

Rehabilitation of War-Damaged Universities

The British Association Committee has under survey the position regarding teaching material, apparatus, books and staff in universities which have been destroyed, damaged, disorganized or closed as a result of the War.

The Committee recommends that the United Nations should, at the time of armistice, require the enemy Powers to make full restoration of university property stolen or destroyed in the countries they have temporarily occupied.

Many scientific instruments and much apparatus now being put to war purposes would be of great value for teaching and research, and the Committee recommends that the Governments of the United Nations either give or lend them to the universities, especially those being rehabilitated after the War, and that they require similar action of the enemy Powers.

The Committee has obtained much information from the London International Assembly concerning war damage to the universities. Lists of up-to-date text-books as well as standard books and works of reference are being compiled. When these are sufficiently complete, they will be sent to British universities and university colleges and to the American University Union. It is then hoped to collect a large number of spare copies of such works. The Committee also recommends that the British Council consider buying certain books, and it is also hoped that publishers may supply, for the use of rehabilitated universities, books at reduced prices. It is also hoped to collect copies of learned journals or microfilms of them. The Committee may be able to arrange for the preparation of such microfilms.

It is the opinion of some members of the Committee, who are citizens of the Allied States in Europe, that it will be necessary for British and American universities to train teachers and research workers for some of the universities whose staffs have been killed or dispersed by the enemy.

¹ NATURE, 148, 331, 388, 393, 424, 426, 454, 456 (1941).

² "The Advancement of Science", 2, No. 7, 255 (1942). British Association, Burlington House, London, W.1. 5c.

³ NATURE, 150, 692 (1942).

RECENT ADVANCES IN OUR KNOWLEDGE OF THE PHOTOGRAPHIC PROCESS*

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WHILE many materials are sensitive to light and can be used for making photographs, the present art of photography is based upon one specific process: the light-sensitive material is silver bromide in the form of extremely small crystals held in a layer of gelatin.

The direction in which advances have been made in recent years is in the elucidation of the structure of the light-sensitive materials and the factors which produce great sensitivity in the silver bromide crystals, so that very small amounts of light are sufficient to make them developable; in the study of

the action of light itself and of the change which occurs in the exposed crystals; and in the study of the development reaction by which the exposed crystals are reduced to metallic silver.

The nature of the silver halide crystals and the origin of their sensitivity were elucidated between 1920 and 1930. An adequate theory of the nature of the reaction of light has only become available in the last three or four years, and our views as to the nature of the development reaction have changed very radically in the last year or two.

About twenty years ago, an attack was made on the origin of the sensitivity of the silver bromide crystals by three groups of investigators—Svedberg and his collaborators in Sweden, the British Photographic Research Association in England and the Kodak laboratories in Rochester, N.Y. Soon after gelatin emulsions were first made, it was found that the exposure required in the camera was greatly lessened if the emulsion had been cooked for some time at a high temperature or if it had been treated with ammonia. It was observed that the grains had grown larger during this treatment, and it was concluded that their greater sensitivity was due to their greater size. This is true, but it is by no means the whole story. For a long time, it had been known that if an emulsion were treated with some chemicals, such as chromic acid, it lost its sensitivity, even though the size of the grains was not changed. Also, sensitivity depends very much upon the particular kind of gelatin used in making the emulsion. No clue to an explanation was found until Dr. S. E. Sheppard studied systematically the various fractions obtained at each stage in the preparation of photographic gelatin.

Photographic gelatin is made from clippings from the skins of calves. For this purpose, the skin of the face and ears is used because these parts are of no value for leather. These clippings are first washed and then treated with lime for a long time to remove the fat and hair. The lime is removed by long washing with weak acid and then with water. Then the material is cooked in steam kettles until the gelatin is extracted, and the extract is concentrated if necessary and allowed to set to a jelly; the blocks of jelly are cut into thin slices and stretched out on nets to dry. Sheppard found that in the acid liquors in which the limed clippings had been washed there seemed to be a concentration of some sort of sensitizer, eventually identified as mustard oil, which contains sulphur.

When mustard oil is treated with alkali, it forms allyl thiocarbamide. If silver bromide is treated with a solution of allyl thiocarbamide, the surface of the silver bromide is attacked and grows a mass of white needles containing both allyl thiocarbamide and silver bromide. When these are treated with alkali, they break down into little black spots which must consist of silver sulphide because of the chemistry of the reaction.

When the development of grains is observed under the microscope, it starts from specks, these increasing in number and size until each grain is transformed into metallic silver. The question arises as to whether these centres of development existed before exposure or came into existence when development started. Sheppard's work put the whole matter beyond doubt. Sensitivity depends upon the existence of specks far too small to be seen in the microscope, and these specks consist of silver sulphide, probably derived from the mustard oil in the gelatin. The amount of

* Abridged from *Scientific Monthly* (Lancaster, Pa.), 55, No. 4, 293-300 (Oct. 4, 1942).

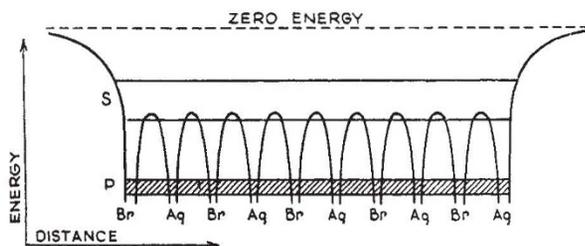


Fig. 1. ENERGY DIAGRAM OF A SILVER BROMIDE CRYSTAL.

mustard oil in an emulsion is very small. A ton of emulsion contains only a couple of drops, and the evidence for the existence of the sulphide specks is therefore indirect.

When Sheppard found that the sensitizing specks consist of silver sulphide, he and his colleagues advanced a theory of the action of light which they called the 'concentration speck theory'. The silver sulphide specks, they suggested, are formed on the surface of the silver bromide crystal and must in some way enter into the lattice of atoms of which the crystal is composed. They produce strains in the crystal, therefore, and these strains stretch into the surface of the crystal as an area of weakness. When light falls on such a crystal, energy travels through the crystal until it reaches the boundary of the speck. At this boundary, owing to the sudden change in structure, metallic silver is set free from the silver bromide. The sensitizing speck thus acts as a nucleus for collecting or concentrating the energy throughout the whole area of the crystal and for liberating metallic silver at the speck itself.

There was still wanting a mechanism for the operation of this concentration speck theory. Such a mechanism has been supplied by the work of Dr. R. W. Gurney and Prof. N. F. Mott and of Dr. J. H. Webb. In the first place, if we consider the energy diagram of a silver bromide crystal as a whole (Fig. 1), there are two energy levels of importance in the photographic process, the *S* and *P* levels, in which the electrons may be situated. The *S* band is normally empty and is referred to as a 'conduction band'. The *P* band is normally completely filled with electrons. Upon exposure of a silver bromide crystal to light which is absorbed in the long wave-length end of the characteristic absorption band, the electrons are transferred from the lower *P* band to the *S* band, and the crystal becomes conducting. This property is well known in other materials, as well as in silver bromide, as 'photo-conductance', and the silver bromide crystal exposed to light may be imagined to be filled with a sort of gas of conducting electrons. This is the primary photographic process—the thing that happens instantly when light falls on the crystal (Fig. 2). When the electrons set free in this way reach a sensitivity speck, either consisting of an impurity or of the silver sulphide derived from the gelatin, the electrons will be trapped and the sensitivity speck will become negatively charged by the electrons that it has absorbed.

In a crystal there are always mobile silver ions in the silver bromide lattice, and these silver ions will travel through the crystal until they reach a sensitivity speck, and there the charge on the ion will be neutralized by the negative charge on a trapped electron and the silver atom freed by the discharge of the ion will be deposited at the sensitivity speck, so that the electrons set free into the conductivity level by the original exposure to light are

eventually transformed into silver atoms deposited on a sensitivity speck. This theory postulates that the production of an image by the action of light occurs in two stages: first, the release of free electrons which occurs instantaneously, and then the transfer of the free electrons by neutralization through the silver ions into silver atoms at the sensitivity specks.

This theory of Gurney and Mott supplies a mechanism for the phenomenon known in photography as the 'failure of the reciprocity law'. Bunsen and Roscoe found that, for the photochemical production of hydrochloric acid, time and intensity were reciprocal. That is, the production of hydrochloric acid was independent of the rate at which light energy was supplied and was dependent only on the total amount of energy. In the case of photography, however, it is well known that the effect of light is not independent of the rate at which it is supplied. There is an optimum rate for the formation of the maximum amount of photographic image, a rate corresponding to an exposure of a small fraction of a second. If the exposure is much greater than this—an hour, for example—two or three times more energy may be required to produce the same density of deposit. On the other hand, if the exposure is much shorter—a ten-thousandth or hundred-thousandth of a second, for example—somewhat more energy will be required. In order to account for the inefficiency of very low intensities of light in producing an image, it must be assumed that the silver atoms formed at the sensitivity specks can easily be lost in the early stages of the formation of the image by acquiring a positive charge owing to thermal action. Thus, for example, newly liberated silver atoms would be more easily lost than those which have entered a silver crystal lattice to form metallic silver.

On the other hand, with high intensities of light the electrons are supplied too rapidly, the silver ions do not have time to reach the sensitivity specks by diffusion through the crystal, and some of the electrons are repelled from the highly charged sensitivity specks before they can be neutralized. Much light has been thrown on the nature of the reciprocity failure by a study of the formation of the image at different temperatures.

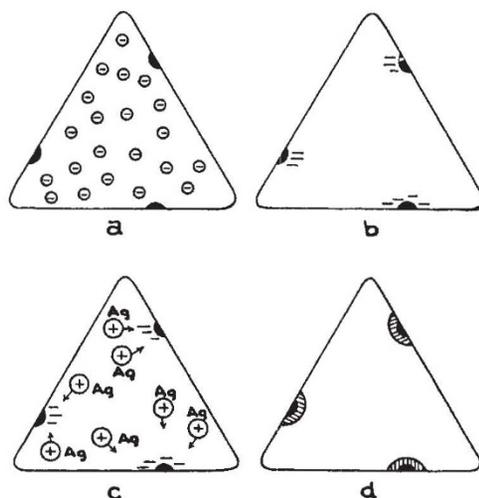


Fig. 2. ACTION OF LIGHT UPON A SILVER BROMIDE CRYSTAL. (a) LIBERATION OF ELECTRONS INTO THE CONDUCTING LEVEL. (b) CHARGING OF THE SENSITIVITY SPECKS BY THE LIBERATED ELECTRONS. (c) MIGRATION OF SILVER IONS TO THE CHARGED SPECKS. (d) DEPOSITION OF SILVER ON THE SPECKS TO FORM THE LATENT IMAGE.

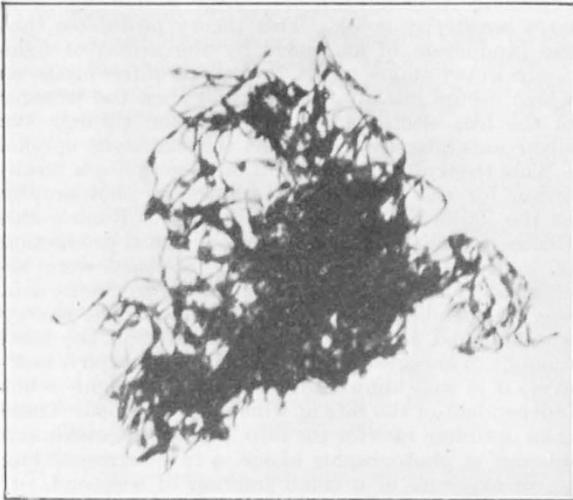


Fig. 3. ELECTRON MICROGRAPH OF A GRAIN OF DEVELOPED SILVER. $\times 50,000$.

The metallic silver deposited at the sensitivity speck and forming a nucleus which facilitates development is what has been known in photography from the earliest days as the 'latent image'. There has been much discussion as to the nature of the latent image, but there is now no question that it consists of metallic silver concentrated at local points in the silver bromide crystal. If the silver bromide is exposed to large amounts of light, a visible discoloration takes place, and this undoubtedly consists of metallic silver. This can be shown by the use of the X-rays in the ordinary crystal structure analysis, when characteristic rings of silver crystals are obtained, and also by the examination of the image by means of the electron microscope, when it can be seen to consist of crystals of silver. Inasmuch as the visible image produced by long exposure to light consists certainly of metallic silver, the latent image produced by short exposure is almost certainly of the same nature.

The mechanism of photographic development has always been very obscure. The general theories as to the nature of development until quite recently were those which conceived it as being similar to crystallization from a supersaturated solution of metallic silver. In the absence of nuclei, deposition of silver would be delayed, and this would check further solution of the silver bromide. In the presence of a latent image nucleus, deposition of silver is facilitated and the solution, reduction and deposition of the silver bromide continues until the crystal is converted into metallic silver. There are many physico-chemical difficulties in this mechanism, but it would undoubtedly have continued as a possible explanation of development had it not been for the evidence recently supplied by the electron microscope as to the form of the silver produced in development.

The silver grains of the developed image are very small and the microscope is unable to distinguish any appreciable structure in them, so that in spite of some suggestions that the silver might be formed as filaments, the general view was that the developed silver grain was a spongy mass of silver crystals somewhat resembling a lump of coke. When developed silver was examined with the electron microscope, however, it was at once seen that the silver grain is a tangled mass of ribbon-like filaments looking very much like

a mass of seaweed (Fig. 3). This is not only very important for the light that it throws on the actual structure of the developed image, but also it at once becomes necessary to account for the production of such an unusual form of silver in the development of the silver bromide. Clearly, the supersaturation theory of development will not do at all. It might be thought that the filaments are formed in cracks in the crystal, but this was disposed of by an examination of the very small crystals of so-called 'Lippmann emulsions', crystals too small to be seen in a microscope. With the electron microscope, these appear as normal silver bromide crystals, but when they are developed, each of them turns into a single filament of silver, these filaments being much longer than the diameter of the crystal from which they were formed. The impression, therefore, becomes overwhelming that the silver filament is formed by ejection from the silver bromide crystal. It is squirted out during the process of development from the solid crystal, and the picture we form of the development reaction is that the reducing ions of the developing agent attack the silver bromide crystal, and in some way the initiation of the formation of metallic silver is facilitated by the presence of the latent image speck.

The mechanism for this is supplied if we consider the potential at the surface of the silver bromide. The surface of the silver bromide grain itself has an excess of bromide ions, which give rise to a negatively charged surface. However, just outside this negative charge, a positive layer of potassium ions must be present to neutralize the negative charge. Without such a neutralizing layer of positive ions, it would be impossible for the surface of the silver bromide grain to be covered with negative bromide ions, since the amount of such a charge in so small a region would give rise to explosive forces. A double-charge layer, consisting of negative bromine ions on the grain and positive potassium ions in the gelatin just outside, may be considered to exist around the surface of each silver bromide grain (Fig. 4). Grains with such a double layer (in a solution) would move under an electric field as negatively charged bodies, since the negatively charged grain would be forced in one direction by the field, and the surrounding movable positive-ion layer in the opposite direction; but since at any point in the liquid there would be positive ions to form the surrounding positive shell, the

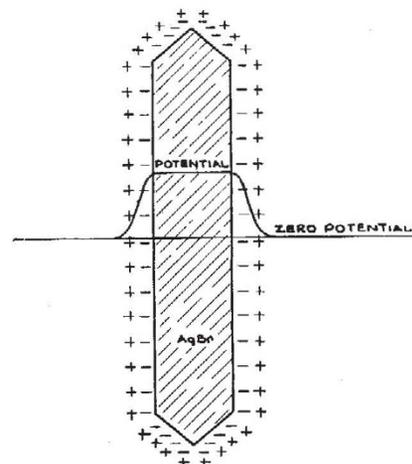


Fig. 4. DISTRIBUTION DIAGRAM OF THE POTENTIAL AND CHARGE OF A SILVER BROMIDE CRYSTAL.

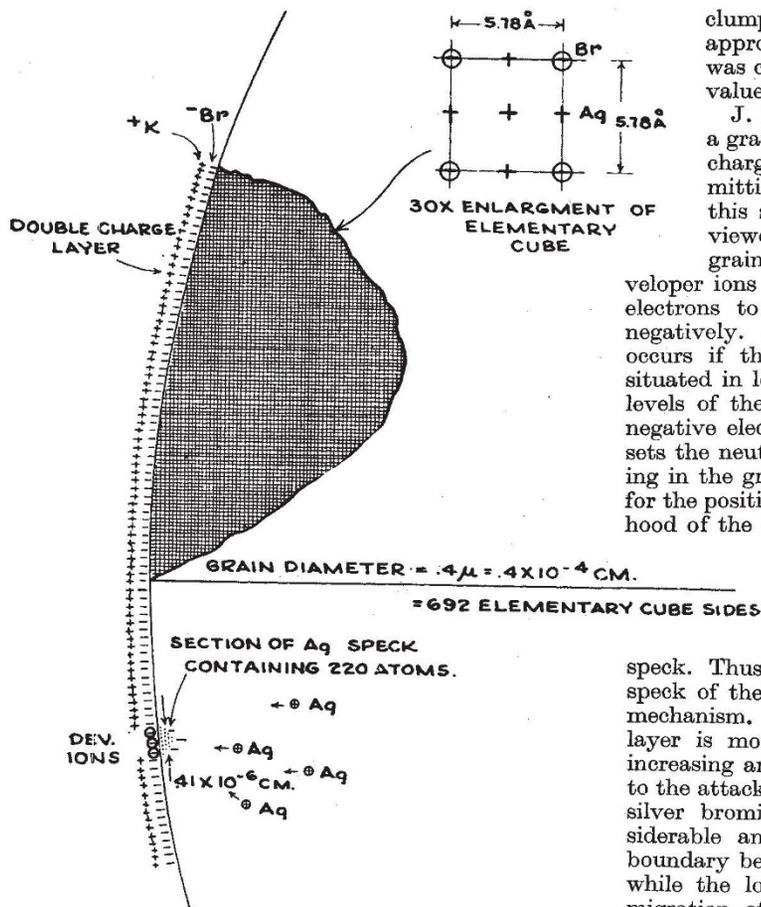


Fig. 5. DIAGRAM SHOWING A LATENT IMAGE SPECK IN A SILVER BROMIDE CRYSTAL ATTACKED BY A DEVELOPER.

double-charge layer would be maintained. That the surface charges on the particles and surrounding charge layers do neutralize each other in the manner outlined is proved by the fact that the colloidal suspension does not possess a net charge of either sign but is neutral as a whole.

It may be assumed that a grain, owing to its double-charge layer, behaves toward outside charges and also those located inside the grain as a neutral body. An electron placed inside such a double-charge layer would experience no force nor, in the same way, would an electron placed outside such a double layer. However, there is a marked difference in potential between the inside and outside of the grain, and the total jump in this potential occurs in the region between the two charge layers. The potential gradient between these charge layers accordingly gives rise to a strong electrical force between the layers, and an electron placed between them would experience a force toward the outside. It is considered that the double-charge layer acts in this way as an effective potential barrier to the entrance of an electron into the silver bromide grain of the emulsion and prevents the developer from attacking the grain.

The conditions existing in the exposed grain containing a latent image silver speck may be seen in Fig. 5. This shows a greatly enlarged scale model of a charged grain surface with a clump of silver atoms on the surface, which is supposed to represent the latent image produced by exposure to light. The

clump shown includes 220 atoms, with approximately the correct spacing. This size was chosen as representing a fair mean of the values given by various workers.

J. H. Webb assumes that development of a grain is initiated by the break in the double-charge layer caused by the silver speck, permitting the negative developer ions to reach this silver speck. The latent image speck is viewed as an electrode penetrating into the grain. The tendency on the part of the developer ions to release electrons to the silver causes electrons to pass to the electrode and charge it negatively. As explained by Gurney and Mott, this occurs if the electrons of the developer ions are situated in levels above the highest occupied energy levels of the silver metal. The penetration of this negative electrode into the silver bromide grain upsets the neutral electrical condition previously existing in the grain, and there arises an attractive force for the positively charged silver ions in the neighbourhood of the latent-image speck.

Positive silver ions always exist in the crystal lattice owing to temperature motion, and these diffuse to the speck under the attraction of the negative charge there and enlarge the silver speck. Thus, it is supposed that the original silver speck of the latent image continues to grow by this mechanism. As this proceeds, the protective double layer is more and more ruptured, and a rapidly increasing area of the silver halide grain is exposed to the attack of the developer. Since the reduction of silver bromide by a developer is exothermic, considerable amounts of energy are liberated at the boundary between the silver and the silver bromide, while the local rise in temperature facilitates the migration of silver ions, so that the metallic silver is extruded as a filament.

The process of development itself involves certain requirements as to absorption and catalysis of the development reaction, which explain why one substance is a developer and another reducing agent having approximately the same reduction potential is not a developer. Much work remains to be done on the chemical reactions involved in development, but the knowledge which has recently become available as to the formation and nature of the latent image and its function in promoting the development of the silver halide grain has enabled us to form a much clearer picture of the phenomena of the photographic process than was possible previously.

EFFICIENCY AND OUTPUT IN AGRICULTURAL SYSTEMS*

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THE measurement of outputs of agricultural systems and their valuation are always a complex proceeding, and the results of any methods of measurement and valuation which have been used up to the present time are to some extent indefinite. Outputs vary in their physical and biochemical characteristics, and in their human uses and values. The only common measure of outputs of varied characters is their

* Excerpts from a paper read before the Royal Society of Arts on November 11.