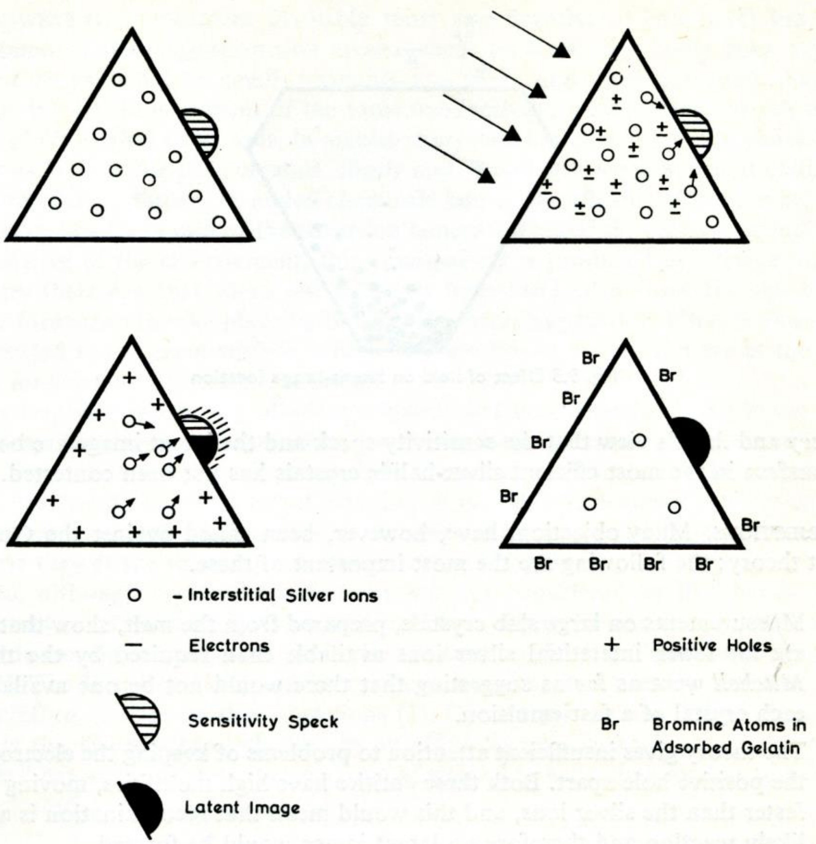
1. Two types of entity are present in a crystal: —
   (a) A sensitivity speck. This is the chemical entity produced during the sensitization process and which may be silver or silver sulphide. This confers the sensitivity by acting as a nucleating centre for the latent-image formation.
   (b) Silver ions which are not located at lattice positions, that is, interstitial silver ions.

   Figure 9.1 represents a light-sensitive crystal before exposure. It must not be assumed that the sensitivity speck is on the edge of the crystal as indicated, in all probability it occurs at a more advantageous place on the crystal.
2. When the exposure occurs, electrons and positive holes are formed. The former rapidly move through the crystal and locate themselves at the sensitivity speck. It is known that the order of mobility of the three important entities in this process is:

   $$\text{electrons} > \text{positive holes} \gg \text{interstitial Ag ions.}$$

   Logically therefore the movement of the electrons could take place in the way *Gurney* and *Mott* suggest. This is shown in Figure 9.2.
2. Sufficient interstitial silver ions will therefore be attracted to the now negatively-charged sensitivity speck to cause the neutralization of this charge and thus form an aggregation of silver *atoms*, the latent image, shown in Figure 9.3.
4. The positive holes escape to the surface, and, as bromine atoms, react with the gelatin as indicated in Figure 9.4. If, on the other hand, the positive hole gets to the sensitivity centre before the silver ion it will recombine with the electron and the results of the absorption of the photon will be lost.

ADVANTAGES. Many of the points of the Gurney-Mott theory are widely accepted today. The most important of these is the separation of the mechanism of latent-image formation into electronic and ionic steps; all subsequent theories have accepted this concept. The existence of these two steps has been supported by experiments in which it has been shown that the latent image is formed very inefficiently at very low temperatures; although the trapping of the very mobile electrons takes place at the low temperature, the subsequent completion of the second stage is retarded because ionic movement is "frozen" and can only occur on warming. This increases the chances of recombination with a positive hole. In addition, work by *Hamm*, *Hamilton* and others on the exposure of large silver-halide grains in the presence of an electric field has shown that the silver is formed nearest to the positive pole of the applied field. This means that the electrons, which have been attracted to the posi-



Figs. 9.1—9.4 Gurney–Mott mechanism for latent-image formation

tive pole, have moved first and the discharge by the silver ions has taken place subsequently. This is shown in Figure 9.5.

One essential feature of latent-image formation, which has been called the *concentration principle*, is that the products of the photolysis must be concentrated at a single point if they are to initiate development efficiently. If they are distributed randomly over the crystal surface, no real latent image would be present; any situation producing such a dispersion of photolysis products will increase the total number of silver atoms required to initiate development. In the Gurney–Mott theory this is achieved by the action of the sensitivity speck of silver sulphide in trapping the electrons at one site. It will be noted how much emphasis *Gurney* and *Mott* place on the crystal surface and when the great increase of sensitivity coming from the chemical sensitization, or digestion treatment is considered, this seems a reasonable approach. Chemical reactions taking place during digestion can occur only on the surface because no change takes place in the habit of the crystals.

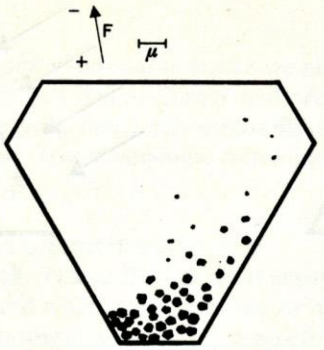


Fig. 9.5 Effect of field on latent-image location

Gurney and *Mott*'s view that the sensitivity speck and the latent image are both on the surface in the most efficient silver-halide crystals has not been contested.

OBJECTIONS. Many objections have, however, been raised against the Gurney–Mott theory; the following are the most important of these.

1. Measurements on large slab crystals, prepared from the melt, show that there are far fewer interstitial silver ions available than required by the theory. *Mitchell* went as far as suggesting that there would not be one available in each crystal of a fast emulsion.
2. The theory gives insufficient attention to problems of keeping the electron and the positive hole apart. Both these entities have high mobilities, moving much faster than the silver ions, and this would mean that recombination is a most likely reaction and therefore no latent image would be formed.
3. The very important part played by imperfections in the formation of internal image in large slab crystals was not appreciated in 1938 and is completely ignored by the theory.
4. The ability of silver sulphide to trap electrons was queried. It is known that silver sulphide, if formed on the crystal surface, can confer some spectral sensitivity in the red region. This is much less efficient than that conferred by dye sensitization; it is not readily detectable on the normal spectrogram but may be detected by heavy exposures through a red filter. The inference was therefore drawn that silver sulphide, assumed to be the sensitivity speck, is more likely to give up electrons, i.e. to trap positive holes.
5. Insufficient emphasis is placed in the Gurney–Mott theory in its original form on the number of silver atoms involved in the critical stage of the latent-image formation. Unless some other factor plays a part no explanation is offered for why two, three or even one silver atom does not constitute a stable latent image and therefore a development centre.

Answers to Objections. Probably most significantly, objection (1) has been countered by the suggestion that measurement on large, and fairly pure, crystals cannot be extended to small, probably less pure, and more distorted emulsion grains. In fact measurement of the ionic conductivity, which occurs by the movement of interstitial silver ions, in emulsion crystals has shown it to be about 1,000 times as high as for pure crystals. *Brady* and *Hamilton's* work makes it clear that because of the influence of added chemicals known to influence silver-ion mobility on this conductivity and of the silver-ion concentration of the surface, as indicated by the pAg of the environment, this conductivity is produced by surface ions. It appears therefore that there *are sufficient* interstitial silver ions for the latent-image formation to take place by the Gurney–Mott hypothesis. What is more they are located in the grain surface, where they are free to move, and are at the right point for forming surface latent image.

The trapping propensity of silver sulphide has been examined and it has been found by *West* and *Saunders* that it will trap both electrons and positive holes. Even the contention that silver sulphide must donate electrons, rather than trap them, because it acts as a spectral sensitizer, is not entirely defensible; many organic sensitizing dyes both sensitize spectrally *and* act as very good traps for electrons because they at the same time desensitize. (See Chapter 6).

Also, although crystal imperfections are not considered in the theory, their important function is likely to be in providing a more reactive site at which silver sulphide can be formed, than would be the case on the plane surface of a perfect crystal. The kinetics of such differences have, however, not been determined.

Therefore, it appears that objections (1), (3) and (4) are not strong arguments against the Gurney–Mott theory. In an effort to overcome all these objections, *Mitchell* has advanced two theories, one of which has been abandoned and will not be discussed.

Mitchell Theory

Basis *Mitchell's* latest theory proposes the following: –

1. The presence of a negligible number of interstitial silver ions in an emulsion crystal before exposure.
2. The existence in the crystal of two types of imperfection:
   (a) a silver ion at a kink site; this is a point, usually on the crystal surface, but it may occur internally, where there is an incomplete layer of ions as shown in Figure 9.6;
   (b) the presence of either a bromide ion at a kink site, analogous to that of the silver ion shown above, or better the existence on the surface of the crystal of an S^{--} ion, this representing the sensitivity centre or what is often called silver sulphide.

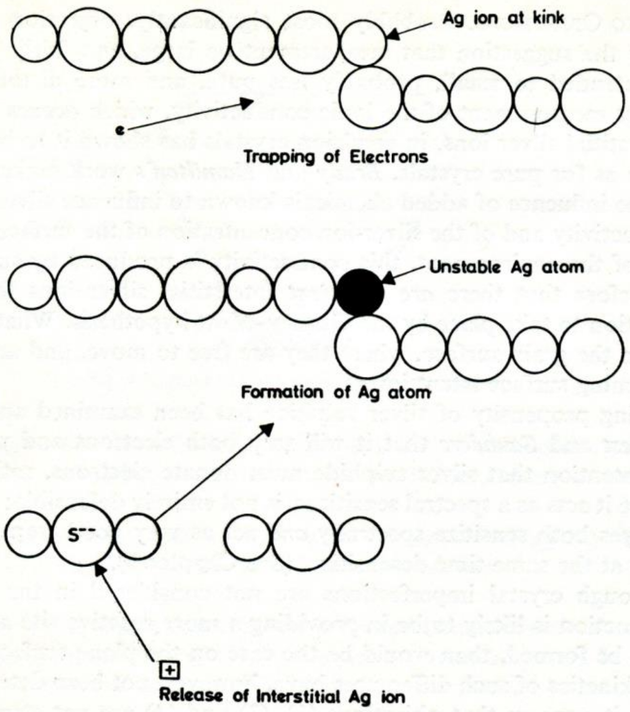


Fig. 9.6 First steps of latent-image formation on Mitchell theory

MECHANISM. On exposure an electron and a positive hole are produced by the first photon to be absorbed in the virgin crystal. The steps of the Mitchell mechanism are: –

1. The photoelectron migrates to a silver ion at a kink site on the surface where it is trapped to give a silver atom (Figure 9.6.). The trapping occurs at these particular silver ions because the positive charge of a kink site silver ion is only partly balanced by the surrounding medium, unlike that of silver ions in the middle of the crystal lattice, although in an imperfect crystal a kink site may be present inside the crystal.

   This silver atom is not very stable. Unless the next stages then occur it will break down into a silver ion and an electron again and the electron may migrate again and locate itself, equally temporarily, at another silver-ion site.

2. The migration of a positive hole, not as fast as an electron, goes to a certain point where there is *either*
   (a) a bromide ion at a kink site, *or*
   (b) a silver-sulphide sensitivity speck.

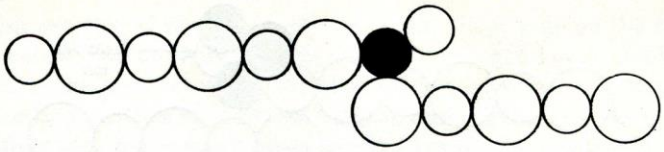


Fig. 9.7 Second step: latent pre-image

The interaction of the positive hole at either of these points, the second type appearing to be more effective because of the well-known effect of chemical sensitization, traps the hole converting the kink bromide ion to a bromine atom or the S^{--} to S^{-} *and releases an interstitial silver ion.*

3. The migration of the interstitial silver ion is fairly slow compared to that of the electron and the positive hole but if the silver ion is released near to the site at which a transient silver atom is located, they will combine and give a pre-latent-image speck, and this situation is shown in Figure 9.7.

   This concept explains the separation of the electron and the positive hole and it also accounts for the location of the all-important silver-atom near the silver sulphide, not because the electron is attracted there as *Gurney* and *Mott* proposed, but because an interstitial silver ion is formed there as a result of the trapping of a positive hole.
4. The unstable pre-latent-image speck now acts as a convenient location point for another photoelectron and interstitial silver ion, formed by a repetition of stages 1, 2, and 3 to give a pair of silver atoms, called the latent sub-image speck, shown in Figure 9.8. However, like the pre-image, the sub image is relatively unstable in that it has no resistance to attack by positive holes.
5. A third electron and positive-hole trapping sequence at the same point produces the arrangement shown in Figure 9.9 in which the trio of silver

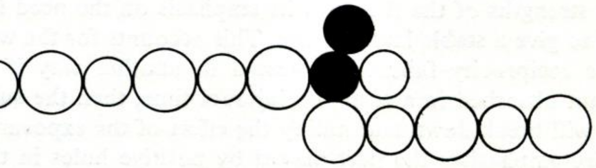


Fig. 9.8 Third step: latent sub-image

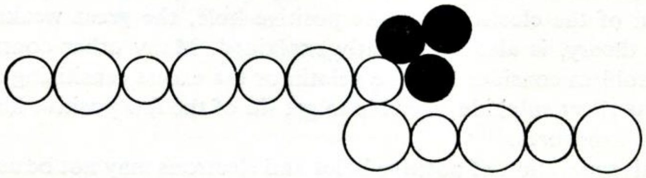


Fig. 9.9 Fourth step: uncharged latent-image speck

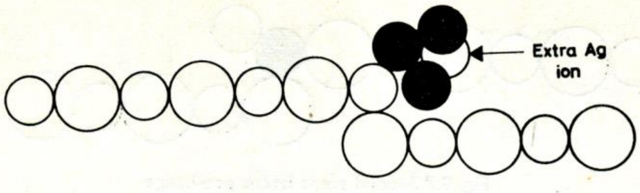


Fig. 9.10 Final state of latent image according to Mitchell theory

atoms is called an uncharged latent-image speck. It is now large enough to act as a development centre.

6. The final stage is the attraction to the trio of silver atoms of an interstitial silver ion to give a positively-charged latent image, Ag^{+}_{4} (Figure 9.10), which is a stable entity and, as *Mitchell* stresses, the latent image will now actually repel positive holes. Also this positively-charged entity will catalyse development, which an uncharged speck might not.

Objection to Mitchell Theory

It must be stressed that, intriguing as this Mitchell theory is, it is based on a number of unproved assumptions. One of these is that once a trio of silver atoms is formed, it will then attract a silver ion to form "a stable tetrahedron". This may be the case but no evidence is available to support it.

One of the most criticized points of the Mitchell theory is that is requires a triple collision, that is the coming together of an interstitial silver ion, formed by the photolysis, with a photoelectron at a particular silver-ion site. Such reactions with three reacting entities meeting at the same time are very rare in chemistry and it is necessary for this to occur three times to produce the latent image.

One of the strengths of the theory is its emphasis on the need for a number of discrete steps to give a stable latent image. This accounts for the well known long-time exposure reciprocity failure. Expressed in another way if the total three photons are not absorbed in a certain minimum time, then the sub-image or pre-image specks will break down and nullify the effect of the exposure. Although the Mitchell theory emphasises the part played by positive holes in this reversion, it must be underlined that *any* process which entails a number of steps before stability must possess the same ability to explain long-time exposure reciprocity failure. The separation of the electron and the positive hole, the great weakness of the Gurney–Mott theory, is also very neatly explained. Many other contributors to this difficult problem consider that the gelatin or the excess sensitizing substances, including excess silver sulphide, are able to get rid of the few positive holes formed in latent-image exposures.

However, this separation of positive holes and electrons may not be as important as *Mitchell* thinks. The electron moves faster than the positive hole. *Hamilton* and

Brady point out that if there are very many free silver ions on the surface, as the measurements of conductivity suggest, then there is a good chance that one of these will collect at the point at which the electron has been trapped, perhaps by silver sulphide, or by a positive kink site (silver ion), and thus form a silver atom. The fact that the silver ions move much more slowly than do the positive holes is offset by the larger number of the former. The difficulty of preventing recombination is further believed not to be a weakness of the Gurney–Mott hypothesis but in fact a strength of it; this point will be dealt with when considering crystals needing more than three photons later on.

Location of Latent Image

There remain some aspects of latent-image formation which have chemical importance quite unrelated to the detailed formation mechanism.

The first of these is the exact location of the latent-image silver speck. In an undigested emulsion crystal there will be sites, such as bromide ions, which could trap positive holes or silver ions able to trap electrons, at kink sites within the crystal which will form latent image in the interior of the crystal, that is *internal latent image*. As digestion proceeds, and preferential trapping sites are formed on the surface of the grains, the latent image is likely to be formed there to give *surface latent image*. It is possible to detect these two types of image chemically and their existence has been well established for many years. Surface latent image only can be detected by developing the emulsion in a strictly non-solvent developer, that is a developer containing no bromide or sulphite. The internal latent image may be detected by first giving the emulsion a brief bleach treatment with potassium-

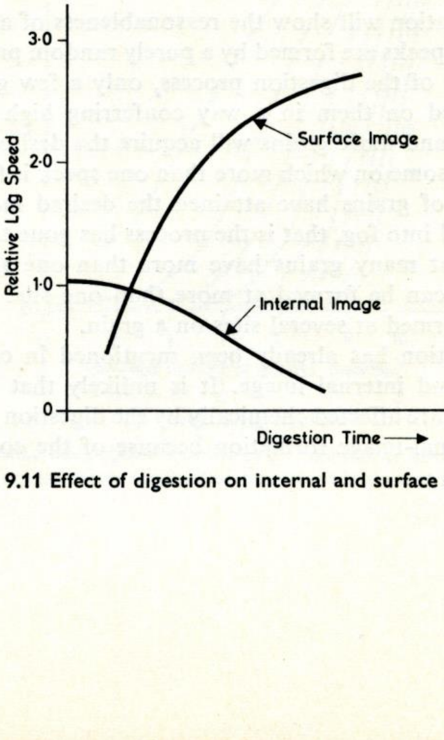


Fig. 9.11 Effect of digestion on internal and surface sensitivities

ferricyanide solution for example and then using a developer containing an amount of thiosulphate designed to etch the grains and expose the latent image in the interior enabling it to catalyse reduction. Alternatively the total amount of latent image, both internal and surface image, may be determined by giving a solvent development without the prebleach. The results depend on the experimental conditions but some generalisations are possible, e.g. the effects of digestion are shown in Figure 9.11 which illustrates that the sensitivity of the emulsion for surface-image formation is increased whilst that for internal-image formation is decreased. This result is consistent with the view that the crystal contains some internal trapping and, therefore, image-forming centres, and as the sensitivity specks form on the surface then latent-image formation becomes more and more likely there instead, until the final optimal condition is reached.

In commercial practice, sensitization is carried out so that surface latent image is at a maximum because it is here that development is most rapid and there is no dependence upon solvent action to uncover the centre.

Grains Needing More Than Four Quanta

So far only the most sensitive grains have been considered. However, even in fast emulsions most of the grains require more quanta than the minimum four. The main reason for this appears to be *competition.* It could be assumed that

1. for some reason more than four silver atoms at one point are needed on many of the grains to render than developable;
2. for some reason the formation of more than four silver atoms *per grain* is necessary to form a development centre of the critical size, that is presumably four atoms.

A moment's consideration will show the reasonableness of adopting the second answer. The sensitivity specks are formed by a purely random process on the grains. During the early stages of the digestion process, only a few grains will have the chemical entities formed on them in a way conferring high sensitivity. As the process proceeds more and more grains will acquire the desired specks but at the same time there will be some on which more than one speck is formed. By the time the maximum number of grains have attained the desired maximum sensitivity, some grains have passed into fog, that is the process has gone too far, and it seems almost unavoidable that many grains have more than one speck, and that, on exposure, silver atoms can be formed at more than one site. Thus, stable latent image centres will be formed at several sites on a grain.

One case of competition has already been mentioned in connection with the formation of surface and internal image. It is unlikely that the internal latent-image-forming agencies are affected chemically by the digestion reaction; the grains become slower to internal-image formation because of the competition provided by the surface centres.

The higher speed produced by using smaller quantities of sulphur sensitizer (see Chapter 5) may also be accounted for by the decreased competition. It seems unlikely, however, that competition between centres is the whole answer to the very broad spread of sensitivities occurring in emulsion grains. Recently, *Hamilton* and *Brady* have drawn attention to this fact and pointed out its significance in considering latent-image theory. In his theory, *Mitchell* pointed out that it is important that the electron and the positive hole must not trap one another, otherwise the effect of exposure is lost, but this may be just what does happen in the majority of cases. In those grains where, for reasons of purely random movement, recombination does not occur, 4 quanta produce 4 silver atoms and the grain becomes developable. In the other grains, which may be identical in structure, an amount of recombination does occur, again purely according to the laws of chance, and then more photons will be needed. In extreme cases a large proportion of the photons recombine, and then perhaps 30 quanta are needed to produce 4 silver atoms.

These considerations have important practical implications; they mean that it is probably not possible ever to make all the grains in an emulsion respond to just four quanta.

There are two types of variation which can occur between individual emulsion grains. The first is the stopping power of the crystals; how many quanta each will absorb, and this depends on grain volume. The second difference is in the number of quanta needed to render a grain developable. These two effects are to a large extent additive and account for the differing grain sensitivities, which, in turn, account for the shape of the well-known characteristic curve. The number of quanta per crystal required to render a grain developable, controls the contrast. This is shown in the Figure 9.12, which was calculated mathematically from the random

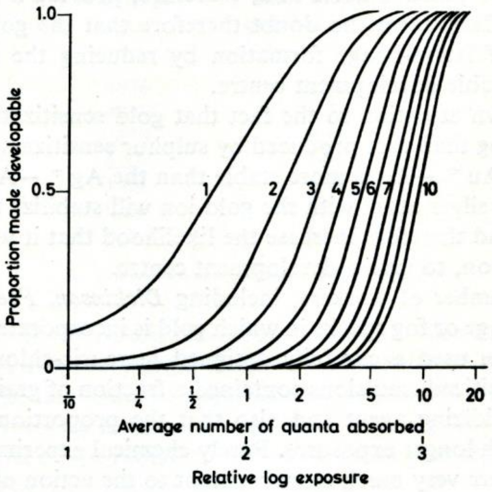


Fig. 9.12 Proportion of grains developable in relation to number of quanta absorbed. Numbers on curves are those required to make a grain developable

absorption of the light by the crystals and is not derived from an experiment. Experimental results, however, show that the faster crystals do give lower contrast.

A special case of competition is high-intensity reciprocity-failure. The loss in speed at very short exposure is believed to be due to the formation of a multiplicity of silver-specks instead of one of sufficient size to initiate development. At high intensities many photo-electrons will be formed in a very short interval. If one of these moves to an appropriate trapping-site but the slower-moving silver-ion cannot neutralize the electron, to give a silver-atom, before a second electron arrives, that second electron will be repelled to another location. The additive effect will therefore be partly lost, with a consequent loss in effective speed. There is good evidence that more latent-image sites are formed by high-intensity exposures. The alternative explanation, that electrons and positive holes are more likely to neutralize one another if formed in very rapid succession is a less widely accepted explanation.

Effect of Gold

The last point to be resolved is that of the function of gold in latent-image formation. Examination of the curves in Figure 5.6 shows that gold increases the speed by reducing the contrast. This is precisely what one would expect, see Figure 9.12, if fewer quanta were needed to produce the latent image. Some authors have suggested that gold appears to be most effective with the faster grains, thus increasing speed and reducing contrast, but there seems no need at all to invoke this additional hypothesis. There is no question of these minute quantities of gold increasing the light absorption and gold or aurous sulphide would not be expected to be good traps for positive holes and, therefore, provide a superior variety of sensitivity centre. There seems no doubt therefore that the gold functions in the secondary stages of latent-image formation by reducing the number of quanta needed to form a stable development centre.

Mitchell has drawn attention to the fact that gold sensitization is always more prone to run into fog than that produced by sulphur sensitizers alone. He suggests this is because the $Au^+ - Ag$ is more stable than the $Ag^+ - Ag$. This means that the association of a silver atom with the gold ion will stabilize the first sub-image, or sub-fog, speck and therefore increase the likelihood that it will collect a further silver atom, and so on, to give a development centre.

In addition, a number of workers, including *Dickinson*, *Faelens* and *Spracklen* have shown that image or fog specks in which gold is incorporated are more difficult to bleach. *Spracklen* used a carefully designed mercuric-chloride treatment and found that gold-sensitized emulsions contained a fraction of grains which were very resistant to that oxidizing agent and also that the proportion of these resistant grains increased with longer exposures. Purely chemical experiments indicated that gold-silver alloys were very much more resistant to the action of mercuric chloride as the gold proportion increased.

All this evidence points to the incorporation of the gold in the latent image, increasing its stability, which could be important in preventing spontaneous decomposition of sub-image specks before additional silver arrives or degradation by positive-hole attack. Whether it is gold metal or aurous sulphide, formed by the parallel decomposition of the gold complex during digestion, is not settled; the two materials are not easily distinguished in the atomic adsorbed state. Some authors favour gold metal since it is claimed that reducing agents *must* be present for gold sensitization.

Effect of X-rays and Gamma Rays

It has been stressed in the above discussion that one absorbed photon produces only one positive hole and one electron and, therefore, can only give one silver atom. This is only true for exposures to light in the visible region. Radiation of much higher energy behaves quite differently because, in addition to giving the primary products of the photolysis, the original absorption gives a whole series of secondary changes, releasing a flood of electrons and positive holes, which give a large number of silver stoms; this is shown in Table 9.2. In extreme cases, more than one silver-halide grain may be affected, something which never occurs with visible light.

TABLE 9.2

NUMBER OF SILVER ATOMS PER QUANTUM FOR VISIBLE LIGHT AND X-RAYS

Wavelength Å	*Silver atoms per quantum absorbed*
4936	0.96
4047	0.92
3658	0.93
1.54	148
1.09	210
0.63	363
0.24	920

This is also true of the action of charged particles, such as sub-atomic species. In these cases therefore every grain struck by the radiation or a particle becomes developable and the latent-image requirements normal for visible light exposures do not apply. Reciprocity failure does not exist with exposures to X-rays. It must be stressed that most of the radiation will still tend to pass through a layer without being absorbed. For this reason films designed for direct X-ray recording are coated at very high coating weights to increase the likelihood of absorption. Emulsions designed for the tracking of nuclear particles have very little gelatin relative to silver, sometimes as little as 20 g per g mole, so that there is very little free space; they are almost solid silver bromide.

Summary of Theories

Most authors today still regard the question as unsolved and further work must be awaited. To sum up:

1. Latent-image formation consists of electronic and ionic steps.
2. The image is formed at or near the site where the electrons are trapped.
3. Until a certain speck size, possibly three silver atoms, is reached, no stable entity is produced.
4. Recombination is a vital factor in producing the desired photographic response.
5. Overall, the present day form of the Gurney–Mott theory is probably the best explanation of the facts.

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X COLOUR PROCESSES

Introduction

Photography started with the formation of black-and-white images and for many years these were the only ones known to the photographer. The production of colour pictures was a dream of the earlier inventors right from the dawn of photography and it is now more than 100 years ago since *Clerk Maxwell* demonstrated photographs in colour at the Royal Institution. His method relied upon the exposure of three black-and-white films through three filters, followed by projection of the correct combination of the processed balanced transparencies through three lanterns, each lantern corrected with a filter to give each of the three primary colours. This type of colour process is still used today for the preparation of many colour pictures via printing blocks. As the chemistry of this process is no different from that of black-and-white processes, it falls outside the scope of this book. The only commercial example of a single exposure colour material based upon an exposure behind three filters, was that of the *Dufay*-type product. The chemical side of this, however, was that of a reversal black-and-white material and, as all products of this type have disappeared from the market, it is not proposed to discuss them. The discussion will be restricted to colour processes where the coloured images are formed as a result of chemical processes, distinctly different from those of black-and-white photography, and where the initial exposure to the subject is a single one.

The physics of the modern three-layer one-exposure colour process was worked out by the year 1873 by *De Hauron* but it was not until the 1930's that it became possible to achieve one of his systems on a commercial basis. In order to obtain a coloured image the layer must contain coloured chemicals in place of the normal black silver image. In every commercial colour material these coloured substances, or dyes, are organic in nature. There is no fundamental reason why inorganic colours should not be used although it is difficult to choose those of satisfactory hue and to produce them by suitable reactions and, therefore, this has never been achieved.

Principles of Colour Photography

There are basically three mechanisms whereby coloured images may be produced by photographic means:

1. The formation of dyes. The vast majority of modern colour processes rely upon this mode of operation. These include *Kodachrome*, *Agfacolor*, *Gevacolor*, *Ektachrome*, etc.

2. The destruction of dyes. This method is best represented by the *Gaspar* colour-bleach process which was commercialized by *Ilford* and which is still the subject of some activity by other companies, e.g. *Cilchrome* of *CIBA*.
3. The migration of dyes. The outstanding example of this type of process is *Polacolor*. The migration may be away from the layer which carries the final image, or towards the layer, thus corresponding with either the formation or the destruction of dyes as in 1 and 2 above.

Processes Based on Dye Formation

The first class will be dealt with in the greatest detail because these represent the materials most widely used, the chemistry of these processes possesses the greatest interest and the general principles of the other types of process can be illustrated with reference to this first class. First, the necessary conditions for obtaining such a colour material will be considered:

1. Each of the emulsion layers must be sensitive to one of the three primary colours, blue, green and red.
2. The processing of the material must result in dyes of the correct hue being formed in the appropriate layer and without appreciable sideways wandering in that layer.
3. The processing must be performed at a moderate temperature and under mild conditions, since the light-sensitive system will be silver-halide-gelatin emulsion.
4. The reactions producing the dyes must form these substances in quantities proportional to the developed silver.
5. The dye-forming reactions must be substantially free from coloured by-products or by-products which would generate colour on storage.
6. The dyes formed must be sufficiently light stable to enable the result to be relatively permanent.

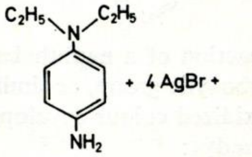
For many years it was not possible to achieve (1) and it was not until the work on sensitizing dyes expanded rapidly in the early 1930's that it was possible to achieve sensitivities in the required positions. Points 3, 4, 5 and 6 exercised the ingenuity of chemists for many years and it was in 1912 that *Fischer* produced the brilliant series of reactions on which every one of the colour processes relying upon the formation of dyes is based today, and which will now be discussed.

The Coupling Reaction

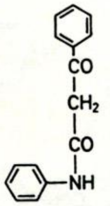
The essential concept which *Fischer* introduced was the use of a developer based upon diethyl-p-phenylenediamine (1) which produces silver by reducing the silver halide while the oxidized developer, which in a black-and-white developer is a waste product which reacts with sulphite and is thus removed from the system, is able to react to form a dye. Diethyl-p-phenylenediamine behaves with regard to the silver-halide in a very similar manner to an ordinary black-and-white developer; it is used for that purpose, acting as a fairly low-energy developer giving fine-grain results.

The oxidized diethyl-p-phenylenediamine may be brought into reaction with three classes of substance, which are called ***colour couplers*** or colour formers.

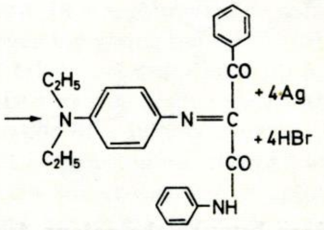
The first class of couplers is a chain compound containing the group $-COCH_2CONH-$ and usually carrying benzene rings at each end of the molecule, e.g. compound (2). These compounds react with the oxidized colour developer to give a yellow dye (3), for example:



(1)

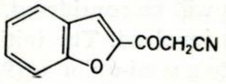


(2)

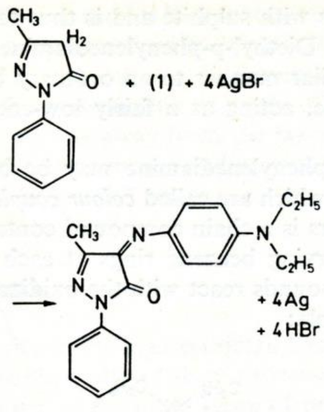


(3)

The second class of compounds contains the group $-COCH_2CN-$ which may either be as a chain, example (4), or as part of a ring, this being the more commonly-used type of compound, such as the pyrazolone (5). A magenta dye (b) is formed from either of these substances by the following type of reaction:

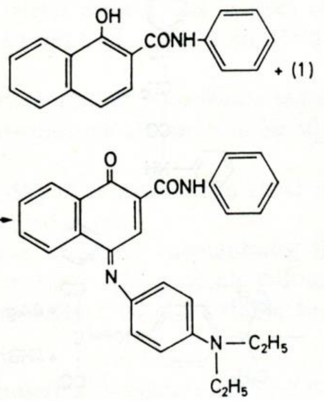


(4)


(5)

(6)

The third class is the reaction of a naphthalene derivative carrying a hydroxyl group and commonly a carboxylic group, or similar residue, such as compound (7). This will also react with oxidized colour developer and give a greeny-blue dye (8), always referred to as a cyan dye:

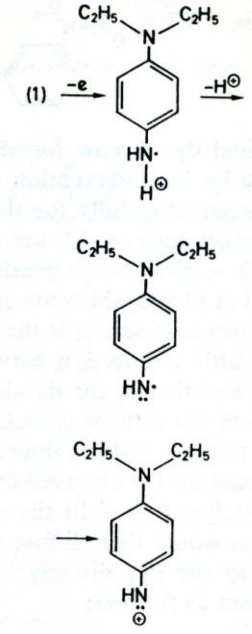

(7)

(8)

These three basic reactions between the colour developer molecule and three selected colour formers of these general types provide the means of forming the coloured images in the vast majority of present-day colour films.

Mechanism of Coupling Reaction

Before proceeding to analyse the methods and their applications in more detail, the mechanism of the reactions will be considered. Recent work has led to a clear understanding of the processes involved. The initial stage is a conversion of the colour developer substance (1) to a semi-quinone (9), by the action of one silver ion from a light-struck, or otherwise fogged, silver-halide crystal.

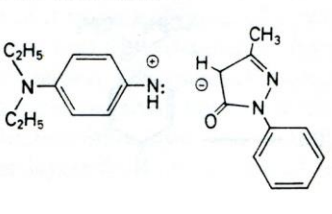


(9)

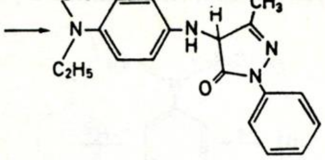
(10)

(11)

After losing an electron the initial neutral colour developer acquires a positive charge, and the semi-quinone (9) formed is also a free radical, that is, the molecule contains an unpaired electron. In a highly alkaline solution this semi-quinone ion now loses a proton or hydrogen ion giving the entity (10), which is still a free radical because the proton has not taken any electrons with it, but is no longer charged. The semi-quinone radical (10) now very easily reacts with a further silver ion to give silver metal, by the transference of a further electron, being itself converted into the quinone di-imine (11). It is this quinone di-imine which is the reactive species giving rise to the dye. All the colour-forming or colour-coupling substances are moderately strong acids and are converted into negatively-charged ions in an alkaline solution, all of them being strong enough to dissolve in aqueous sodium carbonate, for example. There is then a rapid reaction between the positively-charged quinone di-imine (11) and the negatively-charged anion of the colour former, e.g. (12), to give the reaction:



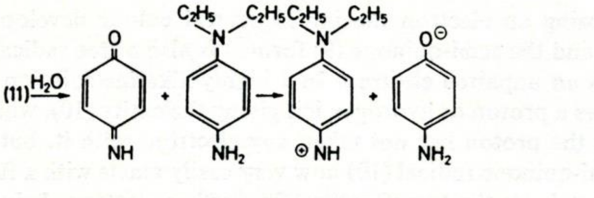
(12)



(13)

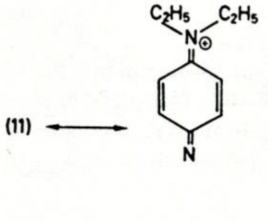
The carbon structure of the final dye is now formed and substance (13) is very rapidly converted into the dye by the intervention of two more silver ions thus completing the process, and accounting fully for the equation. This last stage is such an easy one that if substances such as (13) are prepared they are so unstable that they easily oxidize in the air to give the dye bearing two fewer hydrogen atoms.

The dye is frequently formed at places which are remote from the site where the silver-halide crystal is being reduced. Indeed it is the general rule of many of these colour processes that there is little connection between the grain pattern of the original silver-halide emulsion and that of the developed dye image. The quinone di-imine was at one time believed not to be very stable and it was suggested that it could not exist for a sufficient time to enable coloured image to be formed remote from the grain. In order to account for the observed facts, therefore, it was proposed that the quinone di-imine hydrolyzed to yield the mono-imine (14) and diethylamine, Et$_2$NH. The mono-imine would then diffuse through the layer. Clearly the mono-imine cannot give rise to the dye directly but on neeting an unoxidized developer molecule it could react as follows:



(14)

thus forming oxidized developer by an indirect process at another point. It seems unnecessary, however, to invoke this kind of process in all cases because there seems good reason for supposing that the quinone di-imine would be stabilized by resonance. The structure of the substance may be represented by either formula (11) or (15), and, as discussed in Chapter 7, a system of this type will be more stable than any of its individual contributors, and, therefore, the quinone di-imine probably possesses the required order of stability.



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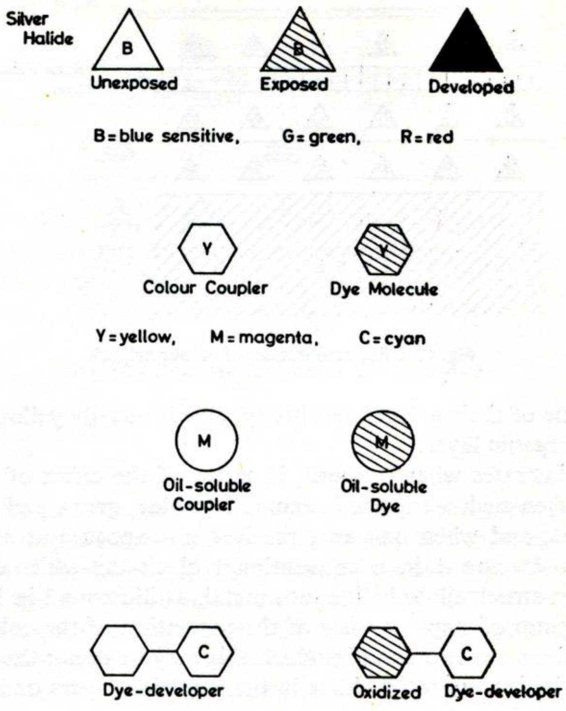


Fig. 10.1 Convention for illustrating colour processes

Types of Commercial Colour Process

In order to simplify the presentation, a convention is used for representing the emulsion components and the colour of dyes formed in the various processes, which is shown in Figure 10.1. There are basically two ways of using these dye-forming reactions in commercial products.

Reversal Processes

The first one is the *Reversal Method* and produces a direct positive. The sensitive layer consists basically of a tripack, Figure 10.2, with a blue-sensitive layer, on top of the green-sensitive layer and the red-sensitive layer on a support, which is usually film although it may be paper. The spectral characteristics of the sensitizing dyes in the red-sensitive and green-sensitive layers will be chosen to confer correct colour rendering, while the blue-sensitive layer will be undyed emulsion. The yellow filter layer protects the lower layers from the action of blue light to which they are also

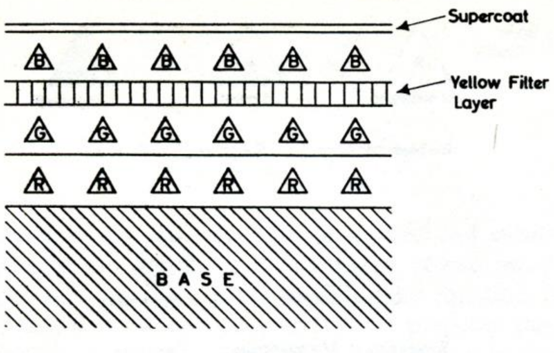


Fig. 10.2 Representation of colour tripack

sensitive by virtue of their natural sensitivity; this is usually yellow colloidal silver but may be an organic layer.

Figure 10.3 illustrates what happens, in terms of the effect of the light on the whole system, when such a tripack is exposed to blue, green, red and white light, in different areas, and when one area receives no exposure at all. This exposed material is now developed in a conventional black-and-white developer which converts the light-struck silver halide into metal, as illustrated in Figure 10.4.

The second group of steps consists of the formation of the coloured images in each layer and there are two ways in which this may be done: the colour-coupling substances may be incorporated either in the emulsion layers or in the processing solutions.

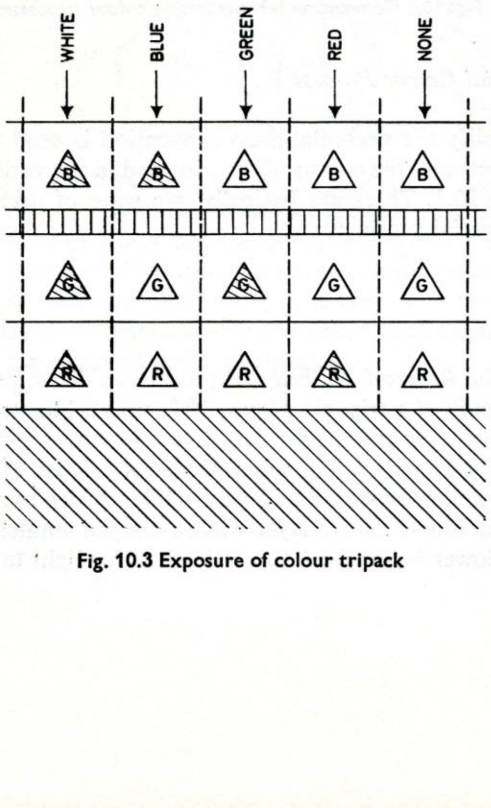


Fig. 10.3 Exposure of colour tripack

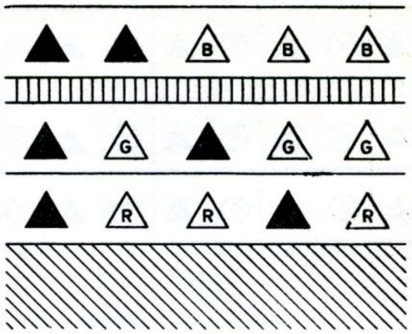
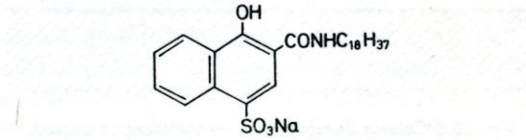


Fig. 10.4 First development — colour tripack

Substantive Process

In the substantive process, the colour couplers are incorporated in each appropriate layer. The original *Agfacolor* method was of this type and the substantive process is still used by that company, *Ferrania, Gevaert* and others. This method places a very severe restriction upon the type of colour coupler used. It will be obvious that the appropriate dye must be formed in the correct layer but if colour couplers of the simple structures shown in formulae (2) (5) and (7) were used, they would readily diffuse from one layer to another or would migrate out of the film altogether in the early stages of the developing process. In order therefore to make correct colour development possible, the colour couplers must be modified chemically in order to locate them in the appropriate layers. This is achieved by incorporating in the coupler molecule a long carbon chain and a strongly acid group, usually a sulphonic acid. Three examples, one from each class of these couplers, are shown in Formulae (16), (17), and (18), yellow, magenta and cyan respectively.



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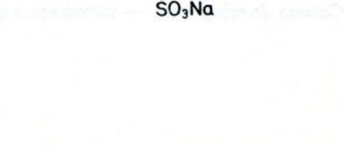

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(18)

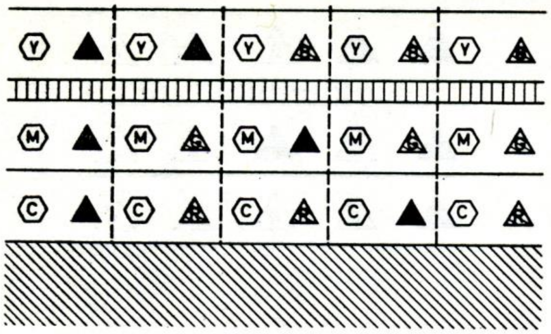


Fig. 10.5 First development and re-exposure — substantive tripack

After the black-and-white development, the film is exposed in order to fog all the remaining silver-halide grains, and the situation at this stage is illustrated in Figure 10.5. This fogging exposure must not be too heavy otherwise some reversal occurs due to solarization. The fogged film is then placed in a colour developer when the remainder of the silver halide is developed with the concurrent formation of a yellow image from the appropriate colour former in the blue-sensitive layer, a magenta image in the green-sensitive layer, and a cyan image in the red-sensitive layer. The result of this stage is represented by Figure 10.6. Finally, it is necessary to bleach all the silver image, with a ferricyanide/hypobleach, leaving the dye images only, as shown in Figure 10.7.

The areas in the image will appear coloured because not all the white light will be transmitted by the layer. In the second area of exposure, the magenta dye will filter out green light, the cyan dye the red light and therefore only the blue light will be transmitted through the layer; the next area will appear green because the blue light and the red light will be removed by the yellow and the cyan dyes respectively, and similarly the next area will appear red. In the area of the film where all three layers were equally affected, that is exposed to white light, there will be no

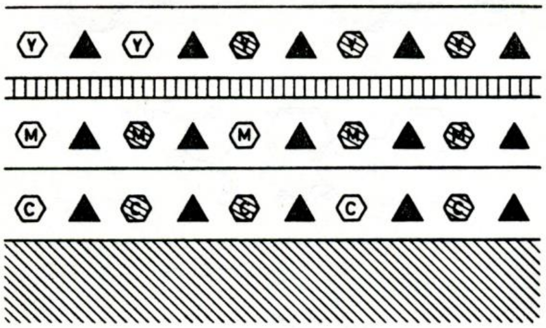


Fig. 10.6 Colour development — substantive tripack

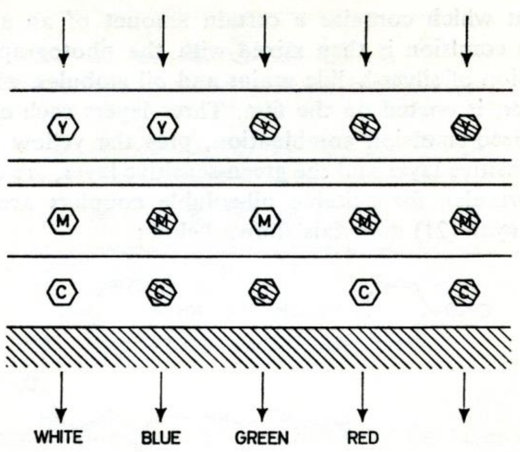
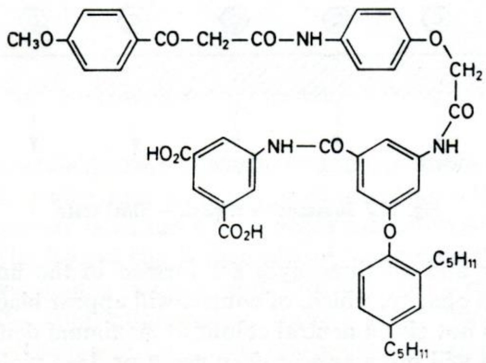


Fig. 10.7 Substantive tripack — final state

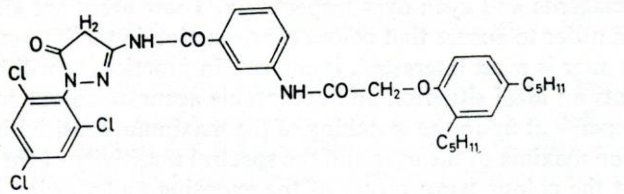
dye image whatever and all three dyes are formed in the unexposed area, thus producing maximum opacity, which, of course, will appear black. In practice many commercial films do not give a neutral colour at maximum density; the completely fogged end of a film will often appear deep green or deep violet corresponding to insufficient magenta and cyan dyes respectively. These areas are allowed to go out of balance in order to ensure that colour reproduction in the intermediate densities, in which the user is most interested, is correct. In practice, as will be seen later on, this represents an ideal situation and acceptable accurate colour rendering by this process is dependent upon the matching of the maximum sensitivities of each layer, the absorption maxima of the dyes and the spectral sensitivity of the eye, also taking into account the colour temperature of the exposing and viewing illumination. In addition the sensitometric curves of each of the emulsion layers must be very accurately matched, otherwise in certain areas the density of colours will go out of balance. The final impression on the eye is of the light which remains after some of it has been absorbed and for this reason this process is called a subtractive process.

Oil-soluble Coupler Process

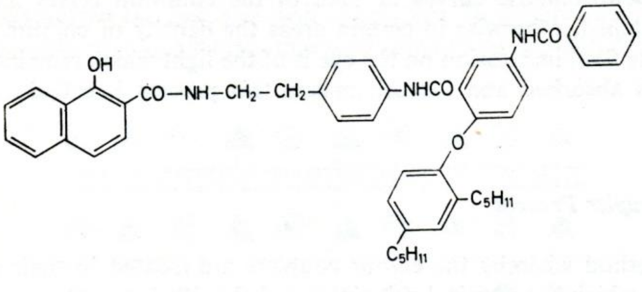
Another method whereby the colour couplers are located in their appropriate layers, and in which the physical principles and the development processes will be basically the same as those of the substantive process, is the oil-dispersion colour-coupler system invented by *Eastman Kodak*, and used, e.g. for *Ektachrome*. Each colour coupler is ballasted with a large water-repellent oil-soluble group. The colour couplers are individually dissolved in a solvent, such as tricresyl phosphate, which is then emulsified in a gelatin solution giving a dispersion of small globules of the oily solvent which contains a certain amount of an appropriate colour coupler. This true emulsion is then mixed with the photographic emulsion and the overall dispersion of silver-halide grains and oil globules, which are similar in size to one another, is coated on the film. Three layers each carrying a suitable coupler/dye-sensitized-emulsion combination, plus the yellow filter between the uppermost blue-sensitive layer and the green-sensitive layer, are coated in a tripack (Figure 10.8). Formulae for suitable oil-soluble couplers are the yellow (19), magenta (20) and cyan (21) materials shown below:



(19)



(20)



(21)

The processing stages will be similar to those described above for the substantive system and the dye formation will take place by the diffusion into the oily layer of the oxidised developer molecule to give the dye image within the globule. Although immiscible with water and suitable as a good solvent for the oil-soluble coupler, the oily solvent is nevertheless polar enough in nature to permit the ready accept-

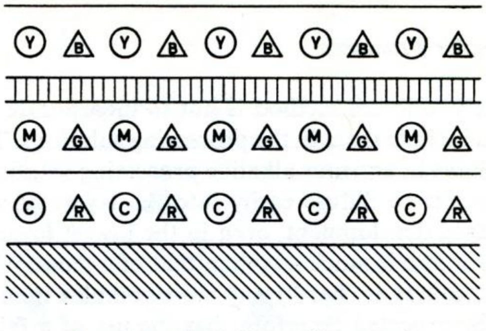


Fig. 10.8 Oil-soluble coupler tripack

ance of the quinone di-imine ion. The final state of the layer after exposure and processing is shown in Figure 10.9.

It the case of the substantive couplers the dye is supposed to be fully dispersed through the emulsion layer but in practice there is a pronounced tendency to clump, and the overall quality produced by the formation of the dye in the small oil globules of the second type of process is generally more acceptable. There are two other considerations which make this *Kodak* method a very satisfactory one. Firstly the purity of the colour produced by the dye, that is the width of the absorption and the density of the maximum light absorption, is very dependent upon the molecular state of the dye. In solution the dye will give a high density and a fairly narrow band but in the solid state the dye will tend to give less pure colour from a broader band. The oil-soluble coupler method gives a dye which is in solution and therefore produces maximum colour purity. The other important advantage is that oil-soluble couplers are free from a very serious shortcoming of the substantive process, namely the severe interaction which frequently occurs between the gelatin and the colour coupler which can cause an undesirable increase in viscosity of the emulsion layer and even cause precipitation of the gelatin.

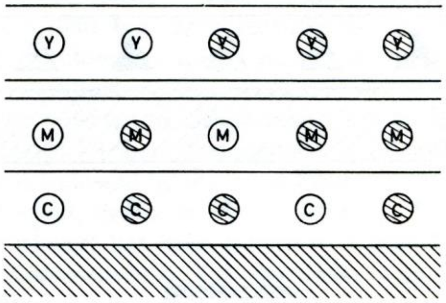


Fig. 10.9 Oil-soluble coupler — final state

Developer-soluble Coupler Processes

The other completely different method is not to incorporate the colour couplers in the film at all but to include them in the processing solutions. The simple couplers, (2), (5) and (7) are soluble in aqueous alkaline processing solution and are of sufficiently small molecular size to diffuse easily into the layers of a tripack coating to effect satisfactorily rapid development, even in the lowest layer. The overall thickness of a modern colour film is much less than that of a modern X-ray emulsion and these simpler colour couplers are hardly any more complex than the usual developer molecules. It would be expected therefore that the use of a fairly standard colour developer containing a colour former, in addition to the dialkyl-p-phenylenediamine should easily diffuse to the appropriate layer and result in the formation of a dye image in the desired emulsion layer as the silver bromide is reduced. In actual fact some "wandering" of the oxidized developer does occur but substantially the desired reactions occur at the required points.

The problem of obtaining the right colours in the right places now remains to be discussed. The light-sensitive layers are sensitized, coated, exposed and given a black-and-white development, as in the incorporated-coupler processes. If, however, all the colour couplers were then added to the next processing bath each layer would develop quite randomly with any of the couplers, so it is necessary to give three separate colour development steps. At one time *Kodachrome*, the most famous process of the soluble-coupler type, was developed by a complicated procedure depending upon graded bleaching, but now the following processing technique is used. After the development of the black-and-white negative image, the washed film is given an exposure to *red light through the back of the film* (Figure 10.10).

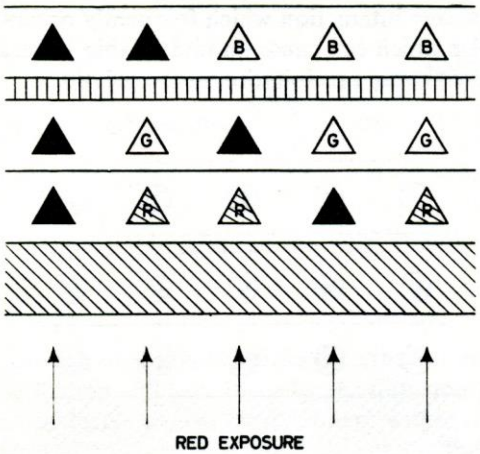


Fig. 10.10 Red re-exposure — Kodachrome type

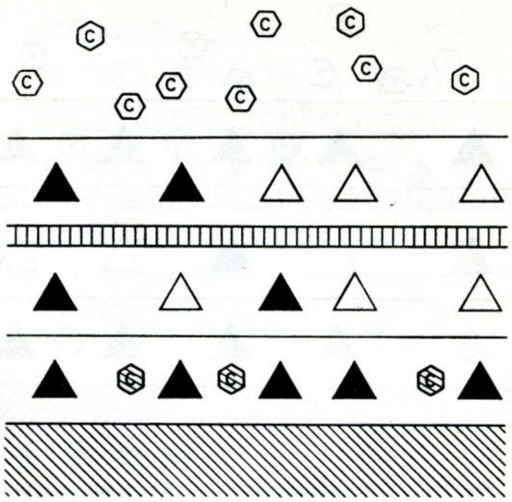


Fig. 10.11 Cyan development — Kodachrome type

This will only fog the red layer because only that layer is sensitive to red light although any migration of the red-sensitizing dye from the red-sensitive layer to the other layers during the first development would cause those layers to be fogged at this stage. This is avoided by the choice of the appropriate red sensitizer and emulsion conditions designed to give it the maximum anchorage. The tripack fogged in the red layer is then treated with a cyan-colour-developing bath to develop the fogged silver halide grains and deposit a cyan image, giving the result shown in Figure 10.11. Next, the face of the film is fogged by blue light which affects only the top emulsion layer because of the yellow filter layer which protects the lower emulsion layer. The fogged film is then developed again, this time in a colour developer containing a yellow colour former as indicated in Figure 10.12. The remaining magenta layer is difficult to fog and develop because of the iodide, released during the development of the other layers, which has deposited on the crystals of this layer. The customary procedure was, therefore, to fog the middle layer with high-intensity light but more recently the use of powerful chemical fogging agents has been disclosed; a *Kodak* patent mentions the use of potassium borohydride, KBH_4, for this purpose. The very small size of the reducing BH_4^- ion suggests that it would be expected to diffuse easily into the layer, and the by-products would not be harmful. The final development is, of course, in the presence of a magenta coupler and is followed by the usual bleach treatment to remove all the silver to yield the final result, shown in Figure 10.13.

This soluble-coupler process has been carried to a high level of perfection, for example in the latest *Kodachrome X*. The sharpness is so good with the thinly-coated high-acutance films of today that 8 mm movies can, at last, give acceptable definition.

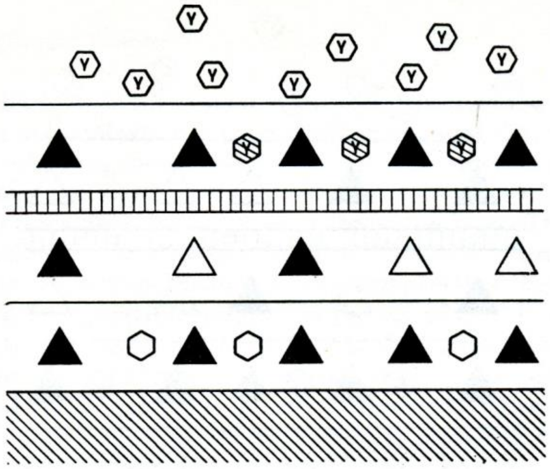


Fig. 10.12 Yellow development — Kodachrome type

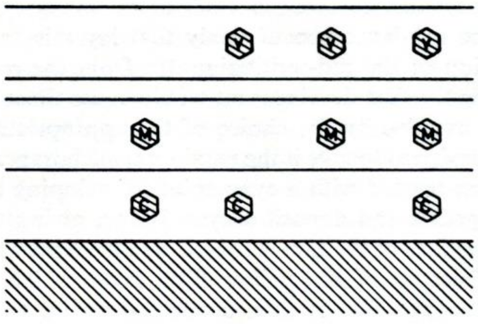


Fig. 10.13 Kodachrome type — final image

The Dye-bleach Process

The second class of process, the *Gasparcolor* method, used for obtaining colour prints, uses the same physics as those methods so far considered but different chemistry. The material consists of a tripack comprising a blue-sensitive layer containing a yellow dye uppermost, an optional filter layer to protect the lower layers from blue light, then the green-sensitive layer containing a magenta dye and the lowest red-sensitive layer containing a cyan dye. All the dyes, therefore, are present in the appropriate layer after coating and before exposure and processing. The dyes used in this process are certain *azo dyes*, which are organic compounds containing as the colour-producing part of the molecule an azo, $-N{=}N-$, link; many commercial dyes used for fabrics are of this type. The tripack is then exposed

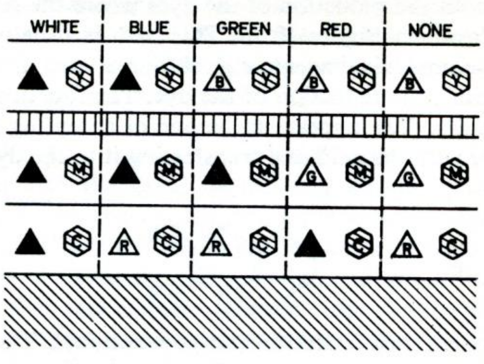


Fig. 10.14 Dye-bleach—first exposure and development

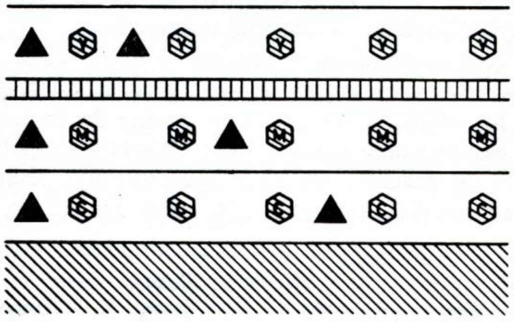


Fig. 10.15 Dye-bleach — after fixation

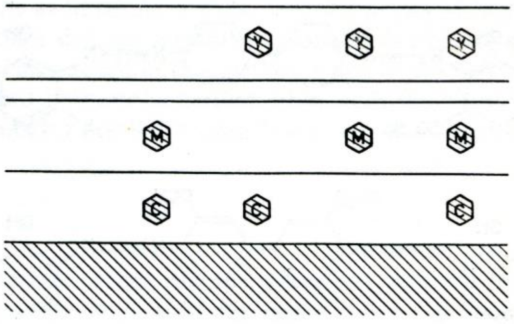
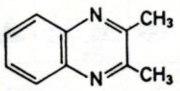


Fig. 10.16 Dye-bleach — final image

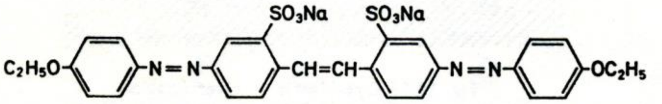
to a coloured object, usually a colour transparency, and is given a black-and-white development step (Figure 10.14). Unreacted silver halide is fixed out to leave a tripack containing silver image and the dyes as shown in Figure 10.15. The layer is then treated with a special bleach bath that dissolves the silver image and at the same time brings about the reduction of the dyes where the silver was present; the final result being shown in Figure 10.16. This bath is usually a strong acid bath containing a silver-complexing agent, e.g. thiourea, and a catalyst designed to effect, at the same time, the reduction of the dye. The function of the catalyst, e.g. 2,3-dimethylquinoxaline (22), appears to be one of accepting hydrogen formed by the reaction of silver with the acid and transferring it to the dye.

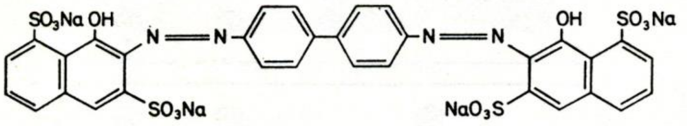

(22)

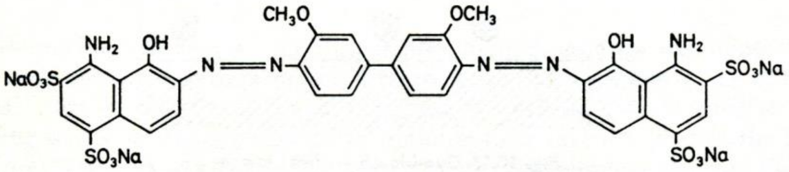
The first development step is simple and conventional. The second stage is the bleaching in which three steps exist, namely:

$$Ag + HCl + NH_2CSNH_2 \longrightarrow [Ag(SC(NH_2)_2)_2]Cl + (H)$$

(H) + 2,3-dimethylquinoxaline → reduced quinoxaline
4 molecules of reduced quinoxaline + azo dye → quinoxaline + reduced dye azo
where (H) is a nascent or very reactive hydrogen atom. Each $-N{=}N-$ group in the dye is reduced to $-NH_2\ H_2N-$, thus separating the molecule into two parts. In some cases the azo dye may contain two $-N{=}N-$ links in which case eight atoms of silver will be required for each dye molecule. Examples of azo dyes useful in this process are (23), (24), and (25), which are yellow, magenta and cyan respectively.


(23)


(24)


(25)

The properties asked of these dyes include:

1. correct hue
2. minimum interference, by desensitization for example, with the silver-halide grains.

3. acceptable ease of reduction by the activated hydrogen atoms.
4. the reduction products must be completely colourless and either removed entirely from the layers of if remaining in the layer must be innocuous, that is they must produce no stain on keeping.

In practice, properties (2) and (4) are very difficult to achieve but there is another difficulty associated with the dyes: by the very nature of the system each layer contains a dye which absorbs light in the same spectral region as that to which the layer is sensitive. In fact the whole coating appears black, because the sum of the light absorptions of all the dyes gives black, and this reduces the overall speed. It must be stressed that this is quite different from the hypothetical all-absorbing layer of maximum speed where *all* the light is used photographically. In the *Gaspar* layer, light absorbed by the azo dyes is wasted from the point of view of forming latent image.

Advantages of the system include fairly easy processing, certainly free from the complications of the soluble coupler-tripack systems. It is not difficult to synthesize dyes of correct hue and, generally speaking, azo dyes are more light stable than are the azomethines used in the more conventional chromogenic development systems. Another useful property is that high tinctorial power is obtainable in this system because the dyes are molecularly dispersed throughout the layer, presumably in association with the gelatin by virtue of their sulphonic-acid groups. This means that only low coating weights of the dyes, and therefore of silver halide also, because the two must be in balanced chemical proportions, are needed, which means thin layers and high sharpness. This latter property is enhanced because the azo dyes function as fairly perfect acutance dyes, by reducing scatter in the emulsion layer of light in the wavelength region to which the emulsion is sensitive. The high tinctorial power of the dyed layers and a fair degree of freedom, probably greater than that available in the azomethine system, can give prints of high brilliance.

There are therefore distinct advantages for the dye-bleach system and further technical advances may result in this method being in the forefront of colour-print processes. The speed limitations derived from both the physics and chemistry of the tripack will probably prevent it from being used in a negative system.

Dye Diffusion

A recently-introduced colour process, *Polacolor*, depends on migration to give the coloured image. The tripack of the negative layer is composed of the usual three emulsion layers. Beneath each sensitive layer there is present a compound of a unique character in that it combines the reducing part of a developing agent with a dye unit. These two parts of the molecule are effectively separated so that they are able both to act independently but move together. The red-sensitive layer contains a cyan dye-developer, the green a magenta and the blue a yellow, very much in the same way as the tripack chromogenic and *Gasparcolor* processes; it is

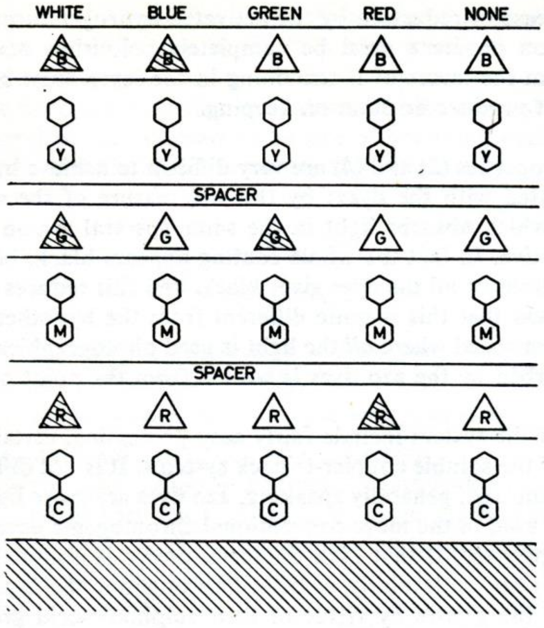


Fig. 10.17 Polacolor — representation of negative layer

represented by Figure 10.17. After exposure the material is brought into contact with an alkaline agent, introduced in pods, and squeezed into contact with a receptor layer, in the same fashion as the black-and-white *Polaroid* film (see Chapter 11) although, in the case of the colour film, the contents of the pods are different. Under the influence of the moisture and the alkali, the development commences. Where the dye-developer molecule is oxidized in reducing the exposed silver-halide grains, it becomes immobilized, but where there is less or no oxidation, the coloured developer molecules are free to migrate across to the receptor layer, as shown in Figure 10.18. Since the three layers are placed one on top of the other, unoxidized developer molecules from the lowest red-sensitive layer will have to pass through the green-sensitive and yellow-sensitive layers to reach the receptor layer. This could cause difficulties if exposed, but undeveloped, silver-halide grains were still present in these upper layers but these are avoided by correct balancing of the activities of the dye-developers and the rate of migration.

The receptor layer, which will be the positive, is also of sophisticated composition. It consists, see Figure 10.19, of three layers coated on a paper support. These are a dye-receiving layer, a spacer layer and, next to the base, an alkali-neutralizing layer. As the dyes move across from the negative, they are accepted by the dye-receiving layer and held there, in the same way as textile dyes are held on fibre; the term mordant is used in this connection by the manufacturers and this implies some

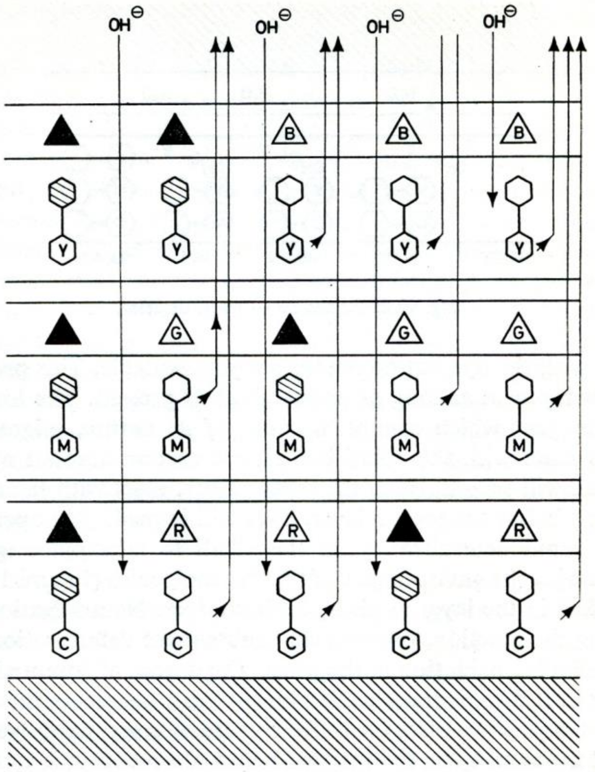


Fig. 10.18 Polacolor — development

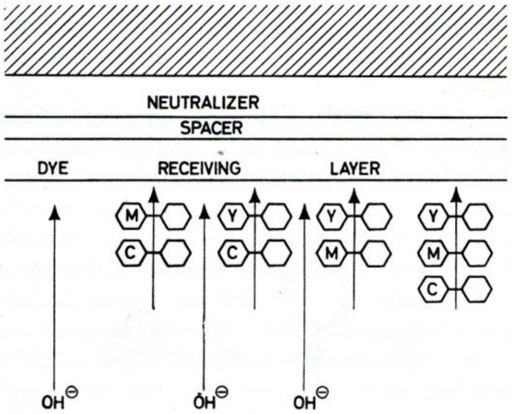


Fig. 10.19 Polacolor — dye acceptance

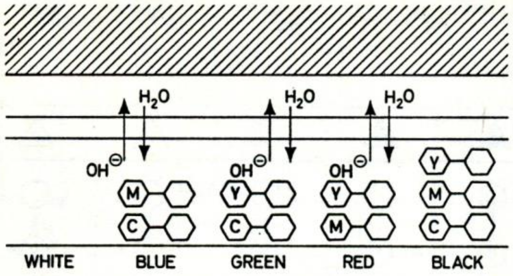
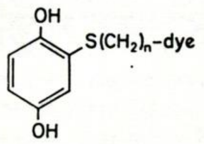


Fig. 10.20 Polacolor — neutralization

special linkage with the dye but no details are yet available. This process continues throughout development as long as excess alkali is present. The lowest layer contains an acid reagent which cannot, because of its nature, migrate through the spacer layer to react with the alkali but after a certain amount of time, a small amount of alkali will seep through the spacer layer, react with the acid, and water will be produced below the spacer layer. This will immediately open up the spacer layer enabling rapid neutralization of the alkali to take place which stops the process and changes the environment of the dye molecules (Figure 10.20). They are now firmly locked in the layer as clear, brilliant dyes. Neutralization of the alkali, besides stopping the reaction, prevents any subsequent deterioration of the colour images due to alkaline oxidation in the print. The degree of completion of the reactions occurring in *Polacolor* is controlled by carefully balancing the rates of the reactions. As the temperature rises the diffusion rate of unoxidized dye-developer will increase *but*, at the same time, the interval before the reaction is terminated is correspondingly shortened, so that, unlike other colour products, the effect of temperature on the processing of *Polacolor* is not critical.

Polaroid make no reference to a yellow filter layer between the blue-sensitive and green-sensitive layers; however, the yellow dye coupler is located beneath the blue-sensitive layer and it is likely that this acts as a yellow filter to prevent blue light affecting the other layers.

No publication has yet been made of the exact structure of the dye-developers although *Polaroid* have referred in a recent patent to molecules in which hydroquinone is linked via a sulphur atom and a hydrocarbon chain to a dye, as in Formula (26).



(26)

Negative-positive Systems

All the processes so far considered give positive images directly, either giving transparencies from a camera film as *Kodachrome* or prints as the *Gaspar*-type processes. The process, now to be considered, operates by giving colour negatives which are then printed to give the final positive. This method is very similar to that of black-and-white photography but relies upon three colour records instead of one neutral density. A normal kind of tripack with blue-sensitive, green-sensitive and red-sensitive layers containing an appropriate colour coupler in each layer is used.

After exposure, the tripack is developed in a colour developer, similar to that discussed earlier, to give colour negative images in each layer. Next, the silver halide remaining and the silver image are removed by fixation and bleaching to leave a negative colour image. The negative is then printed on to a colour-sensitive tripack paper, substantially similar to an incorporated-coupler reversal film, except that the spectral sensitivities of the layers must match those of the dyes in the negative rather than that of the eye. Each layer of the paper contains a colour former to match the sensitivies of the original film, and after processing by colour development, fixation and bleaching, finally gives a print reproducing the subject; all this is demonstrated in Figure 10.21.

The silver-halide emulsions used for the negative material will be of the fast iodobromide type but those used for the print material vary with the manufacturer. A fast chlorobromide emulsion may be used in the positive material for the two lower layers and in this case it is unnecessary to include a yellow filter because the inherent blue speed of the green-sensitive and the red-sensitive layers is so much lower than the speed in the dye-sensitized region.

The couplers may be incorporated by either the substantive method, as used in *Agfacolor*, or by the oil-dispersion techniques, as used in *Kodacolor;* either system gives very satisfactory results. Developer-soluble couplers are not used for this type of process because it is quite impossible to devise means of obtaining the correct colour image in each layer. In all the commercial systems in use today, these couplers are designed to give the complementary colours, i.e. the blue-sensitive layer contains a yellow coupler and so on, as in the case of reversal films, but there is no reason why this should be so, as long as the light sensitivities of the material are matched to the absorption maxima of the negative images. In practice, the hues of the negative dyes, and the spectral sensitivities of the positive material, are spread a little wider than those of reversal films so as to obtain better separation of the three records.

A very important aspect of this type of product must now be mentioned. The light absorptions of the three dyes forming the image are not ideal. The desired curves are shown in Figure 10.22; usually the yellow dye is satisfactory, but the magenta and cyan dyes contain extraneous absorption in the blue region and green regions respectively as shown in Figure 10.23. The effect of these additional absorptions is to add a yellow hue to the magenta, and a red one to the cyan, and thus to degrade the reds and blues of the image. In reversal materials this is not a very serious matter; by careful selection of the couplers, dyes may be chosen which are acceptable. In a negative-positive process, however, the extraneous absorptions will cause serious colour degradation and this fault is overcome by the use of self-masking colour couplers, an invention made at the same time at *Kodak* and *Ansco;* colour couplers of the required type had been prepared some years earlier. The discussion of this technique will be restricted to the magenta colour; the cyan behaves in an analogous way. A group is introduced into the original colour coupler, usually colourless, conferring upon it absorption in the same region as the unwanted blue absorption of the final dye image, and, therefore, the coupler is now yellow. This group is expelled during the

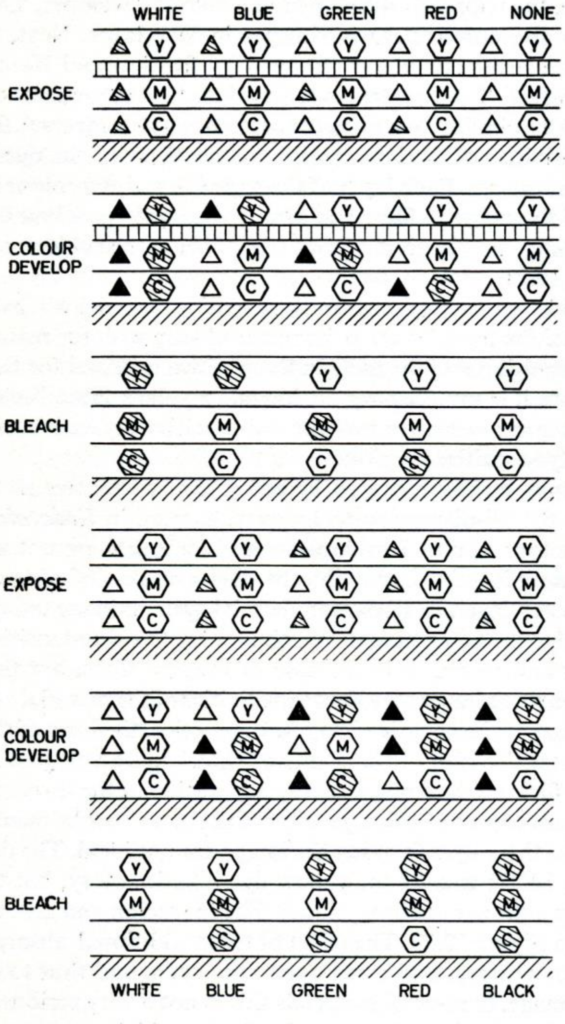


Fig. 10.21 Negative-positive colour process

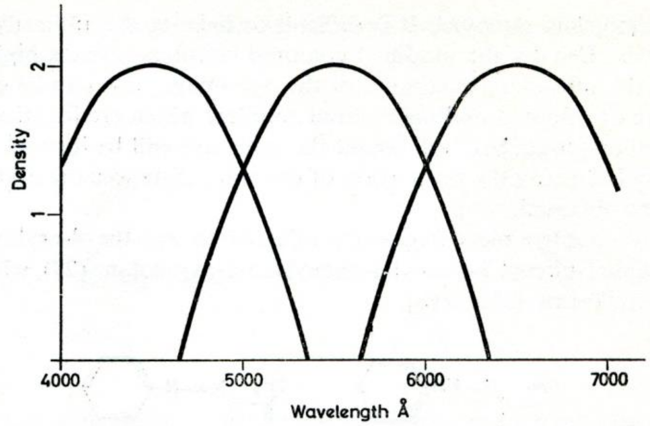


Fig. 10.22 Absorption curves for 'ideal' images

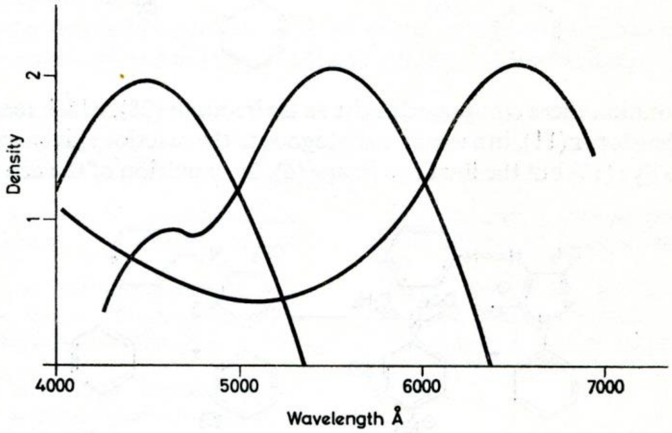


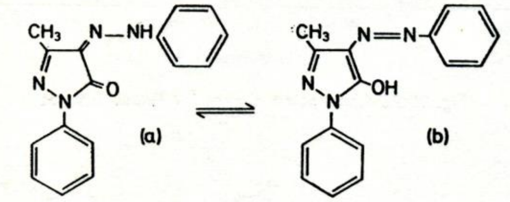
Fig. 10.23 Absorption curves for actual images

reaction giving the dye. Therefore, two processes are taking place during development. In the silver-halide image areas:

oxidized developer + coloured coupler → magenta image with unwanted blue absorption

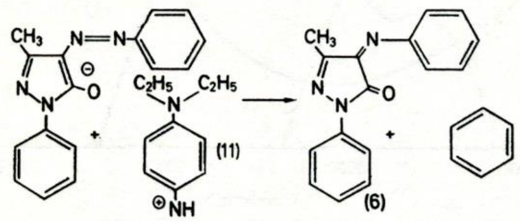
and in the non-image areas, the blue-absorbing coupler remains; in areas of intermediate exposure a mixture of coupled and uncoupled coupler will remain. If the wavelength and intensity of the absorption are accurately balanced between the two parts, then, *in terms of image*, only the magenta part remains. Apart from that, there is a yellow filter layer in the negative and provided the sensitivities of the print layers are balanced (the blue layer of the print material will have to be relatively faster or the exposing light give higher blue intensity), the unwanted imagewise blue absorption will be completely removed. It is difficult to balance the intensity of the two blue absorptions. Usually the modified coloured couplers possess higher blue absorption than the subsidiary maximum of the dye image; this can be overcome by using a mixture of coloured and uncoloured couplers which are identical except for the blue-absorbing group. In development the same dye will be formed from either of them and by balancing the proportion of the two substances the desired level of masking may be obtained.

The coloured couplers most frequently referred to are the 4-arylazo-5-pyrazolones, for example 1-phenyl-3-methyl-4-phenylazo-5-pyrazolone (27), which can exist in two tautomeric forms, (a) and (b).



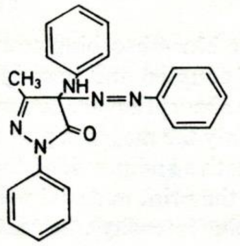
(27)

In alkaline solution these compounds exist as their anions (28), which react with oxidized colour developer (11), in a manner analogous to the reactions given earlier, to give not the leuco dye (13) but the final dye image (6), by expulsion of the azo group.



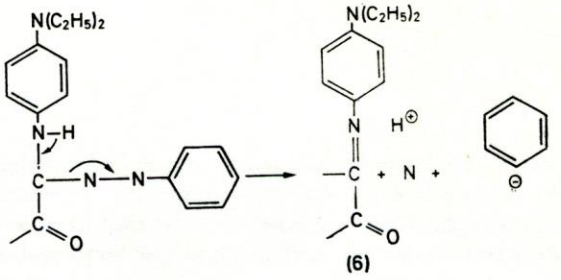
(28)

It will be noted that only two Ag^+ ions are involved in the formation of the dye molecule instead of the usual four; there is no intermediate stage such as the substance (13). The intermediate in this reaction, formed first by the direct union of the positive and negative entities is probably (29).



(29)

The electronic shift resulting from the loss of a proton, easily achieved in an alkaline solution, is as follows:



(30)

and the very transient negative phenyl ion will instantly abstract a proton from water to become benzene. Similar azo derivatives of a α-naphthol (7) behave as magenta masks for the cyan dye.

The compounds used in practice will be more complicated substantive or oil-soluble compounds related to (16, 17, 18) and (19, 20, 21) respectively.

References for Further Reading

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XI NON-CONVENTIONAL PROCESSES

Introduction

So far only the formulation and behaviour of silver-halide processes which are used in a strictly conventional manner have been considered, that is, those processes in which a dispersion of silver-halide microcrystals is exposed to produce a latent image and is then developed to give a negative. The development step may be to give a black-and-white image or a colour image and there may also be subsequent steps leading to reversal, use of the gelatin for forming dye images, etc. Materials of this type include *Technicolor*, still used for movie films, and *Verifax*, *Kodak*'s document copying process. These are, however, later treatments, and the essential features of the emulsion are the same in all cases. Development, the very important step which greatly affects the response of the silver-halide emulsion, is not being discussed in detail in the present work; the reader is referred to a companion volume given in the list for further reading.

One important class of products depending upon non-conventional development chemistry is that using silver-salt diffusion transfer and these will be considered here. Apart from this, there are a number of ways of obtaining images which rely on different latent-image chemistry and different formulations of the silver-halide layer; these two groups will be treated separately.

The Silver-salt Diffusion-transfer Process

This process uses, as its light-sensitive element, a conventional negative emulsion-layer, which is exposed to give the latent-image. This is brought into contact with a receptor layer and the sandwich is treated with a special developer. In addition to containing a reducing agent, the latter includes a silver-halide solvent which will dissolve the silver-halide grains; the behaviour of the process may be followed by reference to Fig. 11.1. In the light-struck areas, the very active developer reduces the grains to give silver in the usual way, but elsewhere the silver halide is dissolved and then diffuses across to the receptor layer. In this layer, the dissolved silver ions, present as a silver complex, come into contact with suitable small catalytic nuclei, such as colloidal silver, silver sulphide, or gold, dispersed in a colloidal binder in which the reduction takes place very easily to give a silver image. It will be appreciated that the final image is formed where no light has fallen in the original exposure, i.e., it is a positive process. Furthermore, the process is capable of giving continuous-tone rendering: the quantity of silver which diffuses is controlled by the amount of original latent image. Generally speaking, because of the high covering-power in the po-

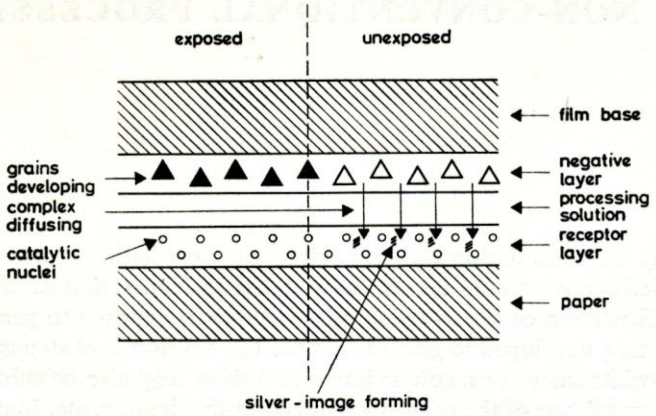


Fig. 11.1 Silver-salt diffusion process

sitive (see below), contrast is high in the final image but nevertheless full tonal range may be produced.

The processing solution may be introduced by passing the two layers into a bath and then bringing them into close contact which must obviously be maintained throughout development. Alternatively, an appropriate solution may be contained in pods affixed to the receptor layer which are broken as the two layers are pressed together; this is shown in Figure 11.2 which illustrates the *Polaroid* camera in diagrammatic form. The final step consists simply of peeling the negative and positive layers apart. In some cases, the negative layer may be placed in contact with one or more further receptor sheets to yield additional copies but, although the production

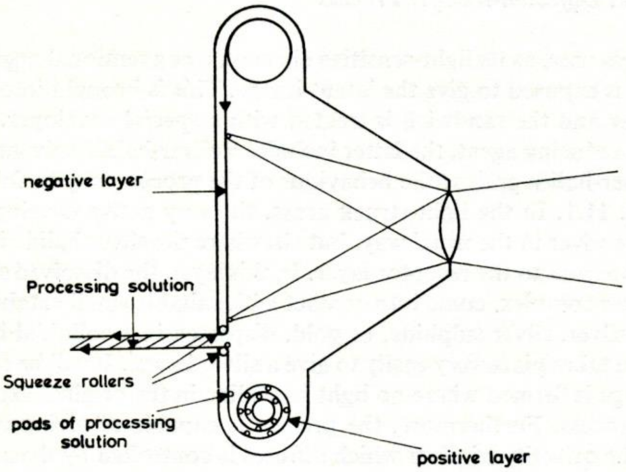
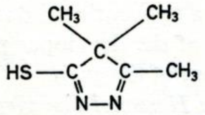


Fig. 11.2 Black-and-white Polaroid camera and process — diagrammatic

of multiple copies has been claimed from time to time, this repeat usage is limited and the subsequent copies are usually poorer in maximum density and contrast. The processing time is short and takes between 10 seconds and 1 minute in present-day materials.

Although simple in outline, there are a number of important factors which must be correct if good results are to be obtained from this method. A very accurate balance must be achieved between development and solution in the negative layer; this usually means that the development must be very fast and this is obtained by using a very active developer such as one containing Phenidone. The silver-solvent is usually sodium thiosulphate. In order to produce image-wise diffusion, the reduction on the catalytic nuclei in the positive sheet must be very fast otherwise diffusion would spread out and produce unsharp pictures. The state of the developed image is also important; in its simplest form the diffusion-transfer method gives an unpleasant yellow-brown image and in commercial processes a suitable toning agent is always added. Among the commonly-mentioned toners are 2-mercaptobenzothiazole (Chapter 7, formula 9), 5-mercapto-1-phenyltetrazole (Chapter 7, formula 15) and 3-mercapto-4,4,5-trimethylpyrazolenine (1):



(1)

These agents are adsorbed to the surface of the silver image during growth and change its structure and surface reflectivity.

Two interesting and useful points may be noted in connection with the development step. Firstly, it seems very probable that it takes place by physical development because the active nuclei are those best suited for that mode of action. The second aspect is that the amount of silver in the final image is very low indeed; it may contain only a few milligrams of silver per sq. dm. in an image of high density. This means that the amplification factor in a diffusion-transfer system is very high indeed. Thus exposure that would give exceedingly low density in a conventional negative may produce a high density by diffusion-transfer. This factor, probably combined with the use of very-active catalytic-nuclei utilizes the foot of a modern fast-negative emulsion to obtain very high speeds. Thus the *Polaroid* black-and-white process gives speeds up to 3000 A.S.A., which are well beyond that obtainable by conventional methods from similar emulsions. Apart from the *Polaroid* camera film, diffusion transfer is the basis of the *Gevacopy* and *Agfa Copyrapid* document-copying methods in which a slow negative-material is used in subdued lighting. In all three of these processes, the final image is formed on paper. The prints may be rendered fully stable by washing or treating with an aliphatic polyhydric alcohol and zinc acetate; the latter agent prevents the formation of silver sulphide. Lacquering is also used with the *Polaroid* prints in order to give final stability to atmospheric degradation.

Direct-positive Materials. There are a large number of methods described in the literature for obtaining a positive image, instead of a negative image, by apparently straightforward developing processes. The basis of many of these processes is to cause the developed silver, or by-products formed in the earlier stages of development, to interfere with the development of the main bulk of the available silver-halide. They are, therefore, development effects and will not be discussed. One process is quite different and is used in many materials today. This is based on the *Herschel effect.*

In addition to the straightforward formation of latent image, there are many other changes which can take place when a silver-halide layer is exposed, usually by abnormal exposure methods. One of these is *solarization* which is a reversal of the D-log E curve brought about by excessively heavy exposures, (Figure 11.3). This reversal is usually incomplete unless special developers are used to process the image. It seems very likely that the very high exposure causes the release of relatively large quantities of bromine from the interior of the crystal which then brominate the surface silver latent image, thus rendering the grain non-developable in a surface developer; extended development in a conventional developer removes the solarization, because the mild solvent action of the developer permits the interior latent-image specks to catalyse the development of the grain.

As long ago as 1840, *Sir John Herschel* discovered that the exposure of printed-out silver-chloride to a spectrum produced a bleaching of the image in the area

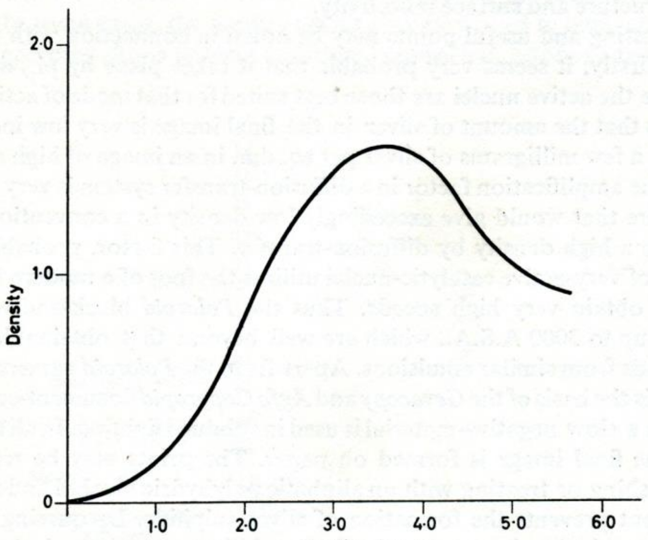


Fig. 11.3 Solarization

where the red light had fallen. The *Herschel effect* is the name given to the bleaching of a latent image by exposure to light of longer wavelength than that used to form it. This effect can be complete in a silver-chloride emulsion but is only partial in silver-bromide emulsions. Much work has been done in this field and the present views have been summarized by *Hillson*.

The usual photographic effect in silver-halide is given by the equation:

$$e + Ag^+ \longrightarrow Ag$$

the electron coming from a bromide ion and the process continuing until a sufficient number of silver atoms produce a latent image.

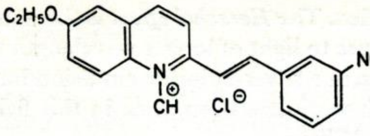
On the other hand, it is also possible that the reverse of this reaction can take place,

$$Ag \longrightarrow Ag^+ + e.$$

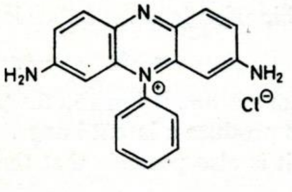
The first possibility is that the silver of the latent image can absorb the light of the second exposure. This is in accord with the long-wavelength response found by so many workers, for example *Carroll* and *Kretchman* reported a broad maximum at 6500 Å while *Hilsch* and *Pohl* found quite a strong maximum at 6900 Å in large single crystals of exposed silver bromide. Having absorbed the light, the excited state of the silver atom will then give a silver ion and the electron.

There are a number of possible mechanisms for the secondary steps of the Herschel effect. The electron may move to another part of the crystal and there combine with another intersitial silver ion to reform a silver atom; this must happen many times before a latent image is decreased in size sufficiently that it is no longer large enough to initiate development. This can in turn happen in three ways, all of which have been observed.

1. The electrons may collect at another point on the crystal surface, there producing a latent-image speck. No change would be detectable in the behaviour of the crystal.
2. The electrons may all migrate into the interior of the crystal and produce an internal image which would not be revealed by a surface developer. This particular change, and the opposite effect, namely the transfer of internal image to the surface, has been well established by experiment.
3. The released electrons may be scattered throughout the crystal and may form a number of small centres of silver atoms by combining with interstitial silver ions at a number of points, none of these new centres being large enough to catalyse development. An image will then no longer be obtained in any developer.
4. The released electrons are trapped permanently by a substance added to the emulsion for that purpose. This can happen in two ways. It was found many years ago that the Herschel effect is very much more effective in the presence of a desensitizing dye. Two dyes used for this purpose are pinakryptol yellow (2) and phenosafranine (3), which in spite of the structural resemblance of (2) to



(2)



(3)

sensitizing dyes, are quite devoid of conventional sensitizing properties and can act only as desensitizers by trapping photolytically-produced electrons and preventing the formation of the latent image.

It has been found that with these dyes the wavelength sensitivity of the Herschel effect is at a maximum at the absorption maximum of the dye, and this is termed a *spectrally-sensitized* Herschel effect. This means that it is most likely that the excited state of the dye is a powerful trap for the electron produced by the breakdown of the silver atom, indeed it virtually brings about the dismutation. This is the reverse of the electron-transfer mechanism for dye sensitization and the behaviour of these dyes is quite different from the usual desensitizing action of sensitizing dyes (see Chapter 6). The mechanism of this process is shown in Figure 11.4. In the other way, a substance is added which plays no part in the light absorption but acts as an excellent trap for the electron; this is called the *sensitized Herschel effect.*

Many compounds are claimed in patents as sensitizers for the Herschel effect but it is not apparent which of these act as both spectral sensitizers and sensitizers and

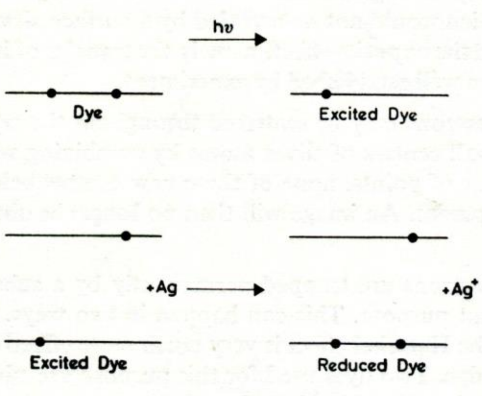
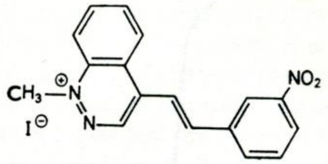
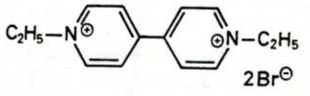


Fig. 11.4 Electronic representation of spectrally-sensitized Herschel effect

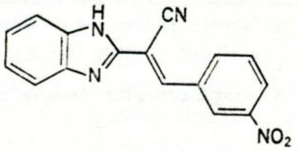
which act as sensitizers only. Among the compounds mentioned are (4), (5) and (6) related to cyanine and merocyanine dyes,



(4)

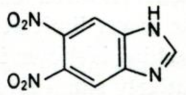


(5)

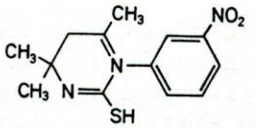


(6)

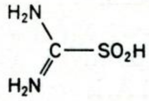
whereas compounds (7) and (8) are akin to stabilizers.



(7)



(8)



(9)

Only compound (4) possesses appreciable absorption in the visual region, so that if spectral sensitization occurs, it is most effective to U.V. light. It has been reported that the most effective wavelength for the Herschel effect in silver chloride is 5200 Å.

All these derivates are readily reduced since they all contain nitro groups, that is, they will all oxidize a latent image. Chemical sensitization in the conventional sense has no part to play in this process. In fact, gold sensitization would probably make the image more difficult to bleach.

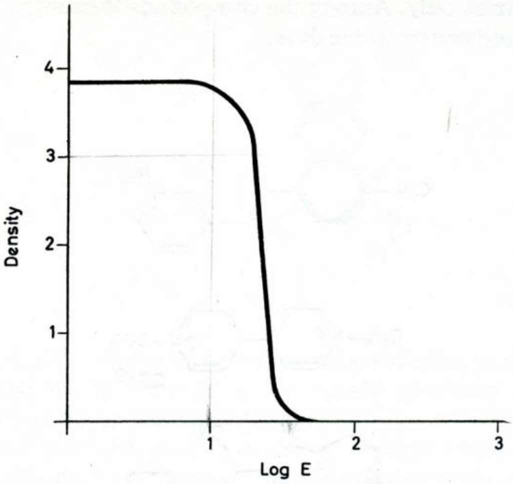


Fig. 11.5 D-log E curve for Herschel bleaching

The other difference between the Herschel bleaching exposure and all the silver image processes discussed earlier is that the light-absorbing entity is removed during the exposure. This makes the process one of very high contrast, because as each silver speck becomes smaller it presents less area for light absorption and therefore all the centres are likely to reach the lower limit at the same exposure. The D-log E curve for an efficient Herschel bleaching is shown in Figure 11.5. Also, of course, the light-absorbing power of the relatively small latent-image speck is very small and therefore the process is a very slow one, even though the effect per quantum absorbed is probably high.

Commercially the Herschel effect is applied in such products as *Kodak Autopositive* paper which uses a fairly fine-grain silver-chloride emulsion. This is fogged either by the action of light or by a chemical fogging agent, e.g. formamidine sulphinic acid, (9), and is then treated with the Herschel sensitizer, quantities from 10 mg to 2.0 g per g.mole of silver are specified for various compounds. This material is then given a straightforward exposure and development; where the light falls, the image is bleached and, therefore, a positive is obtained directly. The use of a yellow filter, absorbing all light below 5000 Å, is preferred for the imaging exposure of these materials. This is presumably because the image in silver chloride is very efficiently bleached by light of 5200 Å and the use of a yellow filter will ensure that no U.V. light reaches the film and reforms the latent image by the usual negative-imaging process. Light sources used for these materials will include mercury vapour and arc lamps which possess considerable emission in the U.V. region. The low speed of these materials means that they may be handled in ordinary artificial light or subdued indirect daylight without any ill effects.

DIRECT WRITING PRINT-OUT MATERIALS. Print-out materials have been known for a long time. This term is used for those materials in which the final image is formed by the exposure, that is, no development stage is used to amplify the latent image. The P.O.P. of amateur photography of many years ago was of this type. These were usually silver-chloride emulsions with excess silver ions present and, after the formation of the image, required fixation in the conventional manner.

More recently however, a new type of print-out recording material has appeared. These are usually coated on paper and are used for the rapid recording and access of high-intensity traces produced by oscillographs, seismographs, etc. The image may initially be formed by high intensity U.V. or short-wavelength visible light or it may come from X-ray, gamma rays or an electron beam. The high sensitivity of the direct-writing materials, e.g. *Kodak Linagraph Direct Print* and *Du Pont Lino-Writ*, permit the recording of an image travelling at 40,000 to 200,000 inches per second. The immediate result of the exposure is a barely detectable image. This may then be brought up to full density by conventional development but the property which makes these products unique is that the image may be "photo-developed" by exposure for prolonged periods to room light or other low-intensity sources. During this "photo-development", the background, that part not affected by the first exposure, produces only a very weak image and the material needs no fixation. Photo-development may be advantageously carried out while the material is heated, for example to 120°–140° C when the exposure need only be from 0.2–15 secs. long thus permitting very rapid processing, and holding back the formation of background density.

Emulsions showing these characteristics have been prepared by adding lead and stannous salts to a silver-bromide emulsion which has already been ripened in excess of bromide ion. For example, *Hunt* describes the addition of 1% molar of lead nitrate and 10% molar of stannous chloride to silver bromide previously ripened in 100% bromide, which is claimed to provide doping at the required level. Amounts of 0.5% and 0.1% molar of stannous and lead salts are said to be incorporated by further ripening under these conditions. Other authors report the doping of silver-bromide and silver-iodobromide emulsions with the combination of lead and cadmium iodides before the final colloid is added for coating.

The latent-image mechanism for these print-out materials is also interesting. Figure 11.6 shows the relative sensitivities for internal and surface latent image of one of these materials for a range of exposures. The image formed by the first short-duration high-intensity exposure will therefore be entirely internal image. When the subsequent low intensity exposure is given, the grains already possessing the internal image will build up at that point to give a high density. The grains not containing the internal centres form some surface image, which has low covering power thus giving very little visual image; the total amount of silver per unit area is identical in image and background. The use of the high temperature for the second exposure is believed to help the already formed internal image to act as an efficient nucleus.

The deliberately introduced lead and stannous ions must play a part in this special latent-image response but no theory of their action has yet been published.

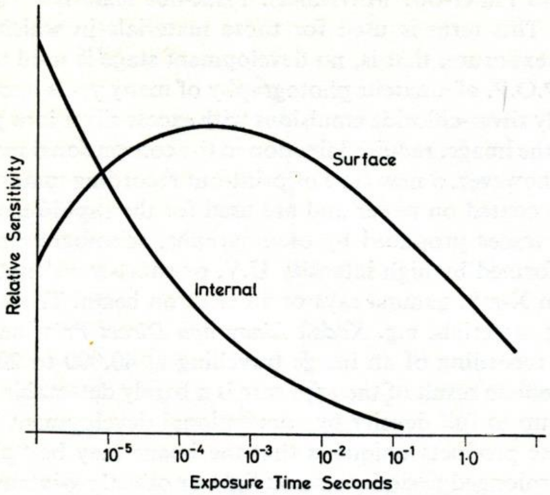


Fig. 11.6 Surface and internal image for print-out emulsion

Non-conventional Silver Halides

Two very novel approaches, both seeking to use the undoubted advantages of silver halide, have been made recently. These are the gelatin-free silver halides of *Technical Operations* and photosolubilization announced in 1964 by *Du Pont*.

GELATIN-FREE SILVER HALIDES. Many attempts have been made to prepare a photographic material in the complete absence of gelatin. In 1960, *Technical Operations* announced a fine-grain material of low speed, A.S.A.1, obtained by depositing silver halide from a vacuum, about 10^{-4} to 10^{-5} mm Hg (about 10^{-7} atmospheres), at 500° C, onto a support. The silver halide formed under these conditions may be sensitized by building unspecified "activators" into the lattice during the evaporation of the halide. The coating may be spectrally sensitized and is claimed to possess the advantages of high resolution and virtually instantaneous development, because there is no colloid layer through which the developer must diffuse. No further details have been published.

PHOTOSOLUBILIZATION. It has been known for some years that if large quantities of an organic stabilizer are added to a silver halide then it becomes much less reactive to development or fixation. At a conference in Washington in Autumn 1964, *Blake* of *Du Pont* announced a new silver-halide process making use of this information. A silver-halide emulsion is prepared and an organic substance is then added to this emulsion. This substance is defined as containing "an ionizable hydrogen atom attached to sulphur, nitrogen or selenium or capable of enolizing". "A mercapto compound" is mentioned, together with the fact that the additive will be water insoluble and it must give a silver salt of lower solubility than the silver halide. This suggests a compound of the stabilizer type; compounds such as the mercapto derivatives given in Chapter 7 would be expected to be effective. This compound forms a layer over the whole of the surface of the silver-halide, thus rendering it insoluble in silver-halide solvents, e.g. hypo solution; this process is referred to as a high-temperature digestion. Coating and supercoating are then carried out as usual. When the silver-halide, still apparently the light-sensitive material, undergoes photolysis it is said to give two silver atoms. One comes from the usual electron and silver-ion interaction and the other by the action of the positive hole on the silver salt of the organic additive which is thereby removed the grain, presumably in an oxidized state.

The imaged layer is then immersed in a thiosulphate fixing solution, and the photosolubilized silver halide is fixed out while that part not affected by light is still insoluble. Subsequently the remainder of the insoluble silver-halide is reduced by a vigorous agent to give a positive image. This reduction step requires either further light fogging, presumably to create enough silver to initiate development in spite of the layer of adsorbed compound, or a chemical fogging agent deliberately added.

Certain similarities can be seen with the conventional method. Instead of differential reduction we have differential solubilization but it still depends on an initiating point which then results in the whole of the crystal being affected. On the face of it one would suppose that more photons were needed to create a sufficient hole in the insoluble layer (it seems unlikely that *all* the surface layer would have to be oxidized off) to render it soluble than are required to give the very small latent-image speck in the conventional process; this could explain the low sensitivity of the system. No indication is given as to whether this system can be dye sensitized but the difficulties of achieving this in a silver-halide crystal completely coated with a stabilizer molecule are obvious.

However, this does represent a new approach and future developments will be interesting.

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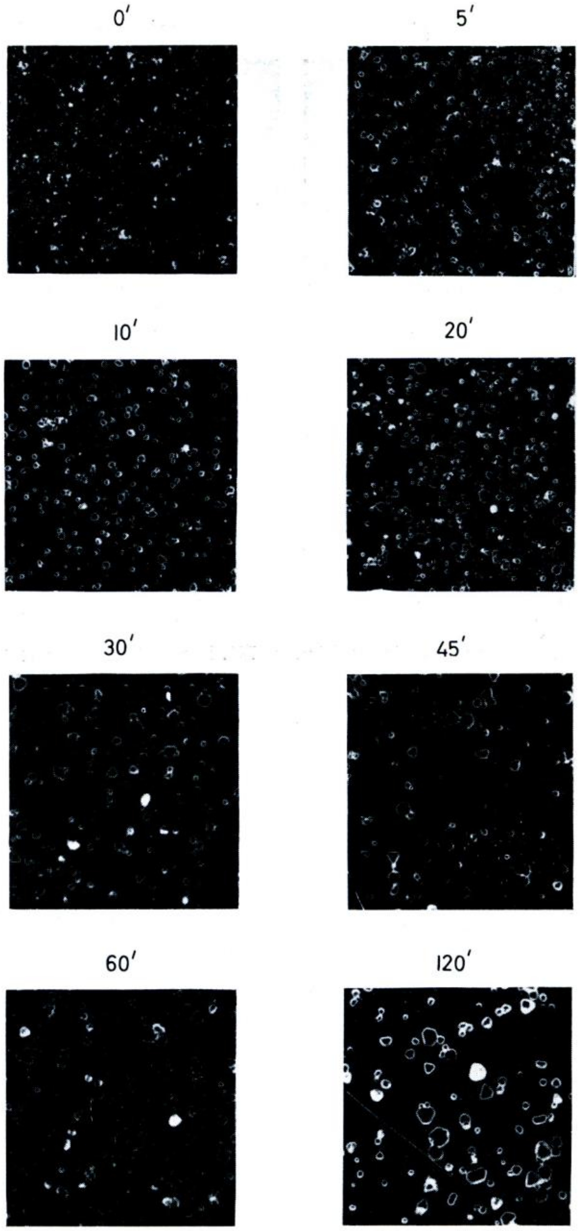


0′ 5′

10′ 20′

30′ 45′

60′ 120′

Plate 4.1 Ripening of octahedral emulsion (p. 66). Photomicrographs × 1000

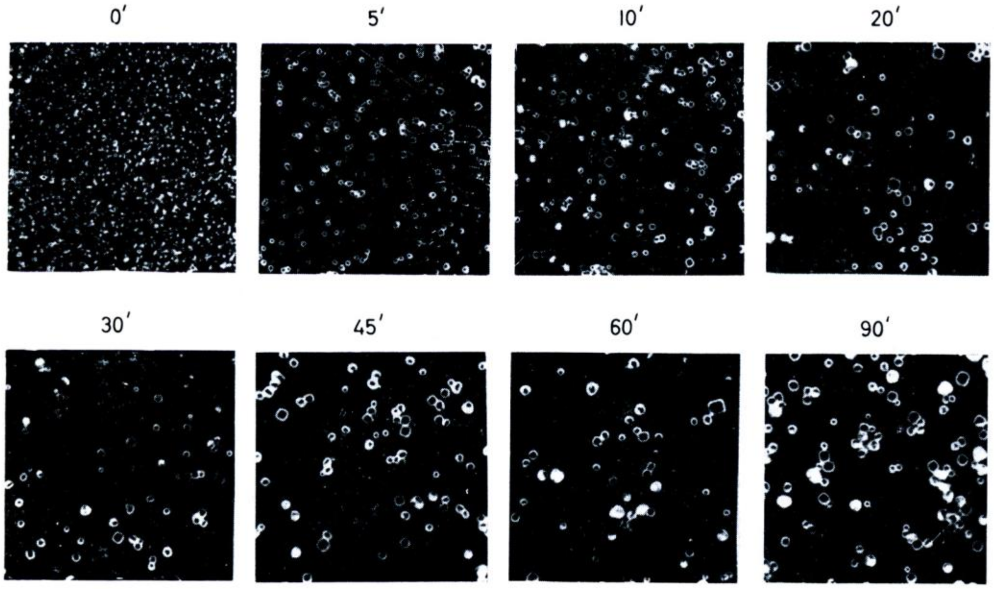
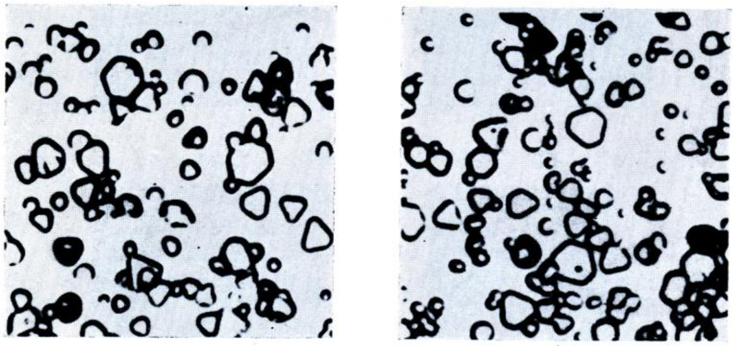


Plate 4.2 Ripening of cubic emulsion (p. 72). Photomicrographs × 1000



UNMODIFIED GELATIN

PHTHALATED GELATIN

Plate 4.3 Photomicrographs of emulsions using modified gelatin
Left: unmodified gelatin; *right:* phthalated gelatin

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by L. F. A. Mason

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