

CHAPTER I

THE BASES OF PHOTOGRAPHY

Sensitivity of silver compounds to light and the discovery of photography

It has been known for a very long time that certain substances are sensitive to light. In particular, silver compounds are darkened when exposed to sunlight. Wedgwood, son of the famous potter, and Sir Humphry Davy made a number of observations on silver chloride. They succeeded in making prints, but failed to make these permanent. Meanwhile Daguerre had made, accidentally, a discovery of fundamental importance. His light-sensitive material was silver iodide, which he prepared by the action of iodine vapour on sheets of silver. Light alone produces metallic silver after very long exposure, but Daguerre found that a plate, exposed for a time insufficient to show a visible image, when placed in a cupboard which contained some mercury, produced a visible image. He had discovered the principle of development and, incidentally, of the latent image. This principle is the basis of all subsequent photography.¹ The light-sensitive system is exposed to light for a short time. Inspection shows no obvious change. When 'developed' an image of silver is formed on the invisible latent image. The second major discovery was that of 'fixing'. The earlier workers had obtained easily some sort of image, but they were not able to remove the unchanged light-sensitive substance and their prints were therefore not permanent but blackened slowly all over.

The direct forerunner of modern photography was Fox Talbot. In 1837 he obtained photographs using a camera obscura with a sheet of paper washed with silver nitrate as his sensitive material. These he rendered permanent by washing in a solution of common salt. Herschel had discovered hypo, sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, in 1819 and observed its extreme efficiency in dissolving silver halides.² Earlier in 1837, the Rev. J. B. Reade had used paper

¹ Photographs can be taken using thallium iodide and bromide in place of silver salts. (Lüppo-Cramer, *Die Grundlagen der photographischen Negativverfahren*, p. 584 and W. J. G. Farrer, *Photogr. J.* 1936, **76**, p. 486.)

² Herschel appears to have been the originator of the word 'photography'.

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soaked in silver nitrate and washed over with a solution of gallic acid. This greatly increased the sensitivity, and he used the process to take photomicrographs, using the sun as light source. He also seems to have been the first person to make use of hypo as a fixer.

The subsequent history of photography is fundamentally no more than an improvement of Fox Talbot's and Daguerre's and Reade's early methods. The first stage was the use of glass plates coated with a suitable mixture of silver salt and some material to hold it in a fine state of dispersion. The first material used for this purpose was collodion. This had the serious drawback that the plates had to be prepared immediately before using. They were coated with a layer of collodion containing a mixture of soluble bromides and iodides. As soon as the collodion had set it was bathed in a solution of silver nitrate. Silver halides were then formed in the collodion, which also retained the other decomposition products of the reaction. The plate had to be used wet, otherwise crystallization of these products occurred in the emulsion. Very fine results were obtained nevertheless with these plates, and collodion plates are still unrivalled where extremely fine grain is required. It should be noted also that development was 'physical' from Fox Talbot's discovery of development of the silver image up to collodion wet plates. The source of silver was the excess of silver nitrate remaining in the negative, and this was reduced by a ferrous salt. In the earliest dry plates, from which the necessary supply of silver nitrate had been washed out, silver nitrate had to be added to the developing solution. This need for physical development must be considered in connection with the remarkable sharpness of the early collodion wet-plate negatives.

The first big improvement consisted in the use of gelatine as the support for the silver halide. The soluble salts, formed by the decomposition of the silver nitrate and soluble halides used, were washed out from the suspension of silver halide in gelatine, which received the name of 'emulsion'. The name is, of course, entirely incorrect, since the system is not an 'emulsion', but the name has persisted.¹ These plates, since they contain only silver halide and

¹ The name 'emulsion' belongs only to stable colloidal dispersions of one liquid in another. Photographic 'emulsions' are suspensions of silver halide microcrystals in the gelatine support.

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gelatine, can be dried without crystallization taking place. It was also found that gelatine plates were intrinsically more sensitive to light than the collodion ones. The gelatine appears to have some specific effect upon the silver halide, which improves it in this manner. This point will be discussed later (p. 9). The gelatine prevents immediate precipitation of coarse amorphous silver chloride so that a fine crystalline form is reached. Fig. 1 (*a*) shows

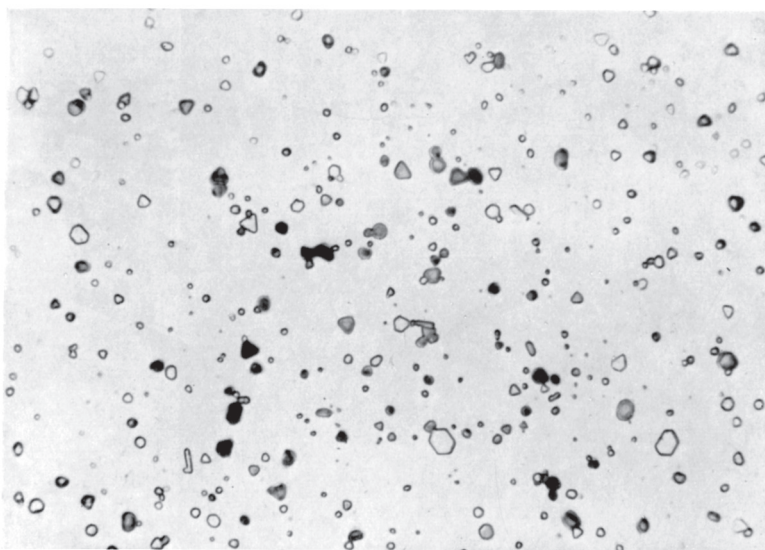


Fig. 1 (*a*). Grains of silver bromide in photographic emulsion. $\times 1500$.

the appearance of the silver halide in an emulsion magnified 1500 times.

The next big advance was the use of celluloid as support for the emulsion in place of glass. This led to the roll film, film pack, and cut film. These have a number of advantages over plates. For convenience of handling, the roll film is superior, and any type of gelatine film has the great advantage for storage that it is very much lighter and takes up less space. Loss of definition by halation is reduced (p. 27).

The subsequent improvements in photographic emulsions consisted of increasing speed, fineness of grain, and sensitivity to all parts of the visible spectrum. In recent years their sensitivity has

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Fig. 2. Spectrogram of iron arc.

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been extended far into the infra-red and ultra-violet regions.¹ It is also found that emulsions prepared for use with visible light are sensitive to numerous radiations of short wave-length, such as X-rays and electrons, and also to α -particles. Becquerel (1896) discovered radio-activity photographically.

Emulsions will be discussed first since, in some cases, they are the only photographic material used in scientific work. The object of photography in scientific work is almost invariably to obtain the most accurate possible record. This includes two and sometimes three quite distinct points: (1) accuracy of reproduction and separation of details—generally called resolving power; (2) accuracy of recording tone values, e.g. recording the range of luminosities on a scale which is identical with, or which bears a simple relation to, the original; (3) equivalence of recording of different colours on the scale of perception of the human eye: or the exact opposite—increasing colour contrast to show important detail more clearly against unimportant confusing background.

Fig. 2 is a spectrogram which illustrates all three points. The large range of wave-lengths from an iron arc is recorded approximately uniformly and the closely distributed lines are separated distinctly. The method used to obtain images of approximately equal intensity of wave-lengths of very widely different actinic action was that described on p. 119.

Theory of photographic action

At one time there was an idea that photographic action could be explained by a single theory. Now, however, it is clear that we have at least three more or less independent points to explain:

- (1) The nature of the emulsion and the cause of its sensitivity to light,
- (2) The mechanism of the absorption of energy and formation of the latent image,
- (3) The nature of development.

The appearance of the emulsion suggests that it is a suspension of crystalline silver halide (Fig. 1*b*). The form is flat hexagonal

¹ Ultra-violet radiations were first detected by their active effect on silver chloride (Wollaston, 1804). Scheele in 1777 had observed that the blue violet end of the spectrum had greatest actinic action on silver chloride.

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plates (silver chloride and bromide belong to the cubic system), but the boundaries are somewhat fuzzy. The fact that the silver halide has the external appearance of a crystalline substance does not mean very much. In the first place, we know that crystals are not to be regarded as homogeneous and that their most reactive parts are edges, corners and cracks. Now although the sensitivity of a silver-halide emulsion is increased by processes which are accompanied by increase of size of the crystallites, these processes

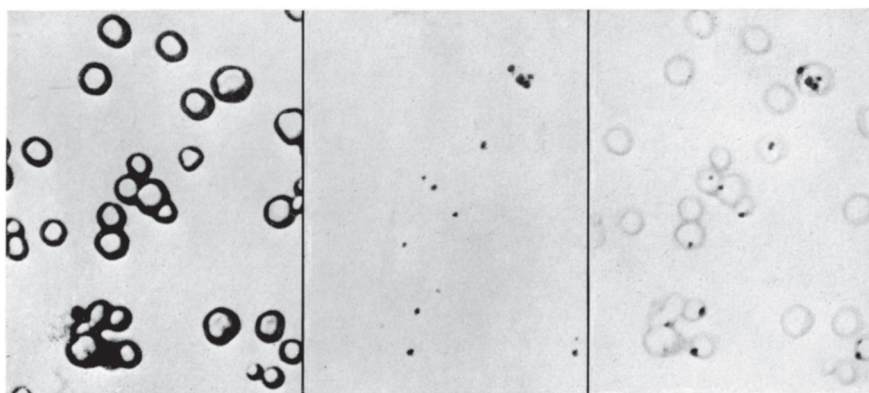


Fig. 1 (b). Svedberg development nuclei.

also involve formation of silver and silver oxide or sulphide; and examination under the highest magnifications shows after suitable treatment that there are in the hexagonal plates black specks¹ which act as nuclei for subsequent development (fig. 1 (b)).

The brilliant work of Sheppard has shown that complex organic substances containing sulphur are present in gelatine and that, in the processes of ripening the emulsion, silver sulphide specks are formed (p. 9).

Recently, Gurney and Mott² have attacked the problem of absorption of energy and have shown that a dispersion of silver or silver-sulphide specks in a silver-halide lattice provides a very efficient electron trap. An electron liberated by the action of light on the emulsion is free to move through the silver-halide lattice

¹ Svedberg, *Photogr. J.* 1922, **62**, pp. 186, 310.

² R. W. Gurney and N. F. Mott, *Proc. Roy. Soc. A*, 1938, **164**, p. 151.

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until it is trapped by a particle of silver. If the work function of the metal is greater than the energy of the electron, then the latter is in a state of lower potential energy when trapped by a metal particle. We know that, once a particle of metal exists in a crystallite, development will convert the whole of the crystallite into metallic silver, given sufficient time. The silver or silver-sulphide specks already described provide the means of trapping electrons. Mott's¹ explanation of development is as follows: When a molecule of developer comes into contact with a silver-halide crystal, it cannot lose an electron to it because the energy level of the electrons in the adsorbed layer of developer molecules lies between the highest occupied level of the metal and the lowest level of the conduction band of the silver halide. But every time that a molecule comes into contact with an uncharged particle of silver, it will lose an electron and the silver will gain a negative charge. It will then attract to itself silver ions.

The nature of photographic emulsions

Photographic 'emulsions' are not emulsions. They are suspensions of silver halide in gelatine. In their earlier stages of preparation the silver halide is formed by double decomposition of silver nitrate and soluble halide in aqueous solution in the presence of gelatine. It is then a protected colloidal dispersion of silver halide. It is allowed to set to a hard gel, cut up and the water-soluble products of the reaction washed out. The emulsion is then heated with water and 'ripened'. 'Ripening' is the trade name given to the two separate processes which increase the sensitivity of emulsions to light—particle growth and formation of nuclei. First, particle growth occurs until the 'emulsion' is a suspension of micro-crystals of silver halide in gelatine. How far we must regard the action of the gelatine as a purely mechanical one of suspending and insulating the micro-crystals and how far there is still definite interaction between the gelatine and the surfaces of the crystals is not clear. Their diffuse outlines seen under the microscope suggest the latter. Silver chloride belongs to the cubic system, but the crystals in an emulsion always have the characteristic form of thin hexagonal plates shown in fig. 1 (*a*). Their size is very important since it seems that, other conditions being the same, the largest

¹ N. F. Mott, *Photogr. J.* 1938, **78**, p. 286.

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crystals are most sensitive to light. Commercial emulsions are remarkably uniform in particle size. Fig. 3 shows the distribution of size in an emulsion.

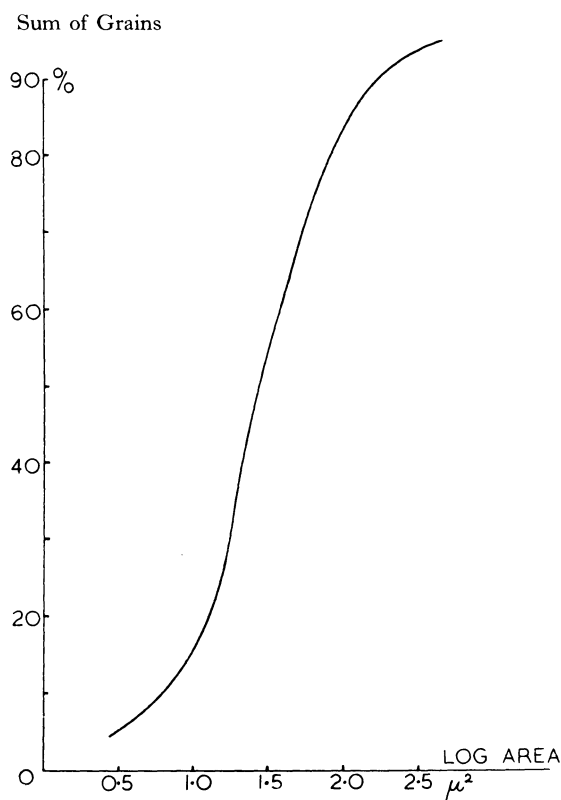


Fig. 3. Grain-size distribution in emulsion.

Abney's observation that gelatine or other colloid is not essential in the first stage of the preparation of the emulsion, since glycerine can replace them as the protector against coagulation of the precipitate, also suggests that there is interaction between the protecting substance and the silver halide amounting to formation of a surface complex.

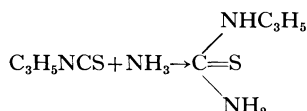
The process of ripening is sometimes visualized as a simple 'ageing' or particle growth analogous to the thermodynamically simple case of growth of large particles of a liquid at the expense of smaller ones which have a higher vapour pressure. Ripening is,

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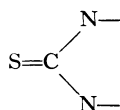
however, much more complex. In the first place, the micro-crystals are not of uniform energy over their surfaces, the corners and edges being most reactive. Ripening consists of two stages, only the first of which is accompanied by grain growth.¹ This first 'ageing' is carried out by heating in the presence of excess of potassium bromide and consists of an increase of crystal size. The potassium bromide is then washed out and the second stage takes place, sometimes in the presence of ammonia. It is believed that the extra sensitivity resulting from this second stage is due to formation of sensitive nuclei either of silver or silver sulphide in the micro-crystals and not to further crystal growth.

Following observations that the final sensitivity of emulsions varied with the history and source of the gelatine used, Sheppard, in a brilliant and classical research,² showed that this was due to the presence of organic sulphur compounds in the gelatine in varying amount. During the second stage of the ripening, these break down and silver-sulphide specks are formed. The manner in which these increase the speed of the emulsion has already been described by the theory of Gurney and Mott.

The exact nature of the organic sulphur compound in the gelatine is uncertain owing to its extremely small amount, which is from one to three or four parts in a million. It is analogous to allyl isothiocyanate. This reacts with ammonia to form a thio-carbamide:



and it is the group (probably acting in a tautomeric form)



which is responsible for sensitizing.

¹ E. J. W. Verwey (*Proc. K. Akad. Wet. Amst.* 1933, **36**, 2, pp. 225-33) has found that the ageing of aqueous sols of silver iodide falls into two parts. The first is very rapid and is accompanied by marked decrease of amount of adsorbed ions. This is followed by a slower ageing consisting of increase of grain size. He suggests that the first is an improvement of an originally very irregular crystal habit accompanied by a decrease of actively adsorbing corners and edges, while the second is a normal crystal growth.

² *Photogr. J.* 1925, **65**, p. 380 and 1926, **66**, p. 399.

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Sensitivity of emulsions and the characteristic curve

In 1890 Hurter and Driffeld made a systematic examination of the response of emulsions to light and devised a system of speed rating which has survived, with added complications, to this day. They determined the density of the image produced by exposures of varying length followed by standard development. When these densities are plotted against the log of the exposure an S-shaped curve is obtained (fig. 4). The reason for using the log of the

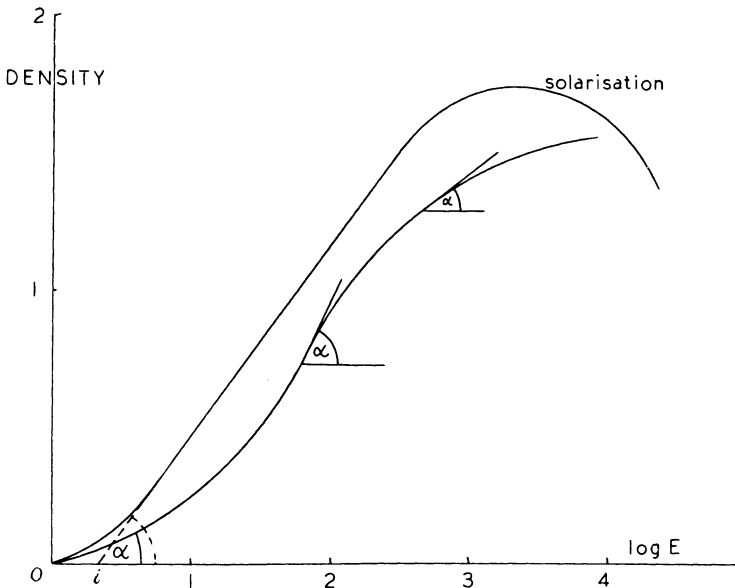


Fig. 4. Characteristic curve.

exposure is because the absorption of light by the developed image is related to the amount of silver present according to the Lambert-Beer law, which states that

$$I = I_0 e^{-kc\theta},$$

where I is the amount of light transmitted through a depth θ , I_0 is the intensity of incident light, k is the molecular absorption coefficient, and c is the concentration of absorbing substance. Taking logs, we get

$$k = \frac{\log_e I_0 - \log_e I}{c\theta}.$$