

THE THEORY OF THE PHOTOGRAPHIC PROCESS

REVISED EDITION

C. E. KENNETH MEES, D.Sc., F.R.S.

Vice President in Charge of Research

Eastman Kodak Company

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REVISED EDITION
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PREFACE TO REVISED EDITION

Since the first edition of *The Theory of the Photographic Process* was published in 1942, much progress has been made in the development of the subject. The second edition is therefore completely revised and largely rewritten. The content and order of the chapters are changed. New chapters on The Action of Charged Particles on the Photographic Emulsion, The Latent Image Produced by X Rays, and The Sensitometry of Color Films and Papers have been added. The chapter on the Photographic Aspects of Sound Recording has been omitted. To provide space for new data, much of the historical material of the first edition has been omitted.

The revised edition has been written in collaboration with the author's colleagues in the Kodak Research Laboratories, both in Rochester and in Harrow, England. In the Contents are given the names of the editors of the sections and of the authors of the chapters.

I am indebted to many other members of the staff of the Laboratories for assistance in revision and also to Dr. J. W. Mitchell for contributions to Chapters 4 and 13. My secretary, Miss Isabel A. Schmitt, and Helen Jacobs Edelman have been responsible for the revision and preparation of the manuscript for publication.

C. E. KENNETH MEES

ROCHESTER, N. Y.

PREFACE TO FIRST EDITION

During the last fifty years, scientific workers interested in the study of the photographic process have built up a fund of knowledge which is scattered through the literature in several languages and in a great diversity of journals. The purpose of this book is to provide a general handbook of the subject as a guide to the literature and as a summary of its conclusions.

Such an undertaking is possible only by the co-operation of a large number of specialists, and the author is fortunate in the generous assistance which he has received from his colleagues in the Kodak Research Laboratories.

The book as a whole owes much to Dr. K. C. D. Hickman and Mr. R. M. Evans.

Dr. S. E. Sheppard contributed much material to Chapters I, III, and IV. Chapter II was revised by Mr. A. P. H. Trivelli and Mr. R. P. Loveland; and Chapter III, by Dr. J. A. Leermakers. Dr. J. H. Webb added much to Chapters IV, V, VI, and VII. A considerable part of the Section on Development, including the whole of Chapters IX, X, and XII, was written by Dr. Arnold Weissberger. Chapters XIII, XIV, and XV were revised by Mr. J. I. Crabtree and Dr. W. Clark. Mr. C. M. Tuttle wrote part of Chapter XVII, and Dr. L. A. Jones revised the Section on Sensitometry and wrote Chapter XX. Chapter XXI was revised by Dr. F. H. Perrin; and Chapter XXII, by Dr. O. Sandvik and Mr. W. K. Grimwood. Chapter XXIII was written by Dr. L. G. S. Brooker and Dr. B. H. Carroll; and Chapter XXIV, by Dr. Brooker. Dr. Carroll and Dr. Leermakers revised Chapter XXV. Dr. E. E. Jelley contributed several sections of chapters.

The author is indebted to Dr. G. Kornfeld for much assistance in revision and, above all, to his secretary, Miss I. A. Schmitt. Acknowledgment should be made of the usefulness of K. V. Chibisoff's book, *Theory of the Photographic Processes*.

One omission in the book requires explanation. A book on the theory of photography should contain a chapter on emulsion-making, discussing various methods of procedure and their effect upon the finished product. The author's knowledge of this subject has been acquired in confidence, how-

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ever, and he is not entitled to publish the material with the frankness which alone would justify any publication.

C. E. KENNETH MEES

ROCHESTER, N. Y.

July, 1942.

INTRODUCTION

The photographic process involves the following operations: An image is formed by means of a lens upon a layer containing light-sensitive material. After exposure, the layer is *developed* by chemical treatment, and a visible image is produced. The unexposed and unchanged material is now removed by solution. This is termed *fixing* the image. The image so obtained is usually a *negative*, in which the bright parts of the original scene appear dark and the dark parts, bright. The negative is printed upon another light-sensitive layer, which, in turn, produces a visible image which is termed a *print*, or *positive*. In this process, the colors apparent in the original scene are not recorded as such, but the negative and positive images represent them in monochrome.

Special processes can be used to produce photographs in color. These utilize a combination of monochrome processes by which the colors of the scene are reproduced by different proportions of three colors.

The *theory* of the photographic process involves a study of the nature of the light-sensitive layers used, of the factors which control their sensitivity to light, of the changes induced in them by the action of light, of the nature of development, and of the properties of the final image and its relation in tone values to the tone values of the scene from which it was produced.

In modern photographic processes, the light-sensitive material is almost always a compound of silver. Compounds of iron, chromium, and a few other metals are sensitive to light, as are certain organic compounds, such as the diazo compounds, which break down under exposure to light. Iron and chromium have been used extensively in the production of photographic prints; but the photographic process which is considered in this work depends upon the light-sensitivity of the compounds of silver, and the photographic materials discussed are those which are formed by the suspension of halides of silver in a layer of gelatin.

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PART | I

THE PHOTOGRAPHIC MATERIAL

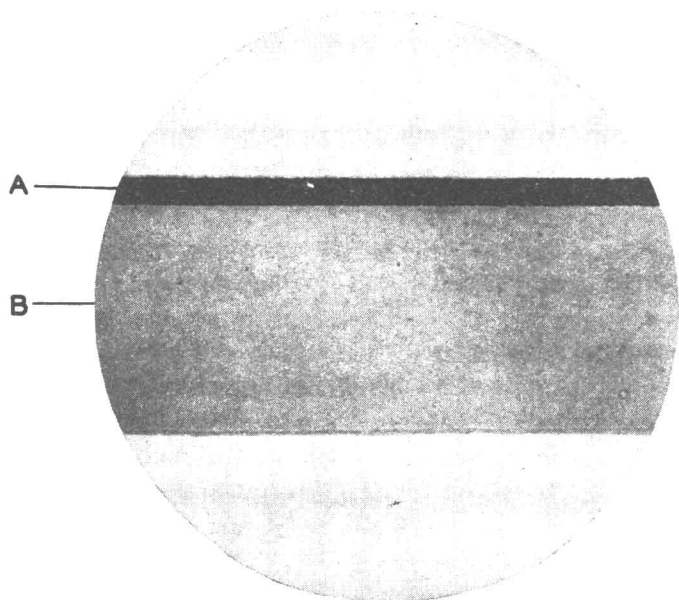


Fig. 1. Photomicrograph of cross section of film, about $\times 500$. A, emulsion; B, support.

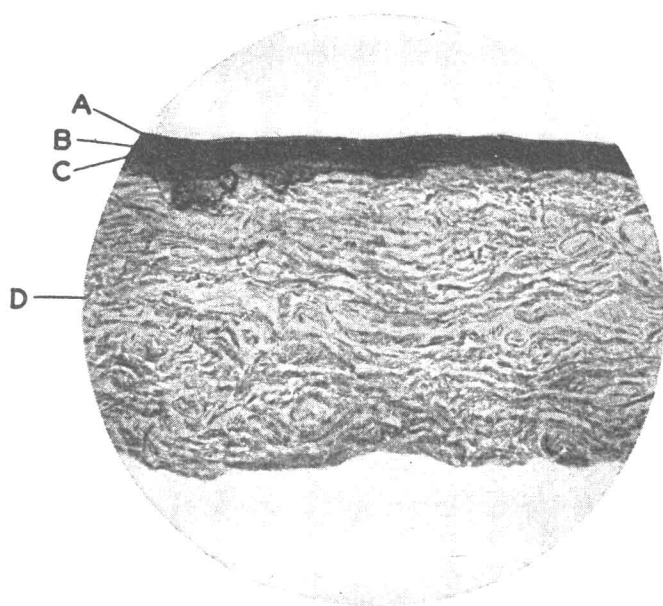


Fig. 2. Photomicrograph of cross section of bromide paper, $\times 500$. A, overcoating; B, emulsion; C, baryta layer; D, fiber.

THE LIGHT-SENSITIVE MATERIAL

The light-sensitive materials considered in this book consist of dispersions of microcrystals of silver halide in a colloidal medium, which is usually gelatin. These dispersions are known as *photographic emulsions* and are employed as thin layers spread over suitable supports, such as glass, paper, or film base (Figures 1 and 2).

If a drop of diluted emulsion is examined under the microscope, the silver halide crystals are seen to be well defined and to range in size from the limit of visibility to a maximum of perhaps 5μ in diameter, the average diameter for a rapid negative emulsion being about 1μ (Figure 3). The photographic properties of the emulsion depend upon the composition and structure of the individual grains, upon their crystalline forms, and upon the conditions of precipitation and treatment which produce grains of different sizes and distribution of size. The presence of gelatin profoundly modifies the nature of the precipitate (Chapter 3).^{1,2}

The composition of the silver salt in various photographic emulsions may be pure silver chloride or bromide but usually consists of mixtures of silver chloride and bromide, or iodide and bromide. Emulsions of silver chloride or chlorobromide are frequently coated on paper supports, whereas emulsions composed of silver bromide with various percentages of silver iodide generally have a greater degree of light sensitivity and are most commonly coated on glass or film. Photographic materials are frequently designated as *negative* or *positive* types, according to their light-sensitivity, negative materials being the more sensitive.

The making of photographic emulsions is a highly specialized technology involving the application of principles and knowledge from the areas of physical and organic chemistry. Several distinct processes may be recognized which are carried out in the sequence given:

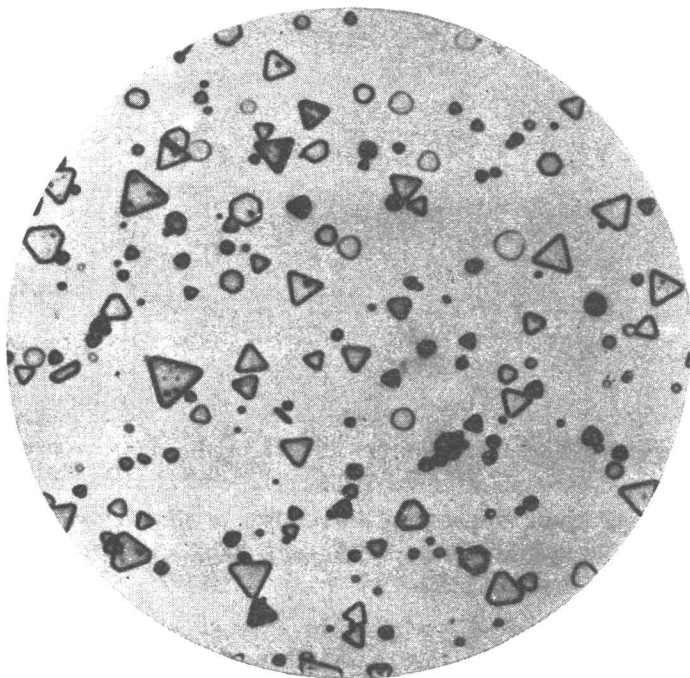


Fig. 3. Photomicrograph of the silver halide crystals of a negative emulsion, about $\times 2500$.

1. The synthesis and dispersal of the microcrystals of silver halide, including the technological stages of *precipitation*, *emulsification*, and *ripening*.
2. The freeing of the emulsion from excess soluble salts, usually by *washing*.
3. A heat treatment, known as *after-ripening*, to obtain the desired light sensitivity.

Several of these processes may be merged into one operation in practice, and in some cases one or more steps may be eliminated from manufacturing procedures. In many cases, photographic papers are coated with unwashed emulsions, since the soluble salts are readily absorbed into the paper support and do not, therefore, crystallize in the emulsion layers.

To prepare a suitable light-sensitive dispersion, the silver halide is pre-

precipitated and emulsified by reacting together solutions of a halide (alkali halide) and a silver salt (commonly silver nitrate) in the presence of the emulsifying agent, which is generally gelatin. The mixing of the halide and silver solutions is done preferably under fixed conditions of temperature, concentrations, and order and rates of addition to produce the dispersion required. Subsequent to or concurrent with the precipitation and emulsification processes occurs the first ripening, which involves maintaining the dispersion in the presence of a solvent for the silver halide to permit the coalescence and recrystallization of the individual particles to the desired crystal (grain) sizes.

When the desired degree of ripening is reached, additional gelatin may be added and the emulsion cooled and permitted to set to a firm jelly. It is then divided into small fragments, usually by squeezing through a grid under pressure, and the soluble salts, consisting of alkali nitrate produced from the reaction and excess alkali halide, are washed from the emulsion with chilled water by osmotic diffusion.

The two stages of ripening differ in the effects which they produce. The first stage is intended to establish the grain size and distribution of the silver halide, and this distribution is affected very little, if at all, in the process of after-ripening, as shown by Chibisov and Mikhailova.³

Before washing, the emulsion generally has low sensitivity and very low contrast; during the after-ripening, the grains undergo important changes in their sensitivity to light owing to chemical reactions caused by heating in the presence of sensitizing materials either present in the gelatin or added to supplement such substances. These sensitizing reactions are discussed in more detail in Chapter 4.

EMULSIFICATION AND RIPENING

The processes of emulsification and ripening determine the distribution of grain sizes of the emulsion and therefore its potential light sensitivity, contrast, and other photographic properties, which, however, must be realized by appropriate after-ripening treatment.

As has been said, negative emulsions generally contain a certain proportion of silver iodide mixed with silver bromide, the amount varying from zero to a maximum of about 10 mol per cent. This iodide may be added at any time during the emulsification or ripening but is generally mixed with the alkali bromide before precipitation. The effect of silver iodide on the photographic properties of silver bromoiodide emulsions is complicated. Because the solubility of silver iodide is lower than that of silver bromide, it tends to produce emulsions of fine grain, and at low con-

centrations it gives emulsions of higher speed and contrast than pure bromide emulsions of the same grain size. Since silver iodide is less readily reduced by photographic developers than silver bromide, emulsions containing larger concentrations of iodide tend to withstand prolonged development and to give lower contrast.

On the basis of their mode of precipitation, there are two classes of emulsions: neutral emulsions and ammoniacal emulsions. In the case of neutral emulsions, a large stoichiometric excess of alkali halide is dissolved in water containing the peptizing gelatin, and to this is added, under controlled conditions, the desired amount of silver salt solution, e.g., aqueous silver nitrate. The excess of alkali halide aids the peptization, and since it is a solvent for the silver halide, it allows recrystallization and Ostwald ripening of the precipitate to take place. Because such ripening action is increased by higher temperature or with time, longer precipitation and ripening and higher temperatures give rise to coarser grained emulsions. Light sensitivity increases with greater average grain size,⁴ and higher speed emulsions are, therefore, obtained by slow precipitation, prolonged ripening, or higher temperatures.

Ammoniacal emulsions are prepared by adding ammonium hydroxide during precipitation and ripening. Ammonia has a strong complexing and solubilizing tendency for silver ion and accelerates the ripening action. The ammonia may be added to the halide solution, or, as is more frequently the case, the silver nitrate solution may be converted by ammonium hydroxide to the silver ammonia complex, which is then added to the halide solution. Upon reaction with the alkali halide, ammonia is released and the silver halide is precipitated and undergoes Ostwald ripening because of the solvent action of the ammonia and excess soluble halide.

Sheppard, Ballard, and Moyses* measured the solubility of silver bromide as a function of concentration of excess bromide and found (Figure 4) that the solubility reaches a minimum at very low concentrations of soluble bromide and then increases with higher bromide concentration. Photographic emulsions are generally precipitated in the presence of a considerable stoichiometric excess of soluble halide, which permits greater solvent action on the silver halides and therefore more rapid ripening of the grain. Similar measurements have been carried out for the system silver chloride: potassium chloride: water by Pinkus and Berkolaiko⁵ and yielded similar results. Lialikov and Piskunova⁶ reported that potassium nitrate also increased the solubility of silver bromide during the ripening process in solutions containing ammonia and potassium bromide.

* S. E. Sheppard, A. Ballard, and A. Moyses, private communication.

Photographic technology utilizes specialized formulas for emulsion preparation adapted to the specific usages intended. Examples of a number of commercial emulsion formulas intended for a variety of purposes are outlined by Ammann-Brass,⁷ who shows the stoichiometric proportions in-

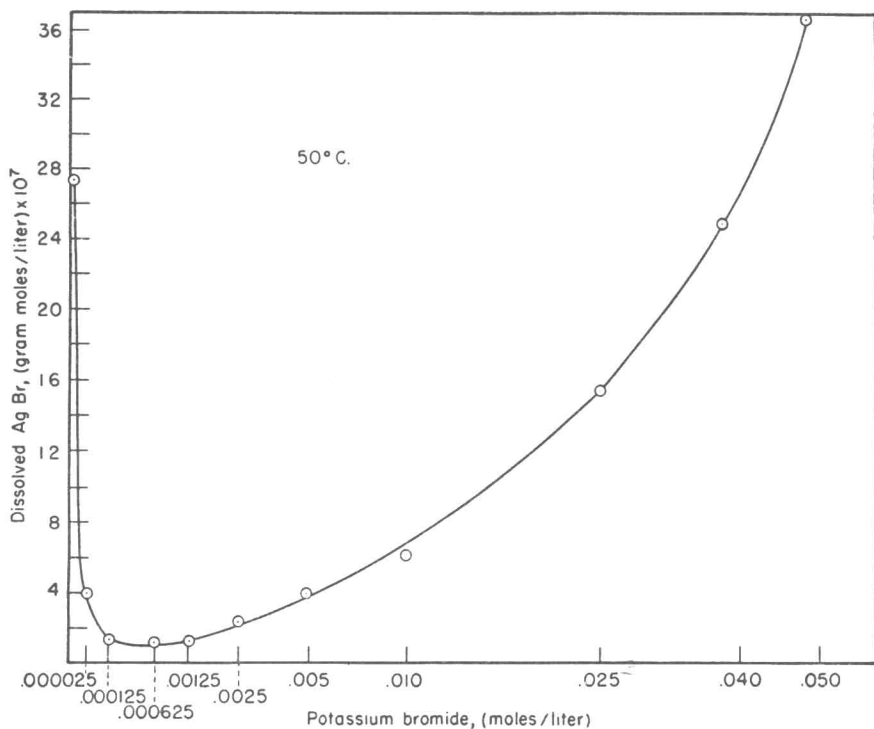


Fig. 4. Solubility of AgBr in aqueous KBr solutions at 50° C.

involved as well as the sequence of precipitation and ripening followed for emulsions intended for X-ray film, roll film, nuclear particle plates, and four grades of photographic paper.

PRECIPITATION IN GELATIN SOLUTION

The precipitation conditions in emulsion making are complicated by the presence of gelatin. Gelatin is one of the best *protective colloids* known. Its effect on the precipitation of silver bromide is very marked. Ordinarily, potassium bromide and silver nitrate in one-hundredth normal solution yield a cloudiness immediately on mixing. In the presence of gelatin, even tenth normal solutions give a clear yellow colloidal suspension of silver bromide, which remains transparent for some time.

The photographic emulsion requires comparatively concentrated solu-

tions of the reactants, and these produce the light-sensitive crystalline grains in two distinct stages: After mixing, there is great supersaturation, followed by the generation of an immense number of nuclei and the growth of these until supersaturation ceases. This is the first stage. The second, already mentioned (p. 5) as ripening, involves clumping and fusion and also the so-

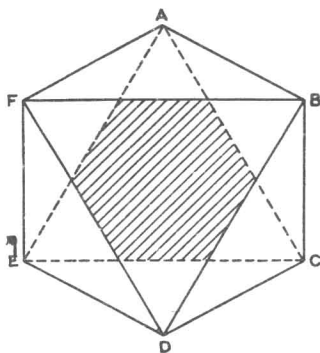


Fig. 5. Diagram of the projection of a regular octahedron showing the generation of a regular hexagon.

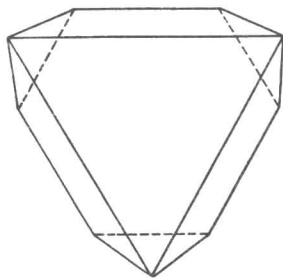


Fig. 6. Diagram of the generation of an equiangular, scalene hexagon.

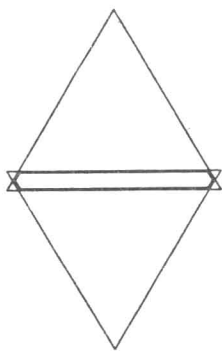


Fig. 7. Diagram of the generation of a needle-shaped crystal.

lution of the smaller particles and redeposition on the larger. Ultimately, well-defined crystals are produced which are visible under the microscope. Finally, these grains undergo coalescence and recrystallization. The existence of these three stages in the precipitation of silver bromide is confirmed by the work of Trivelli and Sheppard,¹ Sheppard and Lambert,^{2b,8} and Chibisov.⁹

The processes of nucleation and growth of crystals are very complex and not yet well understood even in systems which are relatively simple and uniform. For this reason, a thorough comprehension of the factors in-

volved in the first stage of precipitation and grain growth in emulsion making is lacking. Some general observations, however, may be stated and partially explained. The crystals observed in the photographic emulsion generally have octahedral forms, (111) faces. The actual shapes of the crystals can vary enormously, depending upon whether growth takes place equally in three dimensions or is restricted to two or even one dimension. The first gives regular octahedra; the second, plates; and the third, needles. All the variations may be considered derived from a regular octahedron by differential growth or extension of the faces. Let a regular octahedron rest on paper; then, the shadow in parallel projection of the internal area bounded by traces of all its edges is a regular hexagon, as in Figure 5, and the eight facets are discernible after a little study. Thus BDF is one face; and BCD , another. If the rate of growth of all the faces is the same, the crystal increases in size but remains a regular octahedron. If, however, a pair of opposite faces, such as BDF and ACE , have one rate of growth, which is less than that of the other three pairs, a plate in the shape of a regular hexagon is formed. If, in addition, the three faces ABF , BCD , and DEF have a rate of growth different from that of their opposites, CDE , AEF , and ABC , the shape is that of an equiangular hexagon having alternate sides short and long. In the limiting case, a triangular contour results (Figure 6).

The areas of the faces in the fully developed crystal are inversely proportional to their rates of growth. Those faces which acquire material most quickly progress outward, stretching and enlarging neighboring faces, while they themselves remain small. A needle is produced when growth is suppressed at all but the two basal surfaces. These grow in opposite directions, producing a long crystal which is reinforced with but little side expansion (Figure 7). More complicated needle growths are known.

Gibbs,¹⁰ Curie,^{11a} and Wulff^{11b} state that the most stable form is that corresponding to the smallest surface energy for a given volume of the crystal. Thus the growth of a crystal in the mother solution is associated with a change of its surface energy; and, for a given specific distribution of capillary constants among the several faces, the growth of a crystal follows that form for which its total surface energy will be a minimum. This statement is known as the *Gibbs-Curie-Wulff principle of minimal surface energy*. It can be expressed by the equation

$$E = K_1 \cdot F_1 + K_2 \cdot F_2 + K_3 \cdot F_3 + \cdots + K_n \cdot F_n,$$

where $F_1, F_2, F_3, \cdots F_n$ are the areas of the faces of the crystal, to which correspond the capillary constants $K_1, K_2, K_3, \cdots K_n$, while the total surface energy, E , for a given volume, V , of the crystal has to be a minimum.