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PHOTOGRAPHIC
PROCESSING CHEMISTRY



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by

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PREFACE

Photographic Science is an applied science which embraces many branches of chemistry, physics and engineering; the three disciplines are therefore often treated separately, but absolute demarcation is impossible.

The chemistry of conventional silver-based materials is conveniently sub-divided into that of the manufacturing stage and that of the processing stage. This book is concerned with the chemistry of the processing stage of such materials, but includes colour materials as well as the whole range of black and white materials. It does not, therefore, cover the manufacture of photographic materials, nor any aspects of photographic physics and engineering, except where necessary for an understanding of the chemistry involved. Non-silver processes are not considered.

Black and white development is dealt with in the first five chapters, practical formulations being discussed as well as theoretical considerations on the mechanism of development and the chemistry of developing agents. Chapters six and seven are devoted to processing stages other than development, including washing and drying. The last three chapters are on colour processing, current views on the mechanism of the colour development reaction being fully discussed. Typical processing sequences are given for all types of colour materials based on the normal colour development reaction, and several novel processes, which are not yet fully available commercially, are also reviewed.

The book is intended mainly for the graduate in chemistry who wishes to extend his academic knowledge to the chemistry of photographic processing, and also for those in the industry who require an up-to-date reference work on the subject. A basic knowledge of chemistry to B. Sc. General level is therefore assumed, as well as a more elementary knowledge of physics and sensitometry. An extensive list of references is given for those who might wish to consult the original publications.

Finally, it is a pleasure to acknowledge the encouragement and help given by Dr. C. Waller who read the complete manuscript and offered many helpful suggestions. I am also greatly indebted to Dr. G. I. P. Levenson, who performed the final editing, and to Mrs. E. Barnes who typed (and retyped) the whole manuscript.

In acknowledging all the other assistance given, my wife merits special mention, both for her patience during the writing of the book, and for her very practical help during the indexing.

L. F. A. M.

Ilford, Essex.

January, 1966.

PREFACE TO SECOND EDITION

With the need to reprint *Photographic Processing Chemistry*, the opportunity has been taken to carry out some updating. This has been extensive in the section on The Mechanism of Development in chapter IV, the sections on x-ray and graphic arts processing in chapter V, the section on Bleach-Fixing Solutions in chapter VII and the sections on colour negative and paper processing in chapter IX. Throughout the remainder of the book numerous smaller revisions have been made and typographical errors corrected. Additional references are given up to January, 1974.

It is hoped that the book, thus revised, will continue to be of use as one of the main reference works on this subject.

L. F. A. M.

Basildon, Essex.
January, 1974.

I. THE PHOTOGRAPHIC DEVELOPER: GENERAL CONSIDERATIONS

What is Photographic Development?

The photographic 'emulsion' to be discussed in this book consists essentially of a dispersion of microcrystals of silver halides — chloride and bromide, alone or in admixture with each other and often with some iodide — suspended in water-permeable gelatin. Photographic development is the chemical reduction to metallic silver of the silver ions in those silver halide crystals, which have either been exposed to light or have had a latent image produced in them by some other means. The reducing medium, i.e. the developer solution, must therefore be selective in reducing only those crystals possessing a latent image. In practice complete selectivity cannot be achieved, the reduction of both exposed and non-exposed crystals taking place simultaneously. The conditions must therefore be chosen such that the rate of reduction of the exposed crystals is very much faster than that of the non-exposed crystals.

A full discussion on the nature of the latent image will be given later, but for the present purpose it will suffice to state that it is essentially a speck of metallic silver. This may be on or near the surface of the crystal (surface latent image), or in the interior of the crystal (internal latent image). Under the conditions obtaining in photographic development, these silver specks in the exposed crystals exert a marked catalytic effect for the reduction of silver ions to metallic silver, whereas the reduction of those crystals which do not possess latent image specks is uncatalysed, and therefore very much slower. Photographic development might therefore be regarded as an amplification process, the minute specks of silver constituting the latent image being used to induce the production of a very much larger mass of silver. The amplification factor is, in fact, about 10^7 .

The reducing agent (i.e. the developing agent) is always used in solution, and hence the development of the exposed grains is a case of heterogeneous catalysis, the catalyst being in the solid phase, and the reduction occurring at the surface of the catalyst, resulting in the deposition of metallic silver at the latent image speck, and hence its enlargement.

The actual source of silver ions to be reduced is therefore immaterial, as reduction preferentially takes place at the latent image centres. Depending on the source of silver ions, two types of development are to be differentiated, physical and chemical, which must be regarded as the two extreme conditions, most practical developer systems giving rise to both types.

PHYSICAL DEVELOPMENT. In this type of development the silver ions for reduction at the latent image specks are originally supplied from the developer solution. This contains a reducing agent (the developing agent), and buffer ingredients to control the pH to a suitable value. The source of silver ions must be a soluble complex ion, so that the free silver ion concentration is low enough to prevent spontaneous reduction of silver from the solution, but high enough for the catalytic reduction on the latent image specks to proceed. To obtain physical development in its purest form, a post-fixation process must be employed. This involves dissolving all the silver halide from the emulsion layer after exposure, but before development, leaving only the latent image specks in the gelatin. All the silver deposited on these specks during subsequent development is thus derived from the developer solution. Although internal and surface latent image specks are utilised in this process, from five to ten times the normal exposure is required. In prefixation-physical development the silver halide is not removed before development. The process is then more rapid, and the speed loss much less, but some chemical development takes place simultaneously with the physical development.

CHEMICAL DEVELOPMENT. In its purest form, the silver ions for reduction at the latent image speck should be supplied only by the silver halide crystal containing that speck. As this is also in the solid phase, reaction can only take place on the surface of the crystal at the boundary between the latent image speck and the silver halide, that is, around the periphery of the speck. In the usual types of photographic developers, where physical development only takes place to a very small extent, the rate of reduction to metallic silver at this boundary is so rapid that the silver already formed is exuded as a fine filament from the site of the latent image speck. An image fully developed by active chemical development thus appears as a mass of fine silver filaments, with little or none of the structure of the original silver halide crystals remaining. Such a chemical developer requires theoretically to be only a suitable reducing agent in a solution buffered at the optimum pH but, in practice, other compounds such as sulphite and bromide are necessary, and these exhibit some solvent action on the silver halide, increasing the concentration of silver in solution, and hence promoting some physical development.

General Constitution of Developers.

The most important constituent is, of course, the reducing agent, which is nearly always known as the 'developing' agent, in order to avoid confusion with a different operation in photographic processing known as 'reduction', which involves the removal of some of the developed silver so as to reduce the optical density of the image. Chemical reducing agents are only suitable as photographic developing agents if they are capable of differentiating between the exposed and non-exposed silver halide crystals, as already stated. The number of compounds which satisfies this criterion, as well as several other practical criteria, is quite small, only about ten

agents being in common use today for black and white photography. A mixture of two developing agents is commonly used to obtain a result superior to that which can be obtained by the use of a single agent.

The activities of all these agents are greatly influenced by the pH of the solution, and all those in common use today are used in alkaline solution. There is an optimum pH range for each developing agent, and in order to maintain constant activity and characteristics, it is essential that the pH should not change by any significant amount during the useful life of the developer, even though the reactions involved will tend to change the pH. The alkali (sometime referred to as the 'accelerator') is therefore most important, and it should always possess a high buffer capacity.

In alkaline medium the developing agents are very easily oxidised by the air, and additions are usually made to the developer to combat this (the so-called 'preservative'). Sulphites are the most common compounds added for this purpose, but other anti-oxidants such as hydroxylamine and ascorbic acid are sometimes added in addition to the sulphite. The role played by the sulphite is much more complex than that of a simple anti-oxidant, however, and will be discussed later.

In a developer formulated as described so far, the rate of chemical reduction of the non-exposed crystals would still be too high relative to the rate of chemical reduction of the exposed crystals. The silver formed as a result of the development of non-exposed crystals is known as 'fog', and may be greatly reduced by the addition of a soluble bromide to the developer. This retards the development of both exposed and non-exposed crystals, but has a much greater effect on the latter, and hence is often referred to as the developer 'restrainer'.

The restraining action of the bromide ion can be supplemented by small quantities of certain organic compounds, known as 'anti-foggants', 'fog inhibitors', 'stabilizers' or 'organic restrainers'. Benzotriazole is commonly used for this purpose.

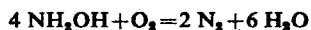
Numerous other additions are often made to developers which already contain the above essential components. These will be discussed in detail later, under the appropriate functions they are intended to influence. The essential components will be discussed in greater detail in the following sections.

The Developing Agents

The above general remarks apply to organic developing agents, to which class belong all those agents in common use today. Considerable interest has been shown in the past, however, in inorganic developing agents. These are of two types — metals capable of forming ions of variable valency states and the non-metallic inorganic reducing agents. Because of the rather unique conditions of use and of recent renewed interest, developers based on metal ions will be discussed later in a separate section.

Non-metallic inorganic developing agents are of academic interest only. Hydroxylamine has found some application as a developing agent in research work where

completely inactive oxidation products are essential, for under alkaline conditions it is a weak developer, and its oxidation products are nitrogen and water:



Hydrazine behaves similarly, but is a somewhat weaker developer. Hydrogen peroxide functions as a weak developer in very strong alkaline solution, but there is much spontaneous decomposition of the hydrogen peroxide on the developing silver. Other inorganic non-metallic species that have been claimed as developing agents include sodium sulphite, sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4$, and sodium formaldehyde sulphonylate, $\text{NaHSO}_2\text{HCHO}$, but these all possess such poor developing properties that they need not be considered further.

The most important and largest group of developing agents are organic compounds. Most of these are aromatic compounds, but there are some notable exceptions. Because of the great number of compounds in this group (which includes all the important agents in use today) several attempts have been made to formulate empirical rules for the basic molecular structure of developing agents. The most successful were those put forward independently by *Andresen*¹ and *Lumière*,² both of which were embodied and extended in a simple rule by *Kendall*³. This stated that compounds are developing agents which satisfy the basic formula:

$\alpha - (\text{C} = \text{C})_n - \alpha'$ where n is zero or any integer, and α and α' are the groups $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}_1$, $-\text{NR}_1\text{R}_2$.

This rule has recently been modified by *Pelz*⁴ to:

$\alpha - (\text{A} = \text{B})_n - \alpha'$, where A is a carbon atom, and B is either a carbon or nitrogen atom. As will be seen later, this modification allows some of the more recently introduced developing agents to be accommodated by the rule. Although such empirical rules have had some limited use in the selection of compounds as new developing agents, their principal use today is as a basis for the classification of this very large group of organic developing agents. The application of these rules in research on new developing agents is now of academic interest only, for much more is now known of the physico-chemical properties required of a developing agent. This classification is used in the following sections, in which are given the important compounds exhibiting developing properties, the date when they were first recorded as developing agents and by whom. More recently, *Tani* has examined these rules from the quantum-chemical viewpoint.^{44a}

(a) TYPE $\text{HO} - (\text{C} = \text{C})_n - \text{OH}$. The special case where $n = 0$, hydrogen peroxide, has already been mentioned. Several compounds have been used in which $n = 1$.



Catechol, Pyrocatechin

Eder and Toth 1880